

Catalytic Coagulation

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We introduce an autocatalytic aggregation model in which the rate at which two clusters merge to form a cluster is controlled by the presence of a third “catalytic” cluster whose mass must equal to the mass of one of the reaction partners. The catalyst is unaffected by the joining event and is available to either 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 rates and show that the total cluster density decays as $t^{-1/3}$, while the density of clusters of any 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.

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 living system might arise, see, e.g., [1–9] 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 to 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 [10–12]. The outcome of from studies such as these is that catalytic activity among a set of molecules is sufficient to promote the appearance of groups of molecules that are able to replicate themselves through catalytic 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 is truly necessary for the emergence of self replication. A missing element in these model is analytical tractability—most of the model 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 and incomplete, it might provide a starting point for analytically determining the kinetics of autocatalytic reactions.

In our *catalytic* coagulation model, some fraction of the reactions 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. This constraint that the catalyst mass is equal to one of the

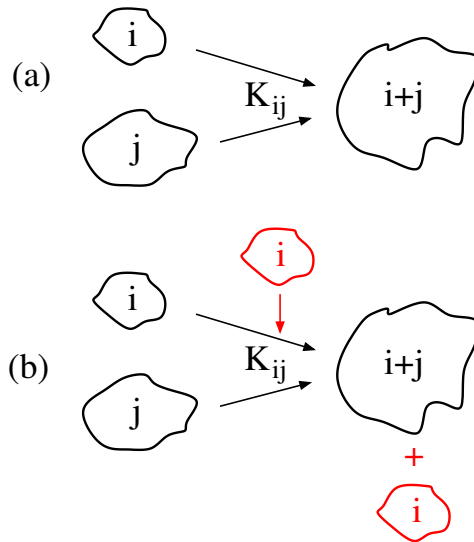
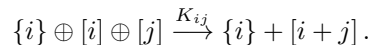


FIG. 1. Schematic of the elemental events in: (a) coagulation and (b) catalytic coagulation. In our catalytic coagulation model, the presence of a catalyst (red) whose mass matches one of the reactants is required. This catalyst is unaffected by the reaction itself.

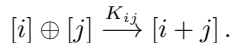
masses of the two clusters that are to be joined is the feature that makes our model analytically tractable. We may represent this reaction as



Here, reactants inside square brackets undergo aggregation, while the reactant within the braces is unaffected by the reaction. In the mean-field or perfect-mixing limit where all reactant concentrations are spatially uniform, we will show that this reaction has slower kinetics compared to that in conventional aggregation. We will extend our theory to treat the case where the efficiency of the catalyst is a function of its mass. We will also treat the situations where only clusters of certain “magic” masses can catalyze reactions and where the reaction is augmented by a steady monomer input.

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 [13, 14]. 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 [15–18].

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 [19–21] describing the evolution of densities in the mean-field limit are particularly simple:

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k c \quad (1)$$

where

$$c(t) \equiv \sum_{k \geq 1} c_k(t) \quad (2)$$

is the total cluster density. Summing Eqs. (1) 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 (1) is

$$c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}}. \quad (3)$$

In the scaling limit of $t \rightarrow \infty$ and $k \rightarrow \infty$, with the scaled mass $kc(t)$ kept finite, the mass distribution (3) has the scaling form

$$c_k(t) \simeq c^2 F(ck), \quad (4)$$

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

Suppose now that merging of two clusters can occur only in the presence of a catalyst according to the reaction $\{i\} \oplus [i] \oplus [j] \rightarrow \{i\} + [i + j]$. 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 obey

$$\begin{aligned} \frac{dc_k}{dt} &= \frac{1}{2} \sum_{i+j=k} c_i c_j (c_i + c_j) - c_k \sum_{i \geq 1} c_i (c_i + c_k) \\ &= \sum_{i+j=k} c_i^2 c_j - c_k^2 c - c_k Q, \end{aligned} \quad (5)$$

involving, in addition to the total cluster density (2), the quadratic moment of the mass distribution

$$Q(t) \equiv \sum_{k \geq 1} c_k(t)^2 \quad (6)$$

The presence of this quadratic moment renders the governing equations (5) intractable. To understand why, we recall that one can solve the rate equations (1) for classical aggregation recursively in terms of the known cluster density. In catalytic coagulation, the governing equations (5) are also recurrent, but they require knowledge of both $c(t)$ and $Q(t)$. Using Eqs. (5), these quantities obey

$$\frac{dc}{dt} = -cQ, \quad (7a)$$

$$\frac{dQ}{dt} = 2 \sum_{i \geq 1} \sum_{j \geq 1} c_i^2 c_j c_{i+j} - 2c \sum_{k \geq 1} c_k^3 - 2Q^2. \quad (7b)$$

Equation (7b) involves moments higher than quadratic, so Eqs. (7a)–(7b) 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 (4). We will see that Eqs. (7a)–(7b) can be solved in this scaling limit. For consistency with (2) and with mass conservation, $\sum_{k \geq 1} k c_k = 1$, the scaling function $F(x)$ must satisfy the conditions

$$\int_0^\infty dx F(x) = 1 \quad \text{and} \quad \int_0^\infty dx x F(x) = 1. \quad (8)$$

By substituting the scaling form $c_k(t) \simeq c^2 F(ck)$ into (6) we obtain

$$Q = Ac^3, \quad A = \int_0^\infty dx F^2(x). \quad (9)$$

Finally, we substitute (9) into (7a) and integrate to obtain the cluster density in the long time limit:

$$c = (3At)^{-1/3}. \quad (10)$$

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

$$\frac{dc_1}{dt} = -c_1^2 c - c_1 Q = -c_1^2 c - Ac_1 c^3. \quad (11)$$

Dividing (11) by $\frac{dc}{dt} = -cQ = -Ac^4$ yields

$$\frac{dc_1}{dc} = \frac{c_1^2 + Ac_1c^2}{Ac^3} \quad (12)$$

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 (12) 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 (11) leads to inconsistent results, and we thus conclude that

$$c_1 = Ac^2. \quad (13)$$

This equation for c_1 is consistent with the scaling form (4) only if

$$F(0) = A = \int_0^\infty dx F^2(x), \quad (14)$$

Collecting (9), (10) and (13) we arrive at

$$c \simeq \frac{1}{(3At)^{1/3}} \quad c_1 \simeq \frac{A^{1/3}}{(3t)^{2/3}}, \quad Q \simeq \frac{1}{3t}. \quad (15)$$

Therefore we have determined the asymptotic behavior of the quadratic moment, while the densities of monomers and clusters are expressed in terms of the unknown amplitude A .

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 (4) into the rate equations (5), from which we can directly obtain the entire scaled mass distribution. After some straightforward algebra, the rate equations transform to the integro-differential equation

$$F^2 - A \left[x \frac{dF}{dx} + F \right] = \int_0^x dy F^2(y)F(x-y). \quad (16a)$$

Notice that for $x = 0$, the condition (14) that $F(0) = A$, is automatically satisfied.

The transformation $\xi = Ax$ and $F(x) = A\Phi(\xi)$ recasts (16a) into

$$\Phi^2 - \Phi - \xi \Phi' = \int_0^\xi d\eta \Phi^2(\eta)\Phi(\xi - \eta) \quad (16b)$$

where the prime denotes differentiation with respect to ξ . In these new variables, Eq. (14) becomes

$$1 = \Phi(0) = \int_0^\infty d\xi \Phi^2(\xi). \quad (17)$$

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 (16b) to find

$$\xi \epsilon' - \epsilon = \xi \quad (18)$$

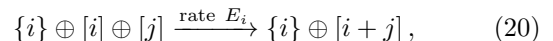
to leading order. The solution is $\epsilon = \xi(\ln \xi + a)$, with a some constant. Thus we conclude that the scaled mass distribution has the small-mass tail

$$\Phi = 1 - \xi(\ln \xi + a) + \dots \quad (19)$$

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.

We can extend the above approach to treat catalytic coagulation in which the reaction rate depends on the mass of the catalyst. 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 write this mass-dependent catalytic reaction as



with mass-dependent reaction rates E_i . 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 emergent behavior is mathematically pathological. In the infinite system the process completes in zero time. This phenomenon is known as instantaneous gelation and its has been studied in the context of classical aggregation [22–24]. This instantaneous gelation also occurs in catalytic coagulation when $\nu > 1$. When $\nu < 1$, catalytic coagulation admits a scaling treatment parallel to that given in this section for the constant-rate model ($\nu = 0$). Details are given in Appendix A.

IV. CATALYSTS WITH MAGIC MASSES

In many catalytic reactions, only a small subset of the reactants are 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 B 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 (20) 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

$$\frac{dc_1}{dt} = -c_1^2(c + c_1), \quad (21a)$$

$$\frac{dc_k}{dt} = c_1^2(c_{k-1} - c_k), \quad k \geq 2. \quad (21b)$$

Essentially the same equations describe the phenomenon of submonolayer islanding [14, 25]. 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 [14, 25]. 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 Eqs. (21).

By introducing the modified time variable

$$\tau = \int_0^t dt' c_1^2(t') \quad (22)$$

we linearize (21) and obtain

$$\begin{aligned} \frac{dc_1}{d\tau} &= -c - c_1, \\ \frac{dc_k}{d\tau} &= c_{k-1} - c_k, \quad k \geq 2, \\ \frac{dc}{d\tau} &= -c. \end{aligned} \quad (23)$$

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

$$c(\tau) = e^{-\tau}. \quad (24a)$$

Then we solve the equation for c_1 and find

$$c_1(\tau) = (1 - \tau)e^{-\tau}. \quad (24b)$$

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

$$c_k(\tau) = \left(\frac{\tau^{k-1}}{(k-1)!} - \frac{\tau^k}{k!} \right) e^{-\tau}, \quad (24c)$$

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

$$c_k(t = \infty) = \frac{k-1}{k!} e^{-1}, \quad c(t = \infty) = e^{-1} \quad (25)$$

While the dependence of the densities in Eqs. (24) in terms of the modified time τ is the same as in submonolayer islanding [14, 25], 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 (21a) to

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

from which

$$c_1(t) \simeq \frac{e}{t}. \quad (26)$$

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:

$$c_k(t) - c_k(\infty) \simeq -\frac{k^2 - 3k + 1}{k!} \frac{e}{t}. \quad (27)$$

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 (21) 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 state. This steady-state behavior often arises in classical aggregation (see e.g., [26–28]). However, the outcome in the present case is continuous evolution, as we now demonstrate.

With monomer input, we add the source to Eq. (21a):

$$\frac{dc_1}{dt} = -c_1^2 c - c_1^3 + J \quad (28)$$

where J is the source strength. The k -mer densities with $k \geq 2$ again satisfy Eqs. (21b). The time dependence of the density of non-catalytic clusters,

$$N = \sum_{k \geq 2} c_k, \quad (29)$$

can be found by summing Eqs. (21b) for $k \geq 2$ and gives

$$\frac{dN}{dt} = c_1^3 \quad (30)$$

It is also useful to rewrite (28) as

$$\frac{dc_1}{dt} = -c_1^2 N - 2c_1^3 + J. \quad (31)$$

Equations (30)–(31) do not admit an exact solution. However, we can determine the asymptotic behavior. The analysis is parallel to that given for the case of sub-monolayer island growth [14, 25, 29]. It turns out (which can be justified a posteriori) that $c_1 \rightarrow 0$ and $N \rightarrow \infty$. Hence from (31) we obtain $c_1^2 N \simeq J$, so that (30) has the asymptotic form $\frac{dN}{dt} = \left(\frac{J}{N}\right)^{3/2}$ leading to

$$c \simeq N \simeq J^{3/5} \left(\frac{5t}{2}\right)^{2/5}, \quad c_1 \simeq J^{1/5} \left(\frac{5t}{2}\right)^{-1/5}. \quad (32)$$

By substituting $c_1 \simeq (2J/5t)^{1/5}$ into (22), we express the modified time in terms of the physical time and thereby express the density in terms of the modified time variable:

$$c_1 \simeq \left(\frac{2J}{3\tau}\right)^{1/3}. \quad (33)$$

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 simply $c_k \simeq c_1(\tau - k)$. Therefore

$$c_k \simeq \left(\frac{2J}{3(\tau - k)}\right)^{1/3}, \quad (34)$$

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

V. SUMMARY

We introduced an aggregation in which the reaction requires the presence of catalysts. These catalysts can both facilitate the aggregation process and they can also directly participate in the aggregation reaction. 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 is analytically tractable. By imposing the constraint that the mass of the catalyst equals that of either of the participant in the aggregation reaction, we have devised a process that is analytically tractable. For the case where the the reaction starts with a population of monomers, we solved the the k -mer density 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 also extended our approach to deal with open systems. This feature of input of elemental reactants is a necessary ingredient to devise models of artificial life. In our modeling, we treated the situation where only monomers are catalytic and they are injected into the system in order to sustain a continuously evolving set of reactions. For this process, we can again solve for the kinetics of the reaction by using classical tools of non-equilibrium statistical physics. Here 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 $t^{-1/5}$.

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Appendix A: Algebraic merging rates

For the catalytic reaction

$$\{i\} \oplus [i] \oplus [j] \xrightarrow{\text{rate } E_i} \{i\} \oplus [i+j], \quad (\text{A1})$$

with the reaction rate $E_i = i^\nu$, the k -mer densities obey

$$\frac{dc_k}{dt} = \sum_{i+j=k} i^\nu c_i^2 c_j - kc_k^2 c - c_k Q_\nu, \quad (\text{A2})$$

with

$$Q_\nu = \sum_{k \geq 1} k^\nu c_k^2. \quad (\text{A3})$$

Similarly, the cluster density evolves according to

$$\frac{dc}{dt} = -cQ_\nu. \quad (\text{A4})$$

Combining (A3) with the scaling form (4) we obtain the analog of Eq. (9):

$$Q_\nu = Ac^{3-\nu}, \quad A_\nu = \int_0^\infty dx x^\nu F^2(x). \quad (\text{A5})$$

Substituting (A5) into (A4) and integrating, we obtain, for the density of clusters,

$$c = [(3-\nu)A_\nu t]^{-1/(3-\nu)} \quad (\text{A6})$$

in the long-time limit. Substituting (A6) into (A5) we then find the asymptotic behavior

$$Q_\nu = \frac{1}{(3-\nu)t}. \quad (\text{A7})$$

The monomer density satisfies

$$\frac{dc_1}{dt} = -c_1^2 c - c_1 Q_\nu, \quad (\text{A8})$$

from which

$$c_1 = (1-\nu)A_\nu c^{2-\nu}, \quad (\text{A9})$$

with c given by Eq. (A6). Equation (A9) is compatible with the scaling prediction $c_1 = c^2 F(x)$ if

$$F(x) = \frac{(1-\nu)A_\nu}{x^\nu} \quad \text{as } x \rightarrow 0. \quad (\text{A10})$$

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 (A2) to give the analog of Eq. (16a):

$$x^\nu F^2 - A \left[x \frac{dF}{dx} + F \right] = \int_0^x dy y^\nu F^2(y) F(x-y). \quad (\text{A11})$$

As in the case of Eq. (16a), the full equation is not tractable, but it is possible to extract partial information about the scaling functions in the limits of small- and large- x .

Appendix B: 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 (5)

$$\{2^i\} \oplus [2^i] \oplus [j] \xrightarrow{\text{rate } 1} \{2^i\} \oplus [2^i + j].$$

The time evolution of cluster densities with non-magic masses, $k \neq 2^n$, obey

$$\frac{dc_k}{dt} = \sum_{2^i+j=k} b_i^2 c_j - c_k Q, \quad (\text{B1a})$$

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

$$\frac{db_i}{dt} = \sum_{2^\ell+m=2^i} b_\ell^2 c_m - b_i^2 c - b_i Q. \quad (\text{B1b})$$

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

$$Q = \sum_{n \geq 0} b_n^2. \quad (\text{B2})$$

With this definition of catalytic clusters, the first of Eqs. (7a) still remains valid

$$\frac{dc}{dt} = -cQ. \quad (\text{B3})$$

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

$$\begin{aligned} \frac{dc_1}{dt} &= -c_1^2 c - c_1 Q, \\ \frac{dc_2}{dt} &= c_1^3 - c_2^2 c - c_2 Q, \\ \frac{dc_3}{dt} &= c_1^2 c_2 + c_2^2 c_1 - c_3 Q. \end{aligned} \quad (\text{B4})$$

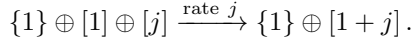
The asymptotic behavior seemingly is

$$\begin{aligned} \frac{dc_1}{dt} &\simeq -c_1^2 c, \\ \frac{dc_2}{dt} &\simeq -c_2^2 c, \\ \frac{dc_3}{dt} &\simeq -c_3 Q. \end{aligned} \quad (\text{B5})$$

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 C: Catalytic monomers with mass-dependent reaction rates

The reaction scheme for this process is



In contrast to models 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

$$\frac{dc_1}{dt} = -c_1^2(1 + c_1), \quad (\text{C1a})$$

$$\frac{dc_k}{dt} = c_1^2[(k-1)c_{k-1} - kc_k], \quad k \geq 2. \quad (\text{C1b})$$

In terms of the modified time (22) we rewrite (C1) as

$$\frac{dc_1}{d\tau} = -1 - c_1, \quad (\text{C2a})$$

$$\frac{dc_k}{d\tau} = (k-1)c_{k-1} - kc_k, \quad k \geq 2. \quad (\text{C2b})$$

Solving these equations recursively subject to the monodisperse initial condition yields [25]

$$c_k(\tau) = e^{-\tau}(1 - e^{-\tau})^{k-1} - k^{-1}(1 - e^{-\tau})^k. \quad (\text{C3})$$

The density of monomers is

$$c_1(\tau) = 2e^{-\tau} - 1, \quad (\text{C4})$$

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

$$c_k(t=\infty) = \frac{k-1}{k} 2^{-k}, \quad c(t=\infty) = 1 - \ln 2. \quad (\text{C5})$$

The latter formula follows from $c(\tau) = 1 - \tau$ that follows by summing all the k -mer densities (C3). 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

$$c_k(t) - c_k(\infty) \simeq -\frac{k-3}{2^k} t^{-1}. \quad (\text{C6})$$

The only exception is the density of 3-mers:

$$c_3(t) - c_3(\infty) \simeq -\frac{1}{4t^2}. \quad (\text{C7})$$

We now inject catalysts with rate J to counterbalance freezing. In the system of equations (C1) only Eq. (C1a) is affected. In the case of initially empty system we find

$$\frac{dc_1}{dt} = -c_1^2(Jt + c_1) + J \quad (\text{C8})$$

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

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

$$c_k(t) \simeq t^{-1} F(k/t) \quad (\text{C9a})$$

More precisely, this happens in the scaling limit

$$t \rightarrow \infty, \quad k \rightarrow \infty, \quad \frac{k}{t} = \text{finite} \quad (\text{C9b})$$

The scaled mass distribution can be extracted from the exact formula in Ref. [25] (which is valid for all $k \geq 2$):

$$c_k(\tau) = (k-1) \int_0^\tau du c_1(\tau-u) e^{-2u} [1 - e^{-u}]^{k-2} \quad (\text{C10})$$

Suppose $k = O(1)$. By substituting $c_1 \simeq t^{-1/2}$ into (22) and dropping terms that vanish as $t \rightarrow \infty$ we deduce that

$$\tau = \ln t + \ln C. \quad (\text{C11})$$

(Fixing the constant C requires an exact solution of (C8) 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 (C10) 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

$$c_k(t) \simeq \sqrt{\frac{\pi}{4kt}}, \quad (\text{C12})$$

which is consistent with the scaling form (C9) and gives the small-mass asymptotic of the scaled mass distribution

$$F(x) \simeq \sqrt{\frac{\pi x}{4}} \quad \text{when } x \rightarrow 0. \quad (\text{C13})$$

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

in (C10). Namely, we write $v = \tau - u$ and obtain

$$c_k(\tau) \simeq (k-1)e^{-2\tau} \int_0^\tau dv c_1(v) \exp[2v - ke^v e^{-\tau}]. \quad (\text{C14})$$

Using (C11) we find $ke^{-\tau} = x/C$. Hence in the exponent we have $2v - ke^v e^{-\tau} = 2v - e^v x/C$. Since $x \gg 1$, we only need the small- v behavior. We obtain

$$c_k(\tau) \simeq k e^{-2\tau - x/C} \int_0^\infty dv c_1(v) e^{-xv/C}. \quad (\text{C15})$$

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 $v > 1/x$. From (C8) we find $c_1 \simeq Jt$ when $t \ll 1$. Substituting $c_1(t) \simeq Jt$ into (22) we obtain $\tau \simeq J^2 t^3/3$, and hence $c_1(\tau) \simeq (3J\tau)^{1/3}$, which recasts (C15) into

$$\begin{aligned} c_k(t) &\simeq \frac{k}{(Ct)^2} e^{-x/C} \int_0^\infty dv (3Jv)^{1/3} e^{-xv/C} \\ &= t^{-1} \left(\frac{3J}{C^2} \right)^{1/3} \Gamma\left(\frac{4}{3}\right) x^{-1/3} e^{-x/C}, \quad (\text{C16}) \end{aligned}$$

which is compatible with the scaling form (C9) and gives the large mass asymptotic of the scaled mass distribution

$$F(x) \simeq \left(\frac{3J}{C^2} \right)^{1/3} \Gamma\left(\frac{4}{3}\right) x^{-1/3} e^{-x/C} \quad \text{as } x \rightarrow \infty. \quad (\text{C17})$$