Borderline Aggregation Kinetics in "Dry" and "Wet" Environments

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ABSTRACT

We investigate the kinetics of constant-kernel aggregation which is augmented by either: (a) evaporation of monomers from finite-mass clusters, or (b) continuous cluster growth – i.e., condensation. The rate equations for these two processes are analyzed using both exact and asymptotic methods. In aggregation-evaporation, if the evaporation is mass conserving, i.e., the monomers which evaporate remain in the system and continue to be reactive, the competition between evaporation and aggregation leads to several asymptotic outcomes. For weak evaporation, the kinetics is similar to that of aggregation with no evaporation, while equilibrium is quickly reached in the opposite case. At a critical evaporation rate, the cluster mass distribution decays as $k^{-5/2}$, where $k$ is the mass, while the typical cluster mass grows with time as $t^{2/3}$. In aggregation-condensation, we consider the process with a growth rate for clusters of mass $k$, $L_k$, which is: (i) independent of $k$, (ii) proportional to $k$, and (iii) proportional to $k^\mu$, with $0 < \mu < 1$. In the first case, the mass distribution attains a conventional scaling form, but with the typical mass growing as $t \ln t$. When $L_k \propto k$, the typical mass grows exponentially in time, while the mass distribution again scales. In the intermediate case of $L_k \propto k^\mu$, scaling generally applies, with the typical mass growing as $t^{1/(1-\mu)}$. We also give an exact solution for the linear growth model, $L_k \propto k$, in one dimension.

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I. INTRODUCTION

Aggregation, fragmentation, and condensation underlie a variety of non-equilibrium phenomena in nature [1-6]. In systems where only one of these mechanisms is operative, the time-dependent cluster mass distribution generally evolves to a scaling form in which the basic variable is the ratio of the cluster mass to the typical mass. These scaling forms have been obtained by exact solutions, numerical simulations, and by direct consistency checks of the scaling description. By these efforts a general understanding has been developed for the connection between microscopic reaction details and macroscopic features of the cluster distribution.

These approaches have also been successfully applied to processes where the mechanisms of aggregation, fragmentation, and condensation are simultaneously active. One important example is aggregation in combination with fragmentation, a process which arises naturally in reversible polymerization [7]. Since the basic elements of aggregation and fragmentation are manifestly opposed, their combined effect generally leads to an equilibrium state in a closed system. Characterizing the approach to and the detailed nature of this equilibrium has been of basic interest [7-11]. Detailed balance considerations can generally be applied to determine the nature of the equilibrium state. If $K_{ij}$ denotes the aggregation rate of $c_i + c_j \rightarrow c_{i+j}$, where $c_k$ is the concentration of clusters of mass $k$, and $F_{ij}$ denotes the fragmentation rate of $c_{i+j} \rightarrow c_i + c_j$, then detailed balance gives $K_{ij}c_i c_j = F_{ij}c_{i+j}$ where $\tau_k$ is the steady-state concentration of $k$-mers.

On the other hand, the situation where the fragmentation matrix $F_{ij}$ has mostly zero elements naturally arises in polymer chain growth kinetics [12,13]. For example, $k$-mers may be unstable to break-off of monomers ("evaporation"), while all other fragmentation events are forbidden. By the nature of these restrictions, the process may be viewed as aggregation in a "dry" environment. For this system, the aforementioned detailed balance argument can no longer determine the equilibrium state. One of our goals is to investigate the kinetics of this composite aggregation-evaporation process in the rate equation approximation. We generally consider the situation where the aggregation rate is independent of the masses of the two incident clusters. We further restrict ourselves to the interesting case of mass conservation, where the monomers which have evaporated remain in the system and continue to participate in the reaction. If the evaporation is sufficiently strong, its dominance over the effects of aggregation results in an equilibrium whose properties are determined analytically. In the opposite case where aggregation dominates, the typical cluster mass increases indefinitely. However, at a critical value of the evaporation rate, the mass distribution decays as $k^{-5/2}$, while the typical cluster mass grows with time as $t^{2/3}$. These intriguing features emerge from both exact solutions to the rate equations and asymptotic arguments.

In a complementary direction, we also explore the kinetics of a combined aggregation-condensation process in which each cluster grows at a specified mass-dependent rate, in addition to the aggregation. This underlying growth can be viewed as arising from a uniform flux of monomers which permeate the system. In this sense, the composite reaction
can be viewed as aggregation in a “wet” environment. Such a process naturally arises in various contexts, such as the growth of breath figures and thin film deposition and growth [6,14,15]. For breath figures, in particular, theoretical models have generally considered the growth rate of each droplet to be a specified function of time. This ultimately gives rise to much faster droplet growth in the composite aggregation-condensation process. In contrast, we consider a droplet growth rate which depends only on the cluster size, and not explicitly on the time. We also employ the rate equations, a description which may not necessarily apply to the stationary droplets which are characteristic of breath figure systems. Within our approximation, we find a number of surprising features in the time evolution of the cluster mass distribution for a mass-independent aggregation rate. When the condensation rate is independent of the cluster mass, the distribution of cluster masses obeys conventional scaling, but with the typical mass growing as \( t \ln t \). On the other hand, for a condensation rate which is proportional to the mass, the typical mass grows as \( e^t \). For a general mass-dependent condensation rate which is proportional to \( k^\mu \) (with \( 0 < \mu < 1 \)), the typical mass grows as \( t^{1/(1-\mu)} \). For all three cases, that is, \( 0 \leq \mu \leq 1 \), scaling generally applies and this approach further predicts that the mass distribution decays exponentially with mass.

A detailed treatment of these two cases of aggregation-evaporation and aggregation-condensation is presented in the following two sections.

**II. KINETICS OF AGGREGATION-EVAPORATION**

The rate equations for mass conserving aggregation-fragmentation are,

\[
\dot{c}_k(t) = \frac{1}{2} \sum_{i,j} K_{ij} c_i(t) c_j(t) - c_k(t) \sum_{i=1}^{\infty} K_{ki} c_i(t) \\
+ [L_{k+1} c_{k+1}(t) - L_k c_k(t)] + \delta_{k,1} \sum_{i=1}^{\infty} L_i c_i(t).
\]  

Here the overdot denotes the time derivative and \( c_k(t) \) is the concentration of clusters of mass \( k \) at time \( t \). In this equation, the first two terms account for the gain and loss of \( k \)-mers due to aggregation, respectively. The prime on the sum in the gain term indicates the restriction of mass conservation, \( i + j = k \). In the evaporation process, a \( k \)-mer produces a \((k-1)\)-mer and a monomer at a rate \( L_k \equiv \lambda k^\mu \). The gain and loss of \( k \)-mers because of evaporation are described by the third and fourth terms of Eq. (1(a)). Finally, the last term accounts for monomer production as a result of evaporation. (If monomers were removed from the system by evaporation, the last term would be absent. This non-conservative process has trivial kinetics in which the mass disappears exponentially in time.)

Let us now determine the conditions for which the system either reaches equilibrium or evolves *ad infinitum*. We focus on the case where the aggregation rates \( K_{ij} \) are all equal (constant-kernel aggregation) and where the evaporation rate is independent of the cluster mass.
mass ($\mu = 0$). Physically, this latter rate is appropriate for linear polymers with evaporation possible only at the chain ends. Although one can easily generalize the discussion to mass-dependent aggregation and evaporation rates, their relative influences are typically of different orders of magnitude. Consequently, it is relatively straightforward to anticipate whether an equilibrium or a scaling distribution obtains. However, for mass-independent aggregation and evaporation, the competition between these two influences is delicate and gives rise to surprisingly rich kinetic behavior.

With the assumptions of constant reaction kernel and size-independent evaporation, the rate equations simplify to

$$\dot{c}_k(t) = \frac{1}{2} \sum_{i,j}' K c_i(t)c_j(t) - c_k(t) \sum_{i=1}^{\infty} K c_i(t) + \lambda (c_{k+1}(t) - c_k(t)) + \lambda \delta_{k,1} \sum_{i=1}^{\infty} c_i(t). \quad (1b)$$

The evaporation rate $\lambda$ and reaction rate $K$ can be absorbed by redefining the concentrations and time by $c_k(t) \rightarrow 2\lambda c_k(t)$ and $t \rightarrow t/\lambda K$, leading to

$$\dot{c}_k(t) = \sum_{i,j}' c_i(t)c_j(t) - 2c_k(t) \sum_{i=1}^{\infty} c_i(t) + (c_{k+1}(t) - c_k(t)) + \delta_{k,1} \sum_{i=1}^{\infty} c_i(t). \quad (1c)$$

For simplicity, consider a monomer-only initial condition, $c_k(t = 0) = \mathcal{M}\delta_{k,1}$. In this case, the total initial mass is the only control parameter, with a large mass corresponding to a small evaporation rate and vice versa.

To gain insight into the kinetics, it is helpful to first write the equations for moments of the mass distribution, $M_n(t) \equiv \sum_{k \geq 1} k^n c_k(t)$. By straightforward manipulations on Eq. (1(c)), these moments obey the equations,

$$\begin{align*}
\dot{M}_0(t) &= -M_0(t)^2 + M_0(t) - c_1(t), \\
\dot{M}_1(t) &= 0, \\
\dot{M}_2(t) &= 2(M_1^2 - M_1 + M_0(t)), \\
\dot{M}_3(t) &= 3M_1 + 3(2M_1 - 1)M_2(t), \\
\dot{M}_4(t) &= 2M_0(t) - 4M_1 + 6(M_2(t) + M_2(t)^2) + 4(2M_1 - 1)M_3(t), \\
\dot{M}_5(t) &= 5M_1 - 10M_2(t) + 10M_3(t) + 20M_2(t)M_3(t) + 5(2M_1 - 1)M_4(t), \\
&\vdots
\end{align*} \quad (2)$$

For the monomer-only initial condition, $M_n(t = 0) = \mathcal{M}$ for all $n$. From the equations for $M_n(t)$ for $n \geq 2$, it is clear that the typical mass and higher moments grow indefinitely, if the initial mass is sufficiently large. In the complementary case, however, an equilibrium state is possible.

More complete information about the kinetics can be obtained by analyzing the rate equations themselves. For this purpose, we introduce the generating function

$$g(z, t) = \sum_{k=1}^{\infty} c_k(t) z^k. \quad (3)$$
By multiplying the rate equation for each $c_k(t)$ by $z^k$ and summing over all $k$, the generating function obeys

$$
\dot{g}(z, t) = g(z, t)^2 - 2g(z, t)M_0(t) + \left( \frac{g(z,t)}{z} - c_1(t) \right) - g(z, t) + M_0(t)z. \quad (4a)
$$

Here we use the equivalence $g(z = 1, t) = M_0(t)$, with $M_0(t)$ the cluster number density. As is often the case in these types of systems, it is more convenient to consider a modified generating function, $h(z, t) \equiv g(z, t) - g(1, t) = g(z, t) - M_0(t)$, in which the value at $z = 1$ is subtracted off. This generating function satisfies

$$
\dot{h}(z, t) = h^2(z, t) + \frac{1 - z}{z} h(z, t) + \frac{(1 - z)^2}{z} M_0(t). \quad (4b)
$$

While we have been unable to solve this differential equation in general, the time independent solution is

$$
h(z) = \frac{z - 1}{2z} \left( 1 - \sqrt{1 - 4M_0 z} \right), \quad (5)
$$

with $h(z) \equiv h(z, t = \infty)$, $M_0 \equiv M_0(t = \infty)$, and the sign of the radical is fixed by requiring that $h(z) \to -M_0$ as $z \to 0$. Once the value of $M_0$ is specified, the equilibrium solution, as well as the conditions for equilibrium to exist can be determined. From Eq. (5), we conclude that equilibrium exists whenever $4M_0 \leq 1$, while if $4M_0 > 1$, the power series representation of the generating function diverges and equilibrium is not reached. The unknown quantity $M_0$ can be related to the initial mass by the requirement that $z \frac{\partial h}{\partial z} \mid_{z=1} = M$, which is the total mass of the system, equals the initial mass $M$. This leads to the condition $M = (1 - \sqrt{1 - 4M_0})/2$, or equivalently, $M_0 = M(1 - \mathcal{M})$. Since $M_0$ must be in the range $(0, 1/4)$ for equilibrium to occur and since $M_0$ must be an increasing function of $M$, the corresponding constraint on the initial mass is $M \in (0, 1/2)$.

The equilibrium properties of the cluster size distribution can be obtained by expanding the generating function in Eq. (5) in powers of $z$ for $4M_0 \leq 1$. Thus the equilibrium cluster mass distribution, $c_k \equiv c_k(t = \infty)$, is given by

$$
c_k = \frac{1}{4\sqrt{\pi}} \left[ \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k + 1)} (4M_0)^k - \frac{\Gamma(k + \frac{1}{2})}{\Gamma(k + 2)} (4M_0)^{k+1} \right], \quad (6)
$$

where $\Gamma(z)$ is the gamma function. When $4M_0 < 1$ (equivalently, $\mathcal{M} < 1/2$), the asymptotic behavior of $c_k$ is dominated by $(4M_0)^k$ and the mass distribution decays exponentially in $k$. On the other hand, when $4M_0 = 1$ ($\mathcal{M} = 1/2$), the mass distribution has the power-law form

$$
c_k = \frac{3}{8\sqrt{\pi}} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k + 1/2)} \propto k^{-5/2}. \quad (7)
$$

The behavior of the moments of the mass distribution reflects the above two possibilities. Since all positive moments approach equilibrium values for $\mathcal{M} < 1/2$, a recursive
solution of the moment equations, Eq. (2), gives

\[
\begin{align*}
M_0 &= \mathcal{M}(1 - \mathcal{M}), \\
M_1 &= \mathcal{M}, \\
M_2 &= \frac{\mathcal{M}}{1 - 2\mathcal{M}}, \\
M_3 &= \frac{3\mathcal{M}(1 - \mathcal{M})}{2(1 - 2\mathcal{M})^3} - \frac{\mathcal{M}(1 + \mathcal{M})}{2(1 - 2\mathcal{M})}, \\
& \quad \vdots
\end{align*}
\]

(8)

On the other hand, for the limiting case of \( \mathcal{M} = 1/2 \) (\( M_0 = 1/4 \)), the power-law form of the cluster mass distribution leads to finite values of the moments \( M_n \) for \( n < 3/2 \) and diverging values for \( n \geq 3/2 \).

When \( \mathcal{M} > 1/2 \), an equilibrium solution of the rate equations does not exist and the transient behavior is of basic interest. To understand this behavior, it is helpful to first consider the equation of motion for \( M_2(t) \). For \( \dot{M}_2(t) \) to remain positive, \( M_0(t) \) must approach a constant whose value is greater than \( \mathcal{M}(1 - \mathcal{M}) \) as \( t \to \infty \) (Eq. (2)). This observation suggests that the cluster mass distribution breaks up into two components for \( \mathcal{M} > 1/2 \). In the scaling component, the typical cluster mass \( M_2(t) \) diverges as \( t \to \infty \). Conversely, the remaining non-scaling (equilibrium) component arises from the continued production of monomers by evaporation which attempts to maintain the number of clusters \( M_0 \) and the mass \( \mathcal{M} \) at their equilibrium values of 1/4 and 1/2, respectively. Thus the scaling part of the mass distribution should contain the remaining mass of \( \mathcal{M} - 1/2 \), while the number of clusters in this sub-population should decay to zero.

Since the non-scaling component of the mass distribution is given by Eq. (7), the corresponding contribution to \( M_n(t) \) is given by \( \dot{M}_n(t) \sim \sum_{k \leq t} k^{n-5/2} \sim t^{n-3/2} \) for \( n > 3/2 \), while \( \dot{M}_n(t) \to \text{const.} < \infty \) for \( n < 3/2 \). These estimates are based on the observation that the mass distribution approaches the steady-state form \( c_k \sim k^{-5/2} \) behind a leading edge which is growing linearly in time, while there are essentially no clusters of larger mass. To determine the relative contribution of the scaling component of the mass distribution to the moments, notice, from Eq. (2), that the typical cluster size \( M_2(t) \propto t \). This suggests that the ratio \( x \equiv k/t \) is the appropriate scaled mass with which one can express the scaling component of the mass distribution as

\[
c_k(t) = t^{-2} \Phi(x). \tag{9}
\]

The prefactor in Eq. (9) is needed to have a finite mass in this scaling part of the distribution. If we are interested only in the asymptotic behavior, then from Eq. (9), the contribution of this component of the mass distribution to the \( n^{th} \) moment is

\[
M_n(t) = t^{n-1} A_n, \quad \text{where} \quad A_n = \int_0^\infty dx \, x^n \Phi(x). \tag{10}
\]
As a result of these estimates, it is evident that the moments with \( n > 1 \) are dominated by the scaling component of the mass distribution. We therefore restrict ourselves to \( n > 1 \) and insert the above scaling expression into the moment equations. Again, retaining only the asymptotically relevant terms, Eqs. (2) are transformed into a system of equations for the amplitudes \( A_n \)

\[
(n - 1)A_n = (2M - 1)nA_{n-1} + \sum_{i=2}^{n-2} \binom{n}{i} A_i A_{n-i}, \quad n \geq 3.
\] (11)

To determine \( A_2 \), we use the third of Eqs. (2) together with the expected asymptotic value \( M_0 = 1/4 \). This gives \( A_2 = 2(M - \frac{1}{2})^2 \). To solve for the remaining \( A_n \) we introduce the generating function

\[
A(z) = \sum_{j=2}^{\infty} \frac{A_j}{j!} z^{j-1}.
\] (12)

It is then straightforward to transform the system (11) into the differential equation

\[
\frac{dA}{dz} = \left( A + M - \frac{1}{2} \right)^2.
\] (13)

Solving Eq. (13) yields

\[
A = \frac{(M - \frac{1}{2})^2 z}{1 - (M - \frac{1}{2}) z}
\] (14)

and therefore

\[
M_n(t) = n! \left( M - \frac{1}{2} \right)^n t^{n-1}.
\] (15)

From the moments given by (15), it is evident that the scaling component of the cluster mass distribution is

\[
c_k(t) = \frac{1}{(M - \frac{1}{2}) t^2} \exp \left[ -\frac{k}{(M - \frac{1}{2}) t} \right].
\] (16)

We therefore arrive at the same expression for the mass distribution as that which arises in pure aggregation with a constant reaction rate [1-4]. The only difference is that the mass which comprises the scaling component is equal to \( M - \frac{1}{2} \).

To summarize, in the weak aggregation regime, \( M < \frac{1}{2} \), the mass distribution approaches the equilibrium form of Eq. (6) at an exponential rate in time. In the complementary strong aggregation regime, \( M > \frac{1}{2} \), the typical mass grows linearly in time. However, there is an anomalous enhancement in the small-mass tail of the mass distribution which is of the form given in Eq. (7). This residue arises from the continued re-introduction of monomers into the system by evaporation.

At the critical point \( M = \frac{1}{2} \), a novel temporal behavior can be anticipated in which the approach to equilibrium occurs at a power-law, rather than an exponential rate. Let
us therefore hypothesize that the number of clusters, $M_0(t)$, approaches its equilibrium value of $1/4$ as $t^{-\nu}$. Employing this assumption in the moment equations gives the series of relations $M_2(t) \sim t^{1-\nu}$, $M_3(t) = \frac{1 + 3t}{2} \sim t$, $M_4(t) \sim t^{3-2\nu}$, $M_5(t) \sim t^{3-\nu}$, etc. Since the exponents of successive reduced moments should be equidistant within a scaling description, the condition $M_4/M_3 \sim M_3/M_2$, e.g., implies $\nu = \frac{2}{3}$. This suggests the general formula,

$$M_n(t) \sim t^{\frac{2n}{3} - 1}$$

for $n > \frac{3}{2}$, while for $n < \frac{3}{2}$ the moments approach finite values.

One can refine this analysis to obtain the amplitudes as well. Writing the expected asymptotic behavior as $M_n(t) = B_n t^{\frac{2n}{3} - 1}$ for $n > \frac{3}{2}$ and substituting into the moment equations, the $B_n$ satisfy recursion relations for integer $n$. Defining $B_0$ via $M_0(t) - \frac{1}{4} = B_0 t^{-2/3}$, we then find $B_2 = 6B_0$, $B_3 = \frac{3}{2}$, and

$$\left(\frac{2n}{3} - 1\right)B_n = \sum_{i=2}^{n-2} \binom{n}{i} B_i B_{n-i},$$

for $n \geq 4$. While we could not solve Eq. (18) generally, we can obtain partial information by a generating function approach. Indeed, introducing

$$B(z) = \sum_{j=2}^{\infty} B_j \frac{z^j}{j!}$$

transforms Eqs. (18) into a Riccati equation

$$\frac{dB}{dz} = B^2 + B_0 z^{-2/3} + \frac{1}{4}.$$  

While Eq. (20) is insoluble when $B_2 \neq 0$, several characteristics can be established without an explicit solution. In particular, the structure of Eq. (20) suggests that a solution exists for $z < z_c$ and it has form of a simple pole, $B(z) \simeq (z_c - z)^{-1}$, in the vicinity of $z = z_c$. Inversion of this singularity yields the large-$n$ behavior for every third amplitude, $B_{3n} \simeq 2(3n)!z_c^{-2n}$, while $B_{3n+1}$ and $B_{3n+2}$ are asymptotically negligible compared to $B_{3n}$. The location of the singularity, $z_c$, depends on the unknown amplitude $B_0$ and should be established from a more comprehensive treatment which, in turn, is equivalent to finding a complete solution of Eq. (20).

III. KINETICS OF AGGREGATION-CONDENSATION

(a) Mass Independent Growth Rate ($L_k = \text{const.}$)

We now consider the complementary reaction where bimolecular aggregation (with mass-independent aggregation rates), is supplemented by single-cluster growth in which a cluster of mass $k$ grows at a rate $L_k \propto k^\mu$. We wish to understand how this additional growth influences the kinetics of the underlying aggregation within the rate equations. Let
us first investigate this composite aggregation-condensation process for a size-independent
growth rate, \( L_k = \lambda \). The rate equations become

\[
\dot{c}_k(t) = \sum_{i,j} c_i(t) c_j(t) - 2c_k(t) \sum_{i=1}^{\infty} c_i(t) + \lambda (c_{k-1}(t) - c_k(t)).
\]  

(21)

To gain qualitative insight into the asymptotic behavior, we begin by solving for the first
few moments of the mass distribution. We then present a complete solution for the mass
distribution, from which the asymptotic behavior may be extracted.

From the above rate equations, the moments evolve according to

\[
\begin{align*}
\dot{M}_0(t) &= -M_0(t)^2, \\
\dot{M}_1(t) &= \lambda M_0(t), \\
\dot{M}_2(t) &= 2M_1(t)^2 + \lambda(2M_1(t) + M_0(t)), \\
&\vdots \\
\end{align*}
\]  

(22)

subject to the initial condition \( M_n(t = 0) = 1 \) for all \( n \). We also set the initial density
equal to unity so the condensation rate \( \lambda \) is the only control parameter. Solving for the
moments successively yields

\[
\begin{align*}
M_0(t) &= \frac{1}{1 + t}, \\
M_1(t) &= 1 + \lambda \ln(1 + t), \\
M_2(t) &= 1 + \lambda \ln(1 + t) + (4\lambda - 2\lambda^2)(1 + t) \ln(1 + t) \\
&\quad + 2\lambda^2(1 + t) \ln^2(1 + t) + 2(1 - \lambda + \lambda^2)t, \\
&\vdots \\
\end{align*}
\]  

(23)

Although the exact expressions for \( M_n(t) \) become cumbersome as the index \( n \) grows, the
asymptotic behavior is simply

\[
M_n(t) \sim n! \lambda^n t^{n-1} (\ln t)^n.
\]  

(24)

To solve the full rate equations we again introduce the generating function \( g(z, t) = \sum_{k=1}^{\infty} c_k(t) z^k \), which reduces an infinite set of rate equations (21) to the differential equation

\[
\dot{g}(z, t) = g(z, t)^2 - \frac{2}{1 + t} g(z, t) + \lambda(z - 1)g(z, t).
\]  

(25)

Notice that \( g(z, t)^{-1} \) satisfies a linear inhomogeneous differential equation whose solution is

\[
g(z, t) = \frac{ze^{\lambda(z-1)t}}{(1 + t)^2} \left[ 1 - z \int_0^t \frac{d\tau}{(1 + \tau)^2} e^{\lambda(z-1)\tau} \right]^{-1}.
\]  

(26)
We now determine the asymptotic behavior associated with this generating function. This information will also suggest the asymptotic form for the mass distribution for general rates of aggregation and condensation, a system for which an analytical solution cannot be found. First, notice that the densities $c_k(t)$ which make a non-zero contribution to the generating function are those whose mass is in the range $0 < (1 - z)k < 1$. If we further assume that $1 - z \gg (\lambda t)^{-1}$, then the integral in Eq. (26) can be approximated by replacing the exponential by unity; this is asymptotically correct over the domain of integration. The generating function now becomes

$$g(z, t) \sim (1 + t)^{-2} e^{-\lambda t} \frac{z e^{\lambda t z}}{1 - z}. \quad (27)$$

Expanding Eq. (27) gives,

$$c_{k+1}(t) \simeq \frac{(\lambda t)^k}{k!} - t^{-2} e^{-\lambda t}, \quad \text{for } 0 \leq k \ll \lambda t. \quad (28)$$

Thus for the range $k \ll \lambda t$, the mass distribution is Poissonian; however, the distribution cannot be written in the conventional scaling form $t^{-\alpha} \Phi(k/t^\beta)$.

On the other hand, for sufficiently large $k$, the mass distribution does exhibit scaling. To determine an appropriate mass scale we expand the exponent $e^{\lambda (z - 1) t}$, compute the integral in the right-hand side of Eq. (26), and then asymptotically balance the various terms. The nontrivial scaling limit arises when $(1 - z) \sim (t \ln t)^{-1}$ and suggests that the appropriate scaling variable is

$$\zeta = (1 - z) \lambda t \ln t, \quad (29)$$

instead of the original variables $z$ and $t$.

In the scaling limit, $t \to \infty$ and $1 - z \to 0$ with $\zeta$ kept fixed, the generating function simplifies to

$$g(z, t) \simeq t^{-1} (1 + \zeta)^{-1}, \quad (30)$$

and the mass distribution approaches the scaling form

$$c_k(t) \simeq \phi(t) \Phi(x), \quad \text{with } x = \frac{k}{\lambda t \ln t}, \quad (31)$$

with the prefactor $\phi(t)$ and scaling function $\Phi(x)$ to be determined. Making use of Eqs. (29) and (31), we express the generating function in terms of $\phi(t)$ and $\Phi(x)$ as,

$$g(z, t) = \sum z^k c_k(t) = \sum \left(1 - \frac{\zeta}{\lambda t \ln t}\right)^k c_k(t) \simeq \lambda t \ln t \phi(t) \int_0^\infty \Phi(x)e^{-x\zeta} dx. \quad (32)$$

Finally, by comparing Eqs. (30) and (32) and performing the inverse Laplace transform, the prefactor $\phi(t)$ and the scaling function $\Phi(x)$ are

$$\phi(t) = \frac{1}{\lambda t^2 \ln t}, \quad \text{and } \Phi(x) = e^{-x}. \quad (33)$$
The scaling solution of Eqs. (31) and (33) agrees with asymptotic expression for the moments (24).

For completeness, we also investigate the large-mass tail of the mass distribution, \( k \gg \lambda t \ln t \). The analysis is similar to that given above so we merely cite the result

\[
    c_k(t) \sim \left(1 - \frac{1}{\lambda t \ln t}\right)^k. \tag{34}
\]

Thus the mass distribution function does not scale in both the small- and large-mass tails. Formally, the condensation process governs the small-mass tail of the distribution, as well as the overall mass. Conversely, the form of the distribution in the scaling region and in the large-mass tail is determined solely by the aggregation process.

(b) Growth Rate Proportional to the Mass \((L_k \propto k)\)

We now consider the case of a condensation rate which is linear in the mass, \( i.e., \) the rate of \( c_k \rightarrow c_{k+1} \) equals \( \lambda k \). The corresponding rate equations are

\[
    \dot{c}_k(t) = \sum_{i,j} c_i(t)c_j(t) - 2c_k(t) \sum_{i=1}^{\infty} c_i(t) + \lambda \left[(k-1)c_{k-1}(t) - kc_k(t)\right]. \tag{35}
\]

Employing the generating function \( g(z, t) \), Eq. (35) becomes

\[
    \frac{\partial}{\partial t} g(z, t) = g(z, t)^2 - 2g(z, t)M_0(t) + \lambda z (1 - z) \frac{\partial}{\partial z} g(z, t). \tag{36}
\]

Notice that the number of clusters \( M_0(t) \equiv g(z = 1, t) \) still satisfies \( \dot{M}_0(t) = -M_0(t)^2 \); hence, \( M_0(t) = (1 + t)^{-1} \). Introducing again the modified generating function, \( h(z, t) = g(z, t) - M_0(t) \), transforms Eq. (36) into a linear equation for \( h(z, t)^{-1} \)

\[
    \frac{\partial}{\partial t} h(z, t)^{-1} + \lambda z (1 - z) \frac{\partial}{\partial z} h(z, t)^{-1} + 1 = 0. \tag{37}
\]

By introducing \( w = \frac{1}{\lambda} \ln \frac{z}{1 - z} \), Eq. (37) becomes a first-order wave equation in the variables \((w, t)\). This equation further simplifies by transforming from \((w, t)\) to \( u = t + w \) and \( v = t - w \) to yield

\[
    \frac{\partial}{\partial u} h(u, v)^{-1} = -\frac{1}{2}, \tag{38}
\]

with solution \( h(u, v)^{-1} = -\frac{u}{2} + f(v) \). Here \( f(v) \) is fixed by the initial conditions. For example, for monodisperse monomer-only initial conditions, we obtain

\[
    h(u, v)^{-1} = -1 - \frac{u + v}{2} - e^{-\lambda v} = -1 - t - e^{-\lambda t} \frac{z}{1 - z}. \tag{39}
\]

By now expanding \( g(z, t) = h(z, t) + \frac{1}{1 + t} \) in powers of \( z \) the exact concentrations are,

\[
    c_k(t) = \frac{e^{-\lambda t}}{(1 + t)^2} \left(1 - \frac{e^{-\lambda t}}{1 + t}\right)^{k-1}. \tag{40}
\]
In the scaling region, \( k \to \infty \) and \( t \to \infty \) with \( x = k/te^{\lambda t} \) finite, Eq. (40) has the asymptotic form

\[
c_k(t) \simeq t^{-2}e^{-\lambda t}e^{-x}. \tag{41}
\]

Notice that the scaling solution for the mass distribution in both the cases of \( \mu = 0 \) and \( \mu = 1 \) may be written as

\[
c_k(t) \simeq \frac{M_0(t)^2}{M_1(t)} e^{-x}, \quad \text{with} \quad x = \frac{M_0(t)}{M_1(t)} k. \tag{42}
\]

Although the mass density, \( M_1(t) \), has a very different time dependence for these two cases, the respective scaling functions are the same and in fact identical to that in pure aggregation with a constant aggregation rate [1-4].

(c) General Mass Dependent Growth Rate \( (L_k \propto k^\mu) \)

We now turn to aggregation-condensation for a general homogeneous mass-dependent cluster growth rate, \( L_k = \lambda k^\mu \), with \( 0 < \mu < 1 \). Although it does not appear possible to solve the governing rate equations, one expects the scaling form of Eq. (42) to hold in the scaling region. This assumption reduces the problem to finding the first two moments, \( M_0(t) \) and \( M_1(t) \). The former task is trivial since the condensation process does not alter the evolution of the number of clusters, and \( M_0(t) = (1 + t)^{-1} \). On the other hand, \( M_1(t) \) is determined by \( \dot{M}_1(t) = \lambda M_1(t)^\mu M_0(t)^{1-\mu} \) which is coupled to an undetermined moment. Fortunately, in the long-time limit we can use the scaling form (42) to estimate \( M_\mu(t) \) as

\[
M_\mu(t) = \sum_{k=1}^{\infty} k^\mu c_k(t) \simeq \left( \frac{M_1(t)}{M_0(t)} \right)^{\mu+1} \frac{M_0(t)^2}{M_1(t)} \int_0^{\infty} dx x^\mu e^{-x} = \Gamma(1+\mu)M_1(t)^\mu M_0(t)^{1-\mu}. \tag{43}
\]

Thus asymptotically \( \dot{M}_1(t) \simeq \lambda \Gamma(1+\mu)t^{\mu-1}M_1(t)^\mu \), which may be solved to yield

\[
M_1(t) \simeq At^{1-\mu}, \quad \text{with} \quad A = [\lambda (1-\mu) \Gamma(\mu)]^{1-\mu}. \tag{44}
\]

It is instructive to compare this asymptotic result for the typical cluster size,

\[
S(t) = \frac{M_1(t)}{M_0(t)} = At^{1-\mu}, \tag{45}
\]

with a naive estimate provided by considering growing, but 

noninteracting, i.e., non-aggregating, clusters. This latter estimate follows from \( \dot{S}(t) = \lambda S(t)^\mu \), which implies

\[
S(t) = A_0 t^{1/\mu}, \quad \text{with} \quad A_0 = [\lambda (1-\mu)]^{1/\mu}. \tag{46}
\]

Therefore the system with growing but non-interacting droplets provides the correct exponent of the time dependence for the droplet growth rate in the interacting system. However, the corresponding prefactor \( A_0 \) is slightly smaller than that of the interacting system.
(d) Scaling Approach for Low Spatial Dimension

For diffusion-controlled aggregation, the above mean-field approaches are typically not applicable for spatial dimension \( d \leq 2 \) (see, e.g., [16,17]). However, for the aggregation-condensation process with a homogeneous growth rate, \( L_k \propto k^\mu \) \((0 \leq \mu < 1)\), it is possible to infer partial results for \( d \leq 2 \) by applying scaling and exploiting known results. In particular, for diffusion-controlled aggregation with a mass-independent cluster diffusivity, the density of clusters (which is not altered by the condensation process) is [16,17]

\[
M_0(t) \sim \begin{cases} 
  t^{-d/2}, & d < 2; \\
  \ln t, & d = 2.
\end{cases}
\]

We now again assume that asymptotically the mass distribution approaches the scaling form

\[
c_k(t) \simeq \frac{M_0(t)^2}{M_1(t)} \Phi_d(x), \quad \text{with} \quad x = \frac{M_0(t)}{M_1(t)} k,
\]

with a general \( d \)-dependent scaling function \( \Phi_d(x) \). The mass density, \( M_1(t) \), is determined from \( \dot{M}_1(t) = \lambda M_\mu(t) \), where the moment \( M_\mu(t) \) is estimated to be (following the steps of the previous subsection),

\[
M_\mu(t) \simeq M_0(t)^{1-\mu} M_1(t)^\mu \int_0^\infty dx x^\mu \Phi_d(x).
\]

Ignoring numerical factors we solve for the mass density to obtain

\[
M_1(t) \sim \begin{cases} 
  t^{\frac{1-\mu}{2}}, & d < 2, \ 0 \leq \mu < 1; \\
  t^{\frac{1-\mu}{2}} \ln t, & d = 2, \ 0 \leq \mu < 1; \\
  \ln^2 t, & d = 2, \ \mu = 0.
\end{cases}
\]

Finally, combining Eqs. (47), (48), and (50) yields

\[
c_k(t) \sim \begin{cases} 
  t^{-\frac{1}{2}} \Phi_d(x), & d < 2, \ 0 \leq \mu < 1; \\
  t^{-\frac{1}{2}} \ln t \Phi_2(x), & d = 2, \ 0 \leq \mu < 1; \\
  t^{-2} \Phi_2(x), & d = 2, \ \mu = 0.
\end{cases}
\]

in all three cases, the scaling variable is \( x = kt^{-1/(1-\mu)} \).

(e) Exact Solution in One Dimension for \( L_k \propto k \)

We now solve the aggregation-condensation process in one dimension when the cluster growth rate is linear in the mass \((L_k \propto k)\) and the diffusivity of each cluster is mass independent, a case particularly amenable to exact analysis. The model is defined on the real line which is populated by point clusters which: (i) diffuse with a mass independent diffusivity \( D \), (ii) grow with a rate proportional to their masses, and (iii) aggregate irreversibly whenever two clusters meet. A convenient way to treat this problem analytically is to introduce [18] the quantity \( P_k(x,t) \), which is the probability that the total mass of
all clusters contained in an interval of length $x$ at time $t$ is equal to $k$. The evolution of the $P_k(x, t)$ are uncoupled and each such function obeys the diffusion equation [18]. If we account for condensation, the $P_k(x, t)$ now evolve according to

$$\frac{\partial}{\partial t} P_k(x, t) = 2D \frac{\partial^2}{\partial x^2} P_k(x, t) + \lambda \left[ (k - 1) P_{k-1} - kP_k \right].$$  \hspace{1cm} (52)

The second term clearly accounts for the change in mass in the interval due to the cluster growth process. The cluster concentrations, $c_k(t)$, are then found from

$$c_k(t) = \frac{\partial}{\partial x} P_k(x = 0, t).$$  \hspace{1cm} (53)

Note also the sum rule, $\sum_{k=0}^{\infty} P_k(x, t) \equiv 1$, which allows us to focus on the $P_k$'s with $k \geq 1$.

To solve this system, we introduce the generating function,

$$P(z, x, t) = \sum_{k=1}^{\infty} z^k P_k(x, t),$$  \hspace{1cm} (54)

to transform Eq. (52) into

$$\frac{\partial P}{\partial t} = 2D \frac{\partial^2 P}{\partial x^2} + \lambda z (z - 1) \frac{\partial P}{\partial z}.$$  \hspace{1cm} (55)

Note that the obvious boundary condition, $P_k(x = 0) = \delta_{k0}$, translates to the condition on the generating function, $P(x = 0) = 0$. If initially the system is composed of monomers which have a Poissonian distribution of positions with density unity, the corresponding initial condition is

$$P_k(t = 0) = \frac{x^k}{k!} e^{-x}, \quad \mathcal{P}(t = 0) = e^{-x(1-z)} - e^{-x}.$$  \hspace{1cm} (56a)

Although the variable $x$ is defined only on the half-line $x \geq 0$, it proves useful to consider Eq. (55) for $-\infty < x < \infty$, and impose the initial condition

$$\mathcal{P}(t = 0) = e^x - e^{x(1-z)}, \quad \text{for} \quad x < 0.$$  \hspace{1cm} (56b)

With this antisymmetric initial data, the boundary condition $\mathcal{P}(x = 0) = 0$ is manifestly satisfied.

Employing the auxiliary variables $u = t + \frac{1}{\lambda} \ln \frac{z}{1-z}$ and $v = t - \frac{1}{\lambda} \ln \frac{z}{1-z}$ introduced earlier, we further simplify Eq. (55) to the diffusion equation

$$\frac{\partial \mathcal{P}}{\partial u} = D \frac{\partial^2 \mathcal{P}}{\partial x^2},$$  \hspace{1cm} (57)
subject to the initial conditions
\[ \mathcal{P}|_{u=-v} = e^{-x/(1+e^{-\lambda v})} - e^{-x}, \quad \text{for } x > 0, \]
\[ \mathcal{P}|_{u=-v} = e^x - e^{x/(1+e^{-\lambda v})}, \quad \text{for } x < 0. \] (58)

Solving Eq. (57) with the above initial conditions yields
\[ \mathcal{P}(u, v, x) = \frac{1}{\sqrt{4\pi D(u+v)}} \int_0^\infty d\xi e^{-\xi} \left[ \exp\left( \frac{\xi}{1 + e^{\lambda v}} \right) - 1 \right] \times \left[ \exp\left( -\frac{(x-\xi)^2}{4D(u+v)} \right) - \exp\left( -\frac{(x+\xi)^2}{4D(u+v)} \right) \right]. \] (59)

Returning to the original variables we find
\[ \mathcal{P}(z, x, t) = \frac{1}{\sqrt{8\pi Dt}} \int_0^\infty d\xi e^{-\xi} \left[ \exp\left( \frac{\lambda t - z}{z} \right) - 1 \right] \times \left[ \exp\left( -\frac{(x-\xi)^2}{8Dt} \right) - \exp\left( -\frac{(x+\xi)^2}{8Dt} \right) \right]. \] (60)

Combining Eq. (60) with Eq. (53) gives
\[ \sum_{k=1}^\infty z^k c_k(t) = \frac{1}{\sqrt{32\pi (Dt)^3}} \int_0^\infty d\xi \xi \exp\left( -\frac{\xi^2}{8Dt} \right) \left[ \exp\left( \frac{\xi}{1 + e^{\lambda t (\frac{1-z}{z})}} \right) - 1 \right]. \] (61)

Eq. (61) is the formal solution to the problem – for example, the concentrations can be found by expanding the right-hand side in powers of \( z \). However, explicit expressions for the concentrations \( c_k(t) \) are cumbersome, even for small \( k \). In contrast, the moments of the mass distribution have simpler form. For example,
\[ M_0(t) = \frac{1}{\sqrt{32\pi (Dt)^3}} \int_0^\infty d\xi \xi \exp\left( -\frac{\xi^2}{8Dt} \right) (1 - e^{-\xi}) \approx \frac{1}{\sqrt{2\pi Dt}}. \] (62)

in agreement with the known result [19]. Furthermore, the mass density is given by \( M_1(t) = e^{\lambda t} \). This is expected since \( M_1(t) \) satisfies \( \dot{M}_1(t) = \lambda M_1(t) \). These two moments provide a useful consistency check of our exact results.

IV. SUMMARY AND DISCUSSION

Our primary result was to elucidate the broad range of phenomenology which arises from the combined effects of: (a) aggregation with evaporation, and (b) aggregation with condensation. In the former case, the interesting situation is that of mass independent rates of aggregation and evaporation in a mass conserving system. An equilibrium state
is reached for sufficiently strong evaporation, while the kinetics is essentially identical to that of pure aggregation when the evaporation is relatively weak. At a critical evaporation rate, there is power-law kinetics in which the typical cluster size grows as $t^{2/3}$, while the mass distribution decays with mass $k$ as $k^{-5/2}$. An essential ingredient in these results is that the aggregation and evaporation rates are of the same order, so that their competition leads to interesting manifestations. Related transition behavior was obtained for combined aggregation-evaporation by Virgil et al. [10], but with both a mass-dependent aggregation rate (proportional to the product of the cluster masses) and evaporation rate (proportional to the cluster mass). For this latter system, the effects of evaporation and aggregation are, in some sense, of the same order of magnitude, leading to a transition between equilibrium and gelation for a critical value of the ratio of the two rates and also distinct power-law behavior at the transition. Another not entirely unrelated example where microscopic effects influence the approach to equilibrium occurs in the one-dimensional reversible reaction $A + A \leftrightarrow A$ [20]. In this case, the relaxation has different functional forms depending on the ratio of the initial density to the final equilibrium density.

For aggregation with condensation, the cluster growth enhances the aggregation, as expected. When the growth rate is independent of cluster mass, this enhancement is relatively weak, however, and the typical cluster mass grows with time as $t \ln t$, compared to a linear growth for aggregation with no condensation. Conversely when the growth rate is proportional to the mass, the typical mass grows exponentially in time. In the intermediate case of a growth rate for clusters of mass $k$ given by $L_k \propto k^\mu$, with $0 < \mu < 1$, a scaling approach indicates that the typical cluster mass grows as $t^{1/(1-\mu)}$, while the scaling function in the mass distribution is a pure exponential for $0 \leq \mu \leq 1$.

Our aggregation-condensation model is related to breath figures [14,15] as well as to other models of droplet growth and coalescence [6]. In these latter systems, the growth rate of individual droplets is generally a specified function of time, rather than of the mass. If one assumes that the mass of individual droplets grow $t^\alpha$, then the typical cluster mass in the combined aggregation-condensation system grows at a faster rate of $t^\beta$, with $\beta = D\alpha/(D - d)$. Here $D$ is the spatial dimension of the droplets and $d$ (which must be smaller than $D$) is the dimensionality of the substrate. It would interesting to understand what relation, if any, exists between these results and our model of aggregation with explicit mass-dependent cluster growth.

The rate equation approach is expected to provide the correct asymptotic behavior for aggregation-condensation when the spatial dimension $d$ is greater than 2 [16,17]. To extend our understanding to $d \leq 2$, a simple-minded approach was developed which suggests that conventional scaling continues to apply. Furthermore, we derived an exact solution for aggregation-condensation in one dimension with a growth rate linear in the cluster mass, $L_k \propto k$, and with a mass-independent diffusivity. The scaling predictions are in satisfying agreement with this exact solution.
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