Transitional aggregation kinetics in dry and damp environments

P. L. Krapivsky[1,2] and S. Redner[2]
[1]*Courant Institute of Mathematical Sciences, New York University, New York, New York 10012-1185*
[2]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*
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We investigate the kinetics of constant-kernel aggregation which is augmented by (a) evaporation of monomers from clusters, which is termed aggregation in a ''dry'' environment, and (b) continuous cluster growth or condensation, termed aggregation in a ''damp'' environment. The rate equations for these two processes are analyzed using both exact and asymptotic methods. In dry aggregation, mass conserving evaporation is treated, in which the monomers which evaporate remain in the system and continue to be reactive. For this reaction process, the competition between evaporation and aggregation leads to several asymptotic outcomes. When the evaporation is weak, the kinetics is similar to that of aggregation with no evaporation, while a steady state is quickly reached in the opposite case. At a critical evaporation rate, a steady state is slowly reached in which the cluster mass distribution decays as $k^{-5/2}$, where k is the mass, while the typical cluster mass, or upper cutoff in the mass distribution, grows with time as $t^{2/3}$. For damp aggregation, several cases are considered for the dependence of the cluster growth rate L_k on k. (i) For L_k independent of k, the mass distribution attains a conventional scaling form, but with the typical cluster mass growing as $t \ln t$. (ii) When $L_k \propto k$, the typical mass grows exponentially in time, while the mass distribution again scales. (iii) In the intermediate case of $L_k \propto k^{\mu}$, scaling generally applies, with the typical mass growing as $t^{1/(1-\mu)}$. The scaling approach is also adapted to treat diffusion-limited damp aggregation for spatial dimension $d \leq 2$. [S1063-651X(96)10210-5]

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I. INTRODUCTION

Aggregation, fragmentation, and condensation underlie a variety of natural nonequilibrium phenomena [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 rates 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 in a closed system and its characterization 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 $c_i + c_j \to c_{i+j}$, where c_k is the concentration of clusters of mass k, and F_{ij} denotes the fragmentation rate of $c_{i+j} \to c_i + c_j$, then detailed balance gives $K_{ij}\overline{c}_i\overline{c}_j = F_{ij}\overline{c}_{i+j}$, where $\overline{c}_k$ is the steady-state concentration of k-mers.

A related situation in which the evolution is driven by both aggregation and fragmentation is polymer chain growth kinetics [12,13], in which k-mers may be unstable to breakoff of monomers—i.e., evaporation—while all other fragmentation events are forbidden. With these restrictions, the process may be viewed as aggregation in a ''dry'' environment. Because the fragmentation matrix F_{ij} has mostly zero elements, detailed balance can no longer determine the asymptotic state of the system. One of our goals is to investigate the kinetics of a simple version of this combined aggregation-evaporation process in the rate equation approximation.

A crucial feature of this system is that the monomers which have evaporated remain in the system and continue to be reactive [Fig. 1(a)]. Physically, this can be achieved by enclosing the system in a box which prevents the escape of material. (In an open system, evaporation eventually dominates leading to a trivial final state of a completely evaporated system.) We consider the generic case where the aggregation rate is independent of the masses of the two incident clusters. This situation nicely illustrates the interesting features that arise from the competition between aggregation and evaporation. If the evaporation is sufficiently strong (which occurs for small concentrations of clusters), its dominance over the effects of aggregation results in a steady state in which the cluster mass distribution decays exponentially in the mass. In the opposite case where aggregation dominates, the typical cluster mass increases linearly in time for an infinite system. Qualitatively, the effect of evaporation is to continuously reintroduce the evaporated monomers into the system, leading to a cluster mass distribution which contains both a vestige of the steady-state distribution and a transient component which is associated with the growing clusters. At a critical value of the evaporation rate, there is a relatively slow evolution toward a steady state in which the cluster mass distribution decays as $k^{-5/2}$. This power law is produced by a slow evolution of the cluster mass distribution in which the typical mass grows with time as $t^{2/3}$. These intriguing features emerge from exact solutions to the rate

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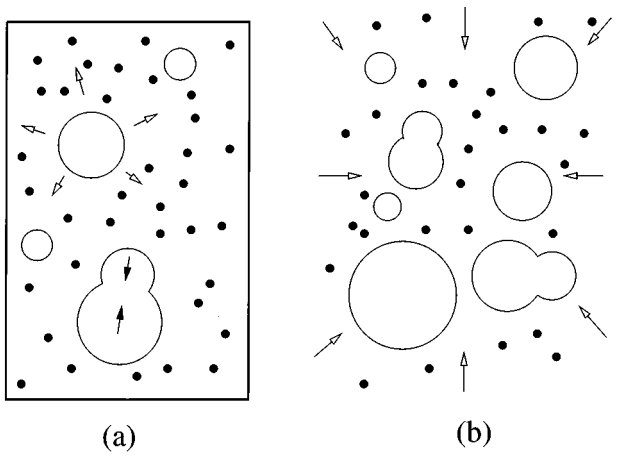

FIG. 1. Schematic illustration of (a) dry aggregation and (b) damp aggregation. Monomers are indicated by small dots, while clusters are indicated by larger circles. In dry aggregation, monomers which evaporate from clusters continue to participate in additional reactions in a closed system. Damp aggregation can be viewed as arising from the continued input of monomers. Consequently clusters can increase in size by either the addition of monomers (continuous growth) or by aggregation.

equations and asymptotic arguments.

The unusual kinetics exhibited by dry aggregation is indicative of the fact that constant-kernel aggregation is sensitive to perturbative influences on the dynamics of the monomers. In particular, sufficiently rapid evaporation of monomers stops the growth of clusters and leads to a steady state. This observation leads us to consider a complementary situation where monomers are continuously added to an aggregating system. We may view this continuous addition of monomers as aggregation in a "damp" environment [Fig. 1(b)]. Such a process naturally arises in various contexts, such as the growth of breath figures and in 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. When this is combined with the effects of the aggregation, the composite aggregation-condensation process exhibits a faster growth law than the underlying single particle growth rate. It is this feature of enhanced cluster growth that we wish to quantify.

For this purpose, we find it more convenient and realistic to consider a version of the condensation process in which the droplet growth rate is a function of the cluster size only, and not of the time. Normally, the growth rate of an individual cluster in a monomer-rich environment would be proportional to its surface area. However, the influence of the condensation already becomes apparent for a much weaker growth rate which is independent of the cluster size. This motivates us to consider the general situation where the cluster growth rate is proportional to k^{μ} (with $0\leq\mu\leq 1$). Within a rate equation description, we find a rich range of kinetic behavior for the cluster mass distribution. When the condensation rate is independent of the cluster mass ($\mu=0$), the distribution of cluster masses obeys conventional scaling, but with the typical mass that grows as $t\ln t$. On the other hand, for a condensation rate which is proportional to the mass ($\mu=1$), the typical mass grows as e^{t}, while for general $0<\mu<1$, the typical mass grows as $t^{1/(1-\mu)}$. For all three cases, i.e., $0\leq\mu\leq 1$, a scaling approach further predicts that the mass distribution decays exponentially with mass.

On a more descriptive level, both dry and damp aggregation involve bimolecular and unimolecular reaction channels. Thus for damp aggregation with a small initial concentration, the unimolecular growth process dominates initially but eventually the concentration becomes large enough so that the bimolecular aggregation process comes into play. Since the typical cluster mass grows indefinitely in damp aggregation, scaling should generally apply, a feature which greatly simplifies the analysis. For dry aggregation, however, even when the typical cluster mass grows indefinitely, conventional scaling does not strictly apply because the concentration of clusters of any fixed mass approaches a finite positive value rather than vanishing. In spite of this complicating feature, the analysis of both dry and damp aggregation has many common technical aspects. A detailed treatment of these two cases is presented in the following two sections.

II. DRY AGGREGATION

The rate equations for mass conserving dry aggregation are,

$$\dot{c}_k(t)=\frac{1}{2}{\sum_{i,j}}' K_{ij}c_i(t)c_j(t)-c_k(t)\sum_{i=1}^{\infty}K_{ki}c_i(t)$$
$$+[L_{k+1}c_{k+1}(t)-L_kc_k(t)]+\delta_{k,1}\sum_{i=1}^{\infty}L_ic_i(t). \tag{1a}$$

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 mass conservation restriction, $i+j=k$. 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 therefore described by the third and fourth terms of Eq. (1a). 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 and the mass would disappear exponentially in time.)

Let us now determine the conditions for which the system either reaches steady state 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 ($\mu=0$). 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 treat mass-dependent aggregation and evaporation rates, their relative influences are typically of different orders of magnitude. Consequently, it is relatively straightforward to anticipate whether a steady state or a scaling distribution arises. However, for mass-independent aggregation and evaporation, the competition between these two influences is subtle and gives rise to surprisingly rich kinetic behavior.

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

$$\dot{c}_k(t)=\frac{1}{2}\sum_{i,j}{}' Kc_i(t)c_j(t)-c_k(t)\sum_{i=1}^{\infty} Kc_i(t)$$

$$+\lambda[c_{k+1}(t)-c_k(t)]+\lambda\delta_{k,1}\sum_{i=1}^{\infty} c_i(t). \quad (1b)$$

The evaporation rate λ and reaction rate K can be absorbed by redefining the concentrations and time by $c_k(t)\to 2\lambda c_k(t)$ and $t\to t/\lambda K$, 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 $\mathcal{M}$ 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 the moments of the mass distribution, $M_n(t)\equiv\Sigma_{k\geq 1}k^n c_k(t)$. By straightforward manipulations on Eq. (1c), these moments satisfy

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

For the monomer-only initial condition, $M_n(t=0)=\mathcal{M}$ for all n; additionally, by construction $M_1(t)\equiv\mathcal{M}$ for all $t\geq 0$. The equations for $M_n(t)$ for $n\geq 2$ indicate that the typical mass and higher moments grow indefinitely, if the initial mass is sufficiently large. In the complementary case, however, a steady 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 equality $g(z=1,t)=M_0(t)$, with $M_0(t)$ the cluster number density. As is often the case in these types of systems [3,4], 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. 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 steady-state solution, as well as the conditions for a steady state to exist, can be determined. From Eq. (5), we conclude that stationary behavior arises whenever $4M_0\leq 1$, while if $4M_0>1$, the power series representation of the generating function diverges and a stationarity is not reached. The unknown quantity M_0 can be related to the initial mass by the requirement that $z\partial h/\partial z|_{z=1}$, which is the total mass of the system, equals the initial mass $\mathcal{M}$. This leads to the condition $\mathcal{M}=(1-\sqrt{1-4M_0})/2$, or equivalently, $M_0=\mathcal{M}(1-\mathcal{M})$. For a steady state to occur, $\mathcal{M}$ must be real, leading to M_0 being restricted to the range $(0,\frac{1}{4})$. As M_0 increases from 0 to $\frac{1}{4}$, $\mathcal{M}$ correspondingly increases from 0 to $\frac{1}{2}$. From this it immediately follows that M_0 is an increasing function of $\mathcal{M}$, with the latter quantity restricted to the range $(0,\frac{1}{2})$ in the steady state.

The properties of the cluster size distribution in the steady state can be obtained by expanding the generating function in Eq. (5) in powers of z for $4M_0\leq 1$. This gives, for $c_k(t=\infty)$,

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

where $\Gamma(z)$ is the gamma function. When $4M_0<1$ (equivalently, $\mathcal{M}<\frac{1}{2}$), 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 $4M_0=1(\mathcal{M}=\frac{1}{2})$, the mass distribution has the power-law form

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

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

$$
\begin{aligned}
M_0 &= \mathcal{M}(1-\mathcal{M}),\\
M_1 &= \mathcal{M},\\
M_2 &= \frac{\mathcal{M}}{1-2\mathcal{M}},\\
M_3 &= \frac{3\mathcal{M}(1-\mathcal{M})}{2(1-2\mathcal{M})^3} - \frac{\mathcal{M}(1+\mathcal{M})}{2(1-2\mathcal{M})},\\
&\vdots
\end{aligned}
\tag{8}
$$

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

When $\mathcal{M}>\frac{1}{2}$, a stationary solution of the rate equations does not exist and the transient behavior is of basic interest. To determine this behavior, it is helpful to first recall the transient behavior in the simpler case of pure aggregation [1,2]. The Smoluchowski rate equations admit only one steady-state solution, namely, $c_k=0$ for all k, corresponding to an empty system. In a sense, the transient solution of Smoluchowski rate equations can be regarded as approaching this steady state, that is, $c_k(t)\to 0$ as $t\to\infty$ for any *fixed* k. Notice, however, that the transient solutions contain a constant *positive* total mass density, $\sum k c_k(t)=\text{const}>0$, while the (empty) steady state contains zero mass density.

In the case of dry aggregation, an analogous behavior may be expected, i.e., the transient solution approaches some steady state. The difficulty is that there exists a continuum of possible steady states which are characterized by different values of $\mathcal{M}$. We *assume* that the transient solution converges to the extreme steady state given by Eq. (7) which contains the maximum possible mass density. This assumption, in particular, implies that $M_0\equiv M_0(t=\infty)$, when written as a function of $\mathcal{M}$, is

$$
M_0 = \begin{cases} \mathcal{M}(1-\mathcal{M}) & \text{if } \mathcal{M}\leq\frac{1}{2},\\ \frac{1}{4} & \text{if } \mathcal{M}\geq\frac{1}{2}. \end{cases}
\tag{9}
$$

This feature that a nonlinear system selects the marginal solution from a continuous family of potential solutions arises in a wide variety of physical situations [16]. While we are unable to demonstrate the validity of the marginal solution hypothesis directly, notice that if the transient solution were to approach another steady state, the dependence of the number of clusters on mass, $M_0=M_0(\mathcal{M})$, would be pathological. It is possible that for some pathological initial conditions, the transient solution which contains the total mass density $\mathcal{M}>\frac{1}{2}$ will approach some steady state which contains the total mass density $\mathcal{M}<\frac{1}{2}$. However, the basins of attraction of these "light" steady states are expected to be negligible compared to the basin of attraction of the extreme steady state (7). This scenario is confirmed by our numerical simulations.

If the transient solution does approach the steady state (7), there then remains a cluster subpopulation, which we refer to as the scaling part of the distribution, which contains the difference $\mathcal{M}-\frac{1}{2}$ between the total mass and the steady-state distribution. That is, the total concentration should have the form $c_k(t)=c_k(\infty)+c_k^{\text{scal}}(t)$, with the stationary component $c_k(\infty)$ given by Eq. (7) and the scaling component $c_k^{\text{scal}}(t)$ to be determined. The number of clusters in the latter subpopulation should ultimately decay to zero, thus playing an analogous role to the transient solution in pure aggregation. While we are unable to verify the correctness of this form by direct substitution into the rate equations, we can validate the intuition that the transient subpopulation, in some sense, scales. To see this, let us return to Eqs. (2) and consider the case of $\mathcal{M}>\frac{1}{2}$. As we have previously argued, $M_0(t)\to\frac{1}{4}$. By inserting this into Eqs. (2) and solving for the moments asymptotically, we obtain $M_2(t)\to 2(\mathcal{M}-\frac{1}{2})^2 t$, $M_3(t)\to 6(\mathcal{M}-\frac{1}{2})^3 t^2$, suggesting $M_n(t)\to n!(\mathcal{M}-\frac{1}{2})^n t^{n-1}$. To derive this result more rigorously, let us suppose that asymptotically the moments exhibit power-law behavior,

$$
M_n(t) = t^{n-1} A_n .
\tag{10}
$$

Substituting Eq. (10) into the moment equations and retaining only the asymptotically relevant terms, Eqs. (2) are transformed into a system of equations for the amplitudes A_n,

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

We have already found $A_2=2(\mathcal{M}-\frac{1}{2})^2$. To solve for the remaining A_n we introduce the generating function,

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

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

$$
\frac{d\mathcal{A}}{dz} = (\mathcal{A}+\mathcal{M}-\tfrac{1}{2})^2,
\tag{13}
$$

whose solution is

$$
\mathcal{A} = \frac{(\mathcal{M}-\frac{1}{2})^2 z}{1-(\mathcal{M}-\frac{1}{2})z}.
\tag{14}
$$

Therefore,

$$
M_n(t) = n!(\mathcal{M}-\tfrac{1}{2})^n t^{n-1},
\tag{15}
$$

in agreement with what we anticipated previously. From the time dependence of the moments, it is evident that the scaling component of the cluster mass distribution is of the form $c_k^{\text{scal}}(t)=t^{-2}\Phi(x)$, where $x\equiv k/t$ is the scaled mass. The precise form of Eq. (15) gives the Mellin transform of the scaling function $\Phi(x)$. Performing the inverse Mellin transform we finally obtain

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

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 $\mathcal{M}-\frac{1}{2}$. The remaining mass is contained in the residual steady-state distribution of Eq. (7).

Note also that Eq. (15) correctly describes the asymptotic behaviors of the moments only for $n>1$. When $n<1$ the steady-state component dominates over the scaling component and the moments approach constant values.

To summarize, in the strong evaporation or weak aggregation regime, $\mathcal{M}<\frac{1}{2}$, the mass distribution approaches the stationary form of Eq. (6) at an exponential rate in time. In the complementary weak evaporation regime, $\mathcal{M}>\frac{1}{2}$, 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 reintroduction of monomers into the system by evaporation.

At the critical point $\mathcal{M}=\frac{1}{2}$, a novel temporal behavior can be anticipated in which the approach to a steady state occurs at a power law, rather than an exponential rate. Let us therefore hypothesize that the cluster number density, $M_0(t)$, approaches its stationary value of $\frac{1}{4}$ as $t^{-\nu}$. Employing this assumption in the moment equations gives the series of relations $M_2(t)\sim t^{1-\nu}$, $M_3(t)=(1+3t)/2\sim t$, $M_4(t)\sim t^{3-2\nu}$, $M_5(t)\sim t^{3-\nu}$, 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

$$M_n(t)\sim t^{2n/3-1} \tag{17}$$

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

III. DAMP AGGREGATION

We now consider the complementary damp aggregation process, where bimolecular aggregation (with mass-independent aggregation rates) is supplemented by unimolecular 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.

A. Mass independent growth rate (L_k=const)

Let us first investigate damp aggregation for a size-independent growth rate, $L_k=\lambda$. For this case, the rate equations become

$$\dot{c}_k(t)=\sum_{i,j}{}' c_i(t)c_j(t)-2c_k(t)\sum_{i=1}^{\infty} c_i(t) +\lambda[c_{k-1}(t)-c_k(t)]. \tag{18}$$

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 rate equations, the moments evolve according to

$$\begin{aligned}\dot{M}_0(t)&=-M_0(t)^2,\\ \dot{M}_1(t)&=\lambda M_0(t),\\ \dot{M}_2(t)&=2M_1(t)^2+\lambda[2M_1(t)+M_0(t)],\\ &\vdots\end{aligned} \tag{19}$$

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

$$\begin{aligned}M_0(t)&=\frac{1}{1+t},\\ M_1(t)&=1+\lambda\,\ln(1+t),\\ M_2(t)&=1+\lambda\,\ln(1+t)+(4\lambda-2\lambda^2)(1+t)\ln(1+t)\\ &\quad+2\lambda^2(1+t)\ln^2(1+t)+2(1-\lambda+\lambda^2)t,\\ &\vdots\end{aligned} \tag{20}$$

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

$$M_n(t)\sim n!\lambda^n t^{n-1}(\ln t)^n. \tag{21}$$

The appearance of the logarithmic factor in the moments stems from the fact that the rate of mass input is proportional to the number of clusters which, in turn, decays as $1/t$.

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, Eqs. (18), to the differential equation

$$\dot{g}(z,t)=g(z,t)^2-\frac{2}{1+t}\,g(z,t)+\lambda(z-1)g(z,t). \tag{22}$$

Notice that $g(z,t)^{-1}$ satisfies a linear inhomogeneous differential equation whose solution is readily found to be

$$g(z,t)=\frac{ze^{\lambda(z-1)t}}{(1+t)^2}\left[1-z\int_0^t\frac{d\tau}{(1+\tau)^2}\,e^{\lambda(z-1)\tau}\right]^{-1}. \tag{23}$$

Although Eq. (23) represents a solution to the problem, we could not find compact formulas for the concentrations $c_k(t)$. A straightforward expansion of Eq. (23) leads to cumbersome expressions as k increases. We therefore restrict ourselves to determination of the asymptotic behavior of $c_k(t)$. 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 nonzero contribution to the generating function are those whose mass is in the range $0<k\lesssim(1-z)^{-1}$. This basic fact follows by approximating the generating function in the physically relevant limit of $z\to 1$ as

$$g(z,t)=\sum_{k=1}^{\infty} c_k(t)z^k \approx \int^{\infty} c_k(t)e^{k\ln z}dk,$$

$$\approx \int^{\infty} c_k(t)e^{-k(1-z)}dk,$$

$$\approx \int^{(1-z)^{-1}} c_k(t)dk. \tag{24}$$

To obtain the last relation, we merely replace the exponential decay by a step function cutoff at $k=(1-z)^{-1}$. Thus as $z\to 1$, the dominant contribution to the generating function arises from clusters whose masses are in the range $k<(1-z)^{-1}$. We now return to Eq. (23) and further assume that $1-z\gg(\lambda t)^{-1}$, so that the integral can be approximated by replacing the exponential by unity; this is asymptotically correct over the domain of integration. The generating function now becomes

$$g(z,t)\cong(1+t)^{-2}e^{-\lambda t}\frac{ze^{\lambda tz}}{1-z}. \tag{25}$$

Expanding Eq. (25) gives

$$c_{k+1}(t)\cong\frac{(\lambda t)^k}{k!}t^{-2}e^{-\lambda t},\quad \text{for } 0\leqslant k\ll\lambda t. \tag{26}$$

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 $e^{\lambda(z-1)\tau}$, compute the integral on the right-hand side of Eq. (23), and then asymptotically balance the various terms. Thus, by inserting $e^{\lambda(z-1)\tau}=1+\lambda(z-1)\tau+\cdots$ into the integral, the expression in the square brackets of Eq. (23) reads $[(1-z)+z/(1+t)+\lambda z(1-z)\ln t+\cdots]$. Clearly, the third term asymptotically dominates over the first term of $(1-z)$, so that the nontrivial scaling limit arises by balancing the second and third terms. Thus $(1-z)\sim(t\ln t)^{-1}$, which suggests that the appropriate scaling variable is

$$\zeta=(1-z)\lambda t\ln t, \tag{27}$$

instead of the original variables z and t.

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

$$g(z,t)\simeq t^{-1}(1+\zeta)^{-1}, \tag{28}$$

and the mass distribution approaches the scaling form

$$c_k(t)\simeq\phi(t)\Phi(x)\quad\text{with } x=\frac{k}{\lambda t\ln t}, \tag{29}$$

with the prefactor $\phi(t)$ and scaling function $\Phi(x)$ to be determined. Making use of Eqs. (27) and (29), we express the generating function in terms of $\phi(t)$ and $\Phi(x)$ as

$$g(z,t)=\sum z^k c_k(t)=\sum\left(1-\frac{\zeta}{\lambda t\ln t}\right)^k c_k(t)$$

$$\simeq\lambda t\ln t\,\phi(t)\int_0^{\infty}\Phi(x)e^{-x\zeta}dx. \tag{30}$$

Finally, by comparing Eqs. (28) and (30) and performing the inverse Laplace transform, the prefactor $\phi(t)$ and the scaling function $\Phi(x)$ are

$$\phi(t)=\frac{1}{\lambda t^2\ln t}\quad\text{with }\Phi(x)=e^{-x}. \tag{31}$$

Notice that the scaling solution of Eqs. (29) and (31) agrees with the asymptotic expression for the moments (21).

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 quote the result,

$$c_k(t)\sim\left(1-\frac{1}{\lambda t\ln t}\right)^k. \tag{32}$$

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 extreme case of a condensation rate which is linear in the mass, i.e., the rate at which $c_k\to c_{k+1}$ equals λk. Because of the simple form of the growth rate, the rate equations turn out to be exactly soluble. As might be expected, an input rate which is proportional to the amount of mass already present leads to a total mass which grows exponentially in time. The detailed consequences of this basic result can be obtained by considering the underlying rate equations,

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

$$+\lambda[(k-1)c_{k-1}(t)-kc_k(t)]. \tag{33}$$

Employing the generating function $g(z,t)=\Sigma_{k=1}^{\infty}c_k(t)z^k$, Eq. (33) becomes

$$\frac{\partial}{\partial t}g(z,t)=g(z,t)^2-2g(z,t)M_0(t)+\lambda z(z-1)\frac{\partial}{\partial z}g(z,t). \tag{34}$$

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. (34) into a linear equation for $h(z,t)^{-1}$

$$\frac{\partial}{\partial t}h(z,t)^{-1}+\lambda z(1-z)\frac{\partial}{\partial z}h(z,t)^{-1}+1=0. \tag{35}$$

By introducing $w=(1/\lambda)\ln[z/(1-z)]$, Eq. (35) 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

$$\frac{\partial}{\partial u}\, h(u,v)^{-1}=-\frac{1}{2}, \tag{36}$$

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

$$h(u,v)^{-1}=-1-\frac{u+v}{2}-e^{-\lambda v}$$

$$=-1-t-e^{-\lambda t}\,\frac{z}{1-z}. \tag{37}$$

By expanding $g(z,t)=h(z,t)+1/(1+t)$ in powers of z, the exact expression for the concentrations are

$$c_k(t)=\frac{c^{-\lambda t}}{(1+t)^2}\left(1-\frac{e^{-\lambda t}}{1+t}\right)^{k-1}. \tag{38}$$

In the scaling region, $k\to\infty$ and $t\to\infty$ with $x=k/te^{\lambda t}$ finite, Eq. (38) has the pure exponential asymptotic form

$$c_k(t)\simeq t^{-2}e^{-\lambda t}e^{-x}. \tag{39}$$

C. General mass dependent growth rate ($L_k\propto k^\mu$)

In both cases of $\mu=0$ and $\mu=1$ the scaling solution for the mass distribution may be written in the unified form

$$c_k(t)\simeq\frac{M_0(t)^2}{M_1(t)}\,e^{-x}\quad\text{with}\quad x=\frac{M_0(t)}{M_1(t)}\,k. \tag{40}$$

Although the mass density, $M_1(t)$, has a very different time dependence for the two cases of $\mu=0$ and $\mu=1$, the respective scaling functions are the same and in fact identical to that in pure aggregation with a constant aggregation rate [1–4]. This universal behavior suggests that the behavior in the intermediate regime of a mass-dependent cluster growth rate, $L_k=\lambda k^\mu$, with $0<\mu<1$, should also be described by scaling.

Thus when $0<\mu<1$, it is reasonable to attempt a solution to the rate equations for damp aggregation by assuming that the scaling form of Eq. (40) holds. 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, so that $M_0(t)=(1+t)^{-1}$. On the other hand, $M_1(t)$ is determined by $\dot M_1(t)=\lambda M_\mu(t)$, which is coupled to an undetermined moment. However, in the long-time limit we can use the scaling form (40) to estimate $M_\mu(t)$ as

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

$$=\Gamma(1+\mu)M_1(t)^\mu M_0(t)^{1-\mu}. \tag{41}$$

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

$$M_1(t)\simeq At^{\mu/(1-\mu)}\quad\text{with}\quad A=[\lambda(1-\mu)\Gamma(\mu)]^{1/1-\mu}. \tag{42}$$

It is instructive to compare the resulting asymptotic behavior for the typical cluster size,

$$S(t)=\frac{M_1(t)}{M_0(t)}=At^{1/(1-\mu)}, \tag{43}$$

with a naive estimate that arises by considering growing, but *noninteracting*, i.e., nonaggregating, clusters. This latter estimate is obtained from the equation $\dot S(t)=\lambda S(t)^\mu$, which implies

$$S(t)=A_0t^{1/(1-\mu)}\quad\text{with}\quad A_0=[\lambda(1-\mu)]^{1/(1-\mu)}. \tag{44}$$

Therefore the system with continuously growing but noninteracting droplets provides the correct exponent for the time dependence of the typical cluster size 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 $d\leqslant 2$ (see, e.g., [17,18]). However, for the damp aggregation process with a homogeneous growth rate, $L_k\propto k^\mu$ $(0\leqslant\mu<1)$, it is possible to infer partial results for $d\leqslant 2$ 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 [17,18]

$$M_0(t)\sim\begin{cases}t^{-d/2}, & d<2\\ \ln t/t, & d=2.\end{cases} \tag{45}$$

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

$$c_k(t)\simeq\frac{M_0(t)^2}{M_1(t)}\,\Phi_d(x)\quad\text{with}\quad x=\frac{M_0(t)}{M_1(t)}\,k, \tag{46}$$

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 preceding subsection),

$$M_\mu(t)\simeq M_0(t)^{1-\mu}M_1(t)^\mu\int_0^\infty dx x^\mu\Phi_d(x). \tag{47}$$

Ignoring numerical factors we solve for the mass density to obtain

$$M_1(t)\sim\begin{cases}t^{1/(1-\mu-d/2)}, & d<2, \quad 0\leqslant\mu<1;\\ t^{\mu/(1-\mu)}\ln t, & d=2, \quad 0<\mu<1;\\ \ln^2 t, & d=2, \quad \mu=0.\end{cases} \tag{48}$$

Finally, combining Eqs. (45), (46), and (48) yields

$$c_k(t)\sim\begin{cases} t^{-1/(1-\mu)-d/2}\Phi_d(x), & d<2, \quad 0\leqslant\mu<1 \\ t^{-(2-\mu/1-\mu)}\ln t\Phi_2(x), & d=2, \quad 0<\mu<1. \\ t^{-2}\Phi_2(x), & d=2, \quad \mu=0 \end{cases} \tag{49}$$

The scaling variable is $x=kt^{-1/(1-\mu)}$ for the first two cases, while in the latter case, the scaling variable is $x=k/t\ln t$, i.e., the same expression that was found in the rate equations.

Making use of the techniques which allow one to solve the one-dimensional diffusion-controlled aggregation process with a mass-independent cluster diffusivity [19–21], we have found [22] an exact solution to diffusion-controlled aggregation in one dimension which is augmented by a cluster growth rate of the form $L_k\propto k$. These results agree with the above heuristic expectations. Unfortunately, we were unable to adapt these exact approaches to solve related one-dimensional problems, such as damp aggregation with constant growth rate or dry aggregation.

IV. SUMMARY AND DISCUSSION

Our primary results were to outline the broad range of phenomenology which arises from the combined effects of: (a) aggregation with evaporation—dry aggregation, and (b) aggregation with condensation—damp aggregation. In the former case, the interesting situation is that of mass conservation, where evaporated monomers remain in the system and continue to participate in further reaction. When the aggregation rate is mass independent, a stationary state is reached for sufficiently strong evaporation, while the kinetics is essentially identical to that of pure aggregation when the evaporation is relatively weak. In the stationary state, the concentration of clusters of mass k, $c_k(\infty)$, decays as $k^{-5/2}$ for small k and is exponentially cut off for k larger than the typical size. At a critical evaporation rate, there is a power-law approach to the steady-state mass distribution, $c_k(\infty)\propto k^{-5/2}$, with the upper cutoff, or typical cluster size, growing as $t^{2/3}$. It is worth noting that a qualitatively similar slow approach to the steady state arises in aggregation with a temporally fixed input of monomers. In this steadily driven system, the typical cluster size grows linearly in t and $c_k(\infty)\propto k^{-3/2}$ for $k\ll t$ [23]. In view of the qualitative similarities between aggregation with steady monomer input and dry aggregation, it might be possible to connect the exponents of the two systems by qualitative arguments.

An essential ingredient in the behavior of dry aggregation is the comparable magnitudes of the aggregation and evaporation rates, so that their competition is relatively delicate. Related transition behavior has been obtained for combined aggregation-evaporation processes by Vigil, Ziff, and Lu [13], 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, however, the effects of evaporation and aggregation were chosen to be of the same order in a scaling sense, leading to a transition between a steady state and gelation for a critical value of the ratio of the two rates and also distinct power-law behavior at the transition in which the mass distribution decays as $k^{-7/2}$. Another not entirely unrelated example, where competition between opposing microscopic effects influence the approach to a stationary state, occurs in the one-dimensional reversible reaction $A+A\leftrightarrow A$ [19]. In this case, the relaxation of the density to its final value decays exponentially in time, but with a characteristic decay time which depends on the initial density.

For damp aggregation, the unimolecular cluster growth was found to enhance the effects of the bimolecular aggregation, as is expected. However, the nature of this enhancement has some unusual features. When the growth rate is independent of cluster mass, a relatively weak enhancement arises, in which the typical cluster mass grows with time as $t\ln t$, compared to linear growth for aggregation with no condensation. The source of the logarithmic correction is that the input rate of new material is proportional to the number of clusters, a quantity which asymptotically decays as t^{-1}. Conversely when the growth rate is proportional to the mass, the typical mass grows exponentially in time, a result which is intuitively obvious. 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 $t^{1/(1-\mu)}$. This behavior is identical to that which arises for pure condensation without aggregation, indicating that an independent particle description is sufficient to determine the cluster growth.

Damp aggregation can also be viewed as a model for breath figures [14,15] and related models of droplet growth and coalescence [6]. In the modeling of these systems, the growth rate of individual droplets has generally been expressed as a function of time, rather than of the mass. Thus in breath figures, if one assumes that the mass of individual droplets grows t^α, then the typical cluster mass in the system which undergoes condensation and aggregation grows at a faster rate of t^β, with β simply related to the system geometry and α through

$$\beta=D\alpha/(D-d). \tag{50a}$$

Here D is the spatial dimension of the droplets and d (which must be smaller than D) is the dimensionality of the substrate. In contrast, for our damp aggregation model a droplet growth rate proportional to k^μ is equivalent to a growth rate which varies in time as $t^{\mu/(1-\mu)}$. Thus in terms of the exponents α and β in the breath figure system, their interrelation is

$$\alpha=\beta/\mu. \tag{50b}$$

It would be worthwhile to understand whether there is a simple way to combine Eq. (50a) and Eq. (50b) in a unified framework.

Finally, we studied the scaling behavior for damp aggregation in systems with spatial dimension $d\leqslant 2$. These results are based on applying known results for the decay of the number of clusters for $d\leqslant 2$ [17–21], to extend the scaling approach in a simple way. This approach suggests that conventional scaling continues to apply, but with dimension-dependent scaling behavior. These predictions smoothly match those given by the rate equations at $d=2$.

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