Kinetic Anomalies in Addition-Aggregation Processes

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We investigate irreversible aggregation in which monomer-monomer, monomer-cluster, and cluster-cluster reactions occur with constant but distinct rates $K_{MC}$, $K_{MM}$, and $K_{CC}$, respectively. The dynamics crucially depends on the ratio $\gamma = K_{CC}/K_{MC}$ and secondarily on $\epsilon = K_{MM}/K_{MC}$. For $\epsilon = 0$ and $\gamma < 2$, there is conventional scaling in the long-time limit, with a single mass scale that grows linearly in time. For $\gamma \geq 2$, there is unusual behavior in which the concentration of clusters of mass $k$, $c_k$ decays as a stretched exponential in time within a boundary layer $k < k^* \propto t^{1-2/\gamma}$ ($k^* \propto \ln t$ for $\gamma = 2$), while $c_k \propto t^{-2}$ in the bulk region $k > k^*$. When $\epsilon > 0$, analogous behaviors emerge for $\gamma < 2$ and $\gamma \geq 2$.

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I. INTRODUCTION

In this work, we investigate a simple aggregation process in which three kinds of reactions occur with constant but distinct rates:

\begin{align}
A_1 + A_1 & \rightarrow \epsilon \rightarrow A_2, \\
A_1 + A_j & \rightarrow j \rightarrow A_{j+1} \quad j \geq 2, \\
A_i + A_j & \rightarrow i \rightarrow A_{i+j} \quad i, j \geq 2.
\end{align}

Equivalently, the reaction matrix $K_{ij}$ has the value $\epsilon$ in the upper left corner, the value 1 for all elements along the top and left edges of the matrix, and the value $\gamma$ in the rest of the matrix.

Despite its simplicity, this model exhibits rich dynamics in which both scaling and universality can be violated. The model was initially studied by Hendriks and Ernst to describe polymerization in which addition processes (reactions involving monomers) occur more readily than aggregation (reactions between $i$ and $j$, with $i, j \geq 2$). They found evidence of unusual kinetic behavior by an implicit solution for the cluster concentrations; see also for related work. Our focus is on the opposite limit in which aggregation dominates over addition. By explicit solutions of the rate equations, we elucidate the full range of behaviors for this system.

From a general perspective, the origin of the anomalous behavior in addition/aggregation stems from the fact that the simplest case of aggregation with a constant reaction rate is actually a marginal system. As discussed by van Dongen and Ernst, aggregation can be broadly categorized by whether reactions among large clusters dominate (type I systems, in their nomenclature) or whether reactions between large and small clusters dominate (type III systems). The former generically leads to monotonically decaying cluster mass distributions, while the latter gives peaked distributions. The constant reaction rate system (type II system) is marginal by being at the boundary between these two behaviors.

Because of this marginality, the kinetics of constant-kernel aggregation is sensitive to small perturbations in the reaction rates. Previously-studied examples of this feature include aggregation involving two distinct monomeric units, so that the reaction rates between two even masses, two odd masses, or an even and an odd mass are naturally distinct. Here non-universal and non-scaling behavior arises as a function of these rates. Another example is aggregation with the rate $A_i + A_j \rightarrow i \rightarrow A_{i+j} \quad i, j \rightarrow \infty$. Although this reduces to a constant-kernel system for $i, j \rightarrow \infty$, the $q$-dependent terms lead to unusual kinetics. The model studied here is in the spirit of the first example, except that we perturb only an infinitesimal fraction of the reaction rates.

In the next two sections, we focus on the special case of “sterile” monomers, where monomer-monomer reactions do not occur. In Sec. II, we first determine the monomer and dimer concentrations and show that different behaviors arise for $\gamma \geq 2$ and $\gamma < 2$. Then in Sec. III, we derive asymptotic results for the cluster concentrations. We then study, in Sec. IV, these same three cases when monomer-monomer reactions can also occur. Sec. V gives a summary as well as a discussion of the equivalence between the model and a diffusion-controlled process in which monomers have different diffusivity than other clusters.

II. STERILE MONOMERS

When monomers do not interact among themselves ($K_{11} = 0$), we shall show that the system exhibits three distinct kinetic regimes, with unusual time dependences and breakdown of conventional scaling in two of these cases.
The rate equation for the density \( c_k(t) \) is \[ \dot{c}_k(t) = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i(t) c_j(t) - c_k(t) \sum_{j \geq 1} K_{kj} c_j(t), \] where the overdot denotes time derivative. The first (gain) term accounts for the formation of clusters of mass \( k \) (\( k \)-mers) as a result of the bimolecular aggregation of \( i \)-mers with \( j \)-mers, with \( i + j = k \). The second (loss) term accounts for the aggregation of the \( k \)-mers with any \( j \)-mer, thus leading to a decrease in the \( k \)-mer concentration. For the processes given in \( \ref{eq:3} \) and with the additional constraint of \( K_{11} = \epsilon = 0 \), the explicit rate equations are

\[
\begin{align*}
\dot{c}_1 &= -c_1 R, \\
\dot{c}_2 &= -c_2 [c_1 + \gamma R] \\
\dot{c}_k &= c_1 c_{k-1} + \gamma \sum_{i+j=k} c_i c_j - c_k (c_1 + \gamma R) \quad k > 2,
\end{align*}
\]

where we drop the time argument for compactness and introduce the shorthand \( R = \sum_{k \geq 2} c_k \) for the concentration of reactive clusters (those with mass \( \geq 2 \)). Notice also that there is no production of monomers and dimers in the reaction; they can only disappear. The governing equation for \( R \) is obtained by summing Eqs. \( \ref{eq:3} \) to give \( \dot{R} = -\frac{1}{2} R^2 \), whose solution is

\[ R = R(0) \tau^{-1}, \quad \tau = 1 + \frac{1}{2} \gamma R(0) t. \]

With the explicit expression for \( R \), we integrate the equation for monomers to give

\[ c_1 = c_1(0) \tau^{-2/\gamma}. \]

The crucial point is that the value of \( \gamma \) controls which of \( R \) or \( c_1 \) decays more rapidly. For \( \gamma < 2 \), monomers are asymptotically irrelevant and conventional constant-kernel aggregation kinetics arises. For \( \gamma > 2 \), however, the large disparity in the reaction rates \( K_{1j} \) and \( K_{ij} \) leads to a long-lived residue of monomers and these profoundly affect the asymptotic kinetics. To see this explicitly, we solve for the density of dimers to find

\[ c_2 = c_2(0) \tau^{-2} e^{-\lambda}, \]

where we define \( \lambda = \int_0^t dt' c_1(t') \). Using Eq. \( \ref{eq:5} \) we express \( \lambda \) in terms of \( \tau \):

\[ \lambda = \lambda(\tau) = \begin{cases} 2r \frac{1-2/\gamma}{\gamma-2} & \gamma \neq 2, \\ r \ln \tau & \gamma = 2, \end{cases} \]

where we further define \( r = c_1(0)/R(0) \).

Depending on the value of \( \gamma \) we obtain three distinct long-time behaviors:

- For \( 0 < \gamma < 2 \), \( \lambda \to \frac{2r}{\gamma-2} \) \( \to \) const as \( t \to \infty \). Thus the dimer concentration has a universal \( t^{-2} \) asymptotic decay; only the amplitude of the decay depends on the initial state.
- For \( \gamma > 2 \), the dimer density decays as a stretched exponential \( e^{-\lambda} \) times a power-law prefactor.
- For \( \gamma = 2 \), the dimer concentration asymptotically decays as \( t^{-2(2+\gamma)} \), where the exponent depends on the initial concentration ratio \( r = c_1(0)/R(0) \).

### III. ASYMPTOTIC MASS DISTRIBUTION

To determine the asymptotic cluster concentrations \( c_k \), we re-write the rate equations \( \ref{eq:3} \) in the form

\[ \dot{c}_k + \alpha c_k = \alpha_k, \]

where

\[ \alpha \equiv c_1 + \gamma R, \quad \alpha_k \equiv c_1 c_{k-1} + \gamma \sum_{i+j=k} c_i c_j. \]

Due to the recursive nature of Eq. \( \ref{eq:5} \), we immediately obtain the formal solution for \( c_k \):

\[ c_k(t) = E(t) \left\{ c_k(0) + \int_0^t dt' \alpha_k(t') \right\} \]

with \( E(t) = \exp \left[ -\int_0^t dt' \alpha(t') \right] = t^{-\gamma} e^{-\lambda} \). Therefore, once we know \( c_1, \ldots, c_k-1 \), we can compute \( \alpha_k \) and then determine \( c_k \).

Before proceeding to general \( k \), it is instructive to compute \( c_3 \). From Eq. \( \ref{eq:10} \), and using the previous results for \( c_1 \) and \( c_2 \), we obtain:

\[ c_3 = \left[ c_2(0) \lambda + c_3(0) \right] \tau^{-2} e^{-\lambda}. \]

As in the case of dimers, there are three distinct asymptotic behaviors for the trimer concentration that are best expressed in terms of \( c_3/c_2 \). We obtain

\[ \frac{c_3}{c_2} \propto \begin{cases} \frac{t^{1-2/\gamma}}{\gamma} & \gamma > 2, \\ \ln t & \gamma = 2, \\ 1 & \gamma < 2, \end{cases} \]

that is, \( c_3/c_2 \propto \lambda^{\gamma-2} \) as \( t \to \infty \) by explicit calculation for small

A. \( \gamma \geq 2 \)

When \( \gamma \) is strictly greater than 2, we easily find that \( c_k/c_2 \propto \lambda^{k-2} \) as \( t \to \infty \) by explicit calculation for small
$k$. We therefore seek an asymptotic solution for $c_k$ of the form

$$
c_k / c_2 = \beta_k \lambda^{k-2} + \ldots
$$

(13)

where $\ldots$ denotes subdominant terms in the limit $t \to \infty$ and the amplitude $\beta_k$ will be determined below.

For concreteness and simplicity, let us consider the bi-dispersal initial condition in which only $c_1(0)$ and $c_2(0)$ are non-zero while $c_k(0) = 0$ for all $k > 2$. To extract the asymptotics of $c_k$ from Eq. (10), only the second term on the right-hand side is needed. Let us suppose that Eq. (13) holds for $c_2, \ldots, c_k$. To leading order, we have $\alpha_k + 1 = c_1 c_k$, and substituting $c_k = c_2 \beta_k \lambda^{k-2}$ into Eq. (10), we obtain

$$
c_{k+1} = E(t) \int_0^t dt' c_1(t') c_k(t') / E(t')
$$

and

$$
c_{k+2} = c_2 \lambda^k / k!
$$

(14)

where to obtain the second line we use $E(t) = \tau^{-2} e^{-\lambda}$. Thus $\beta_2 = 1/(k-2)!$ and we arrive at the remarkably simple asymptotic solution

$$
c_{k+2} = c_2 \lambda^k / k!
$$

(15)

with $\tau$ and $\lambda$ given by Eqs. (11) and (7). Explicitly, we have

$$
c_{k+2} \sim \frac{1}{k!} \tau^{-2+k(1-2/\gamma)} \exp \left( -\text{const.} \times t^{1-2/\gamma} \right).
$$

(16)

Thus $c_k$ has a very different asymptotic behavior than in the constant-kernel system [5]. As discussed previously, this anomaly arises because monomers are very long-lived and these then strongly influence the long-time kinetics.

One important caveat, however, is that the derivation of Eq. (15) applies only for finite $k$. For sufficiently large $k$ the neglected subdominant terms accumulate to provide a relevant contribution. The simplest way to see that Eq. (15) cannot hold over entire mass range is to use this equation to compute the total cluster density. This gives $\sum_{k \geq 2} c_k / c_2 e^k = c_2(0) \tau^{-2}$, in contrast to the correct result $R(0) / \tau^{-1}$ given in Eq. (11).

We therefore conclude that the mass distribution naturally divides into a small-mass boundary layer, $k \leq k^*$, that contains an asymptotically negligible fraction of the total mass, and a remaining bulk region. The extent of the boundary layer may be determined as the maximum of $c_k$ in Eq. (15) and gives $k^* = \lambda / \tau^{1-2/\gamma}$. Within this boundary layer, the mass distribution grows rapidly with mass, but this region contains only an asymptotically negligible fraction of the total mass. On the other hand, most of the mass, which exhibits conventional scaling behavior is contained in the bulk region.

In the marginal case of $\gamma = 2$, the asymptotic solution of Eq. (15) is still valid. Since now $\lambda = r \ln \tau$, the density of dimers decays algebraically in time as $c_2 = c_2(0) \tau^{-2(r+1)}$, and the width of the boundary layer grows logarithmically $k^* = \lambda = r \ln \tau$. The following main part of the mass distribution is again characterized by conventional scaling behavior (see Eq. (19) below). A justification of this picture is given in Appendix. Thus for $\gamma \geq 2$, the mass distribution exhibits two growing scales and conventional single-mass scaling is violated.

B. $\gamma < 2$

By solving $c_2, c_3, \ldots$ exactly, we are led to the hypothesis that for $k \geq 2$

$$
c_k \propto \tau^{-2}.
$$

(17)

This indeed can be directly checked by induction. Moreover, in the scaling limit,

$$
k \to \infty, \quad t \to \infty, \quad \frac{k}{t} = \text{finite},
$$

(18)

the mass distribution admits the conventional scaling form

$$
c_k = \frac{4}{\gamma^2 t^2} e^{-2k/(\gamma t)}.
$$

(19)

Summing $\sum c_k$ we indeed recover $R = 2/(\gamma t)$, while the next moment $\sum k c_k$ equals one (based on the total mass set equal to one initially). Equation (16) also describes the scaling portion of the mass distribution when $\gamma \geq 2$.

The origin of the conventional scaling behavior for the case $\gamma < 2$ is simple. For $\gamma < 2$ monomers disappear quickly, since $c_1 \propto t^{-2/\gamma}$, and their asymptotic influence is negligible. Thus the reaction effectively reduces to a constant-kernel system that begins with dimers. The monomers do influence the small-mass behavior, namely $c_k = A_k t^{-2}$ with mass-dependent amplitudes $A_k$; e.g., $A_2 = c_2(0) \gamma R(0)/2 \tau^{-2} e^{-\lambda}$ and $A_3 = A_2(\lambda + c_3(0)/c_2(0))$. However, as $k$ grows the amplitude $A_k$ approaches the constant value $4 \gamma^{-2}$.

The existence of scaling can be proved rigorously, e.g., by the generating function approach given in the Appendix. A simpler approach is to merely assume that scaling holds and check its consistency a posteriori. In the continuum limit, we have checked the correctness of Eq. (19), which is the conventional scaling form for constant kernel aggregation [5].

IV. REACTIVE MONOMERS

We now assume that monomer-monomer reactions do occur: $K_{11} \equiv \epsilon > 0$. This situation has already been studied by Hendriks and Ernst [3]. The rate equations for monomers and dimers now read

$$
c_1 = -c_1(e c_1 + R)
$$

(20)

$$
c_2 = \frac{r}{2} c_2^2 - c_2 (c_1 + \gamma R),
$$

(21)
while the rate equations for clusters with $k > 2$ are the same as in Eq. 3. Correspondingly, the density of reactive clusters $R$ evolves according to

$$\dot{R} = \frac{1}{2} c c^2 - \frac{1}{2} \gamma R^2. \quad (22)$$

It does not seem possible to solve the coupled nonlinear equations 20 and 22 for $c_t$ and $R$ explicitly. If we treat $c_1$ as a function of $R$, however, we can reduce Eq. 20 and 22 to a single differential equation that can be solved to establish a functional relation between $c_1$ and $R$. From this relation, we can deduce that different behaviors emerge depending on whether $\gamma < 2$ or $\gamma \geq 2$.

A simpler and more fruitful way to proceed is to seek the asymptotic behavior of $c_1$ and $R$ without explicitly solving the governing equations. We anticipate that there are three possible asymptotic behaviors: (i) $c_1 \propto R$, (ii) $c_1 \propto R^{-1}$, and (iii) $c_1 \propto R^{-1/2}$. Substituting each of these scenarios into Eqs. 20 and 22 shows that the latter case is impossible. Let us now analyze the first two possibilities. When $c_1 \propto R$, Eq. 22 gives $R \simeq 2/(\gamma t)$, and then Eq. 20 yields $c_1 \propto t^{-2/\gamma}$. Thus the relation $c_1 \propto R$ holds when $\gamma < 2$. In the complementary regime of $\gamma > 2$, we find that $c_1 \propto R$ is consistent; furthermore, Eqs. 20 and 22 now give $R \propto c_1 \propto t^{-1}$.

We now analyze these two cases in more detail.

A. $\gamma \geq 2$

When $\gamma$ is strictly greater than 2, we substitute the ansatz

$$R \simeq A t^{-1}, \quad c_1 \simeq B t^{-1}, \quad (23)$$

into Eqs. 20 and 22 to get a quadratic equation for the amplitude $A$. The physical requirement that $A$ and $B$ are both positive fixes the solution to be

$$A = \frac{\epsilon - 1 + \sqrt{\epsilon(\epsilon + \gamma - 2)}}{\epsilon \gamma - 1}, \quad B = \frac{1 - A}{\epsilon}. \quad (24)$$

The singularity at $\epsilon = \gamma^{-1}$ is only apparent and may be resolved by applying the l’Hospital’s rule, to give $A = \gamma/[2(\gamma - 1)]$ in this case.

From the formal solution 10, we can check by induction that for finite $k$,

$$c_k \simeq B_k t^{-1}. \quad (25)$$

The amplitude $B_k$ is found by substituting the ansatz 20 into 3 and 4 to give the recursion

$$(\mu - 1)B_k = BB_{k-1} + \frac{1}{2} \sum_{i,j \geq 2} B_i B_j \quad (26)$$

for $k > 2$, where we define

$$\mu = \gamma A + B = 1 + \sqrt{1 + (\gamma - 2)/\epsilon}. \quad (27)$$

Note also that $(\mu - 1)B_2 = \epsilon B^2/2$. To solve the recursion 26, we introduce the generating function $B(z) = \sum_{k \geq 2} B_k z^k$ to reduce 26 to

$$B(z) = \frac{\mu - 1 - Bz}{\gamma} \left\{ 1 - \frac{1}{\sqrt{1 - 1}} \left( \frac{Bz}{\mu - 1 - Bz} \right)^2 \right\}. \quad (28)$$

When $k \gg 1$ but still within the boundary layer, the asymptotic behavior of $B(z)$ leads to the amplitude

$$B_k \simeq C k^{-3/2} \beta^k \quad (29)$$

with

$$\beta = B \frac{1 + \sqrt{\gamma}}{\mu - 1}, \quad C = \frac{\mu - 1}{\gamma \sqrt{2 \pi}} \sqrt{\frac{\sqrt{\gamma}}{1 + \sqrt{\gamma}}}. \quad (30)$$

One can verify that $\beta < 1$ for all $\gamma > 2$ and $\epsilon > 0$; therefore, apart from a power-law prefactor, the amplitude $B_k$ decreases exponentially with $k$.

As in the previous section, the results 20 and 28 are valid only within the boundary layer. Thus the total density of clusters within the boundary layer is asymptotically equal to $A' t^{-1}$, where $A' = \sum_{k \geq 2} B_k = B(z = 1)$, or

$$A' = \frac{\mu - 1 - B - \sqrt{(\mu - 1 - B^2 - \epsilon)/\gamma}}{\gamma}. \quad (31)$$

Since the total density of clusters scales as $A'^{-1}$, only a fraction $A'/A$ of clusters lies within the boundary layer. Using Eqs. 21 and 30, we find $A - A' = 2/\gamma$; this implies that the density of clusters in the bulk decays as $2/(\gamma t)$. The same holds for $\gamma \leq 2$, although in this case the density of clusters in the boundary layer is asymptotically negligible.

To determine the asymptotic behavior in the bulk ($k \to \infty$ and $t \to \infty$), we simplify the rate equations by neglecting the subdominant terms $c_1(c_1 - c_k)$ on the right-hand side of Eq. 3. Further, the sum in 8 has three contributions. When $i$ lies within the boundary layer, we can replace $\sum_c c_i c_{k-i}$ by $c_k \sum_i B_i t^{-1} = c_k A' t^{-1}$; a similar contribution arises when $j$ lies within the boundary layer. In the bulk we replace the sum by the integral. Thus

$$\frac{\gamma}{2} \sum_{i+j=k} c_i c_j = \frac{\gamma}{2} \int \text{d}i \text{c}_{i} \text{c}_{k-i} + \frac{A'}{t} c_k. \quad (32)$$

Combining all terms and using the identity $\gamma (A - A') = 2$ we finally convert Eq. 32 to

$$\frac{\gamma}{2} c_k = \frac{\gamma}{2} \int \text{d}i \text{c}_{i} \text{c}_{k-i}. \quad (33)$$

This equation appears in the standard constant-kernel aggregation and its solution, satisfying the aforementioned conservation laws $\int dk \text{c}_{k} = 2/\gamma$ and $\int dk k \text{c}_{k} = 1$, is given by Eq. 19.
By matching the mass distribution in the boundary layer \((c_k \propto t^{-1/2})\) and in the bulk \((c_k \propto t^{-2})\), we estimate the width of the boundary layer as

\[
k^* \approx \frac{\ln t}{\ln(1/\beta)},
\]

with \(\beta\) given by Eq. 29. This is a much slower growth than in the case of sterile monomers where \(k^* \propto t^{1/2}/\gamma\).

When \(\gamma = 2\), we again expect marginal behavior. Proceeding as in the case of \(\gamma > 2\), we find

\[
R \approx t^{-1}, \quad c_1 \approx t^{-1}(\epsilon \ln t)^{-1}.
\]

From the formal solution (19) we can check by induction that,

\[
c_k \approx B_k t^{-1}(\epsilon \ln t)^{-k}.
\]

For \(k > 2\), the amplitude \(B_k\) is found from the recursion 26 with \(\mu = 2\), \(B = 1\), and \(B_2 = \epsilon/2\). The generating function and the coefficients \(B_k\) and \(C\) are given by taking the corresponding formulae in the \(\gamma > 2\) case and setting \(\gamma = 2\).

This behavior holds in a boundary layer whose width now grows as

\[
k^* \approx \frac{\ln t}{\ln(\Lambda \ln t)}, \quad \Lambda = \frac{\epsilon}{1 + \sqrt{2\epsilon}},
\]

while in the bulk we recover the ordinary scaling mass distribution \(c_k = t^{-2}e^{-k/\tau}\).

### B. \(\gamma < 2\)

We already argued that \(R \approx 2/(\gamma t)\) and \(c_1 \propto t^{-2/\gamma}\) for \(\gamma < 2\). Solving then for dimers we obtain:

\[
c_2 \propto \begin{cases} 
  t^{-2} & 0 < \gamma < 4/3, \\
  t^{1-4/\gamma} & 4/3 < \gamma < 2.
\end{cases}
\]

Generally, we find

\[
c_k \propto \begin{cases} 
  t^{-2} & 0 < \gamma < \frac{2k}{k+1}, \\
  t^{-2} \ln t & \gamma = \frac{2k}{k+1}, \\
  t^{k-1-2k/\gamma} & \frac{2k}{k+1} < \gamma < 2.
\end{cases}
\]

Thus for every \(\gamma < 2\), small-mass clusters have abnormal kinetics: only monomers for \(\gamma < 4/3\), monomers and dimers for \(4/3 \leq \gamma < 3/2\), monomers, dimers, and trimers for \(3/2 \leq \gamma < 8/5\), etc. The remaining clusters decay as \(t^{-2}\), and conventional scaling describes the cluster-mass distribution.

### V. SUMMARY AND DISCUSSION

For irreversible aggregation with distinct monomer-monomer \((K_{MM})\), monomer-cluster \((K_{MC})\), and cluster-cluster \((K_{CC})\) reaction rates, the dynamics depends crucially on the ratio \(\gamma = K_{CC}/K_{MC}\), while \(\epsilon = K_{MM}/K_{MC}\) plays a lesser role — all that matters is whether \(\epsilon = 0\) or \(\epsilon > 0\). For \(\epsilon = 0\) and \(\gamma < 2\), there is conventional scaling with a single mass scale growing linearly with time. For \(\gamma \geq 2\), there are two scales: the boundary layer \(k < k^* \propto t^{1-2/\gamma}\) where the mass distribution has an unusual Poisson form, and the bulk region \(k > k^*\) where conventional scaling holds. When \(\epsilon > 0\) and \(\gamma < 2\), there is conventional scaling, except that light clusters have abnormal kinetics — monomers for \(\gamma < 4/3\); monomers and dimers for \(4/3 \leq \gamma < 3/2\); monomers, dimers, and trimers for \(3/2 \leq \gamma < 8/5\), etc. When \(\epsilon > 0\) and \(\gamma \geq 2\), the behavior in the boundary layer is very different from that when \(\epsilon = 0\). In particular, the mass distribution decays with mass while for \(\epsilon = 0\) the mass distribution is peaked.

A possible application of this model is to clustering on surfaces. Consider a two-dimensional substrate with diffusing single-layer islands that aggregate whenever they meet. In the diffusion-controlled limit, the reaction rate of an island of radius \(R\) and diffusivity \(D\) is proportional to \(D \ln R\). To a good approximation, we can ignore the island radius and think of point-like islands that always occupy a single lattice site. When such a cluster hops onto already occupied site, two clusters immediately coalesce into a single cluster.

If monomers hop with rate \(D\) while all heavier clusters hop with the same unit rate, then the corresponding reaction rates for point-like islands are \(K_{11} = 2D, K_{1j} = 1 + D, K_{ij} = 2\). As a result

\[
\epsilon = \frac{K_{11}}{K_{1j}} = \frac{2D}{1 + D}, \quad \gamma = \frac{K_{ij}}{K_{1j}} = \frac{2}{1 + D}.
\]

For immobile monomers, \(D = 0\), we have \(\epsilon = 0\) and \(\gamma = 2\). In this case, the cluster mass distribution is

\[
c_{k+2} = c_2(0) t^{-(2+\gamma)} \frac{\lambda^k}{k!}.
\]

within a boundary layer that grows logarithmically with time \(k^* = r \ln(1 + R(0)t)\), where \(r = c_2(0)/R(0)\). In the bulk, ordinary scaling holds in which \(c_k = t^{-2}e^{-k/\tau}\).

When \(D > 0\), \(\gamma\) is always less than 2. Therefore,

\[
R = \frac{1 + D}{t}, \quad c_1 \propto t^{-1-D}.
\]

The decay rate for clusters of mass \(k > 1\) is also simple:

\[
c_k \propto \begin{cases} 
  t^{-2} & D > 1/k, \\
  t^{-2} \ln t & D = 1/k, \\
  t^{-1-kD} & D < 1/k.
\end{cases}
\]
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APPENDIX A: GENERATING FUNCTION APPROACH

In the case of sterile monomers, we can employ the generating function approach as an alternative to a direct solution. The generating function

\[ G(z, t) = \sum_{k=2}^{\infty} w_k c_k(t) \]  

recasts an infinite set of rate equations into a single differential equation

\[ \frac{\partial G}{\partial t} = \gamma \frac{G^2}{2} + (z c_1 - \alpha) G. \]  

This is a Bernoulli equation that is readily solved in terms of \( G^{-1} \). The solution is

\[ G^{-1} = \frac{z^2 e^{2(1-z)\lambda}}{c_2} - \int_1^\tau \frac{d\tau'}{R(0)} \left( \frac{\tau}{\tau'} \right)^2 e^{(1-z)(\lambda' - \lambda)}, \]  

where \( \lambda = \lambda(\tau) \) and \( \lambda' = \lambda(\tau') \). For the bi-disperse initial condition, \( c_k(0) = c_1(0) \delta_{k,1} + c_2(0) \delta_{k,2} \), we have \( G(z, 0) = c_2(0) z^2 \) and \( R(0) = c_2(0) \). Using these relations together with \( c_2 = c_2(0) \tau^{-2} e^{-\lambda} \) we re-write (A3) as

\[ G^{-1} = \frac{e^{-z\lambda}}{c_2 z^2} - \int_1^\tau \frac{d\tau'}{(\tau')^2} e^{-(1-z)\lambda'}. \]  

We now consider in detail the marginal case of \( \gamma = 2 \) and justify the two-scale structure of the mass distribution. When \( \gamma = 2 \), we have \( \lambda = r \ln \tau \) and (A4) becomes

\[ G(z, t) = \frac{c_2(t) z^2 e^{\lambda_2} \left( 1 - \frac{1}{1+\tau} \right)}{1 - \frac{\tau}{1+\tau} \left( z - \frac{z^2}{1+\tau} \left[ 1 - \frac{1}{1+\tau} \right] \right)}. \]  

The term \( \tau^{-1-r(1-z)} \) in the denominator can be ignored within the boundary layer. Therefore, the denominator becomes \( (1-z)[1+(1+r)^{-1}z] \), and the generating function simplifies to

\[ G(z, t) = c_2(t) z^2 e^{\lambda_2} \frac{1}{2+r} \left[ \frac{1}{1-z} + \frac{1+r}{1+\frac{1}{1+\tau}} \right]. \]  

To extract the mass distribution, we expand \( G(z, t) \) in a Taylor series in \( z \). This gives

\[ \frac{c_{k+2}}{c_2} = \sum_{\lambda=0}^{k} \frac{\lambda^n}{n!} \left[ \frac{1}{2+r} + \frac{1+r}{2+r} \left( -1 + \frac{1}{2+r} \right)^b \right]. \]  

Thus apart from the leading contribution that equals \( \lambda^k/k! \), in agreement with our previous result in Eq. (15), we find all the correction terms; e.g., the leading correction is \( (1+r)^{-1}\lambda^{k-2}/(k-2)! \).

When both the quadratic and the transcendental terms in the denominator balance each other, the generating function accounts for the main part of the mass distribution. The both terms are comparable when \( 1-z \propto \tau^{-1} \). Writing \( 1-z = \zeta/\tau \) and taking \( z \to 1, \tau \to \infty \), with \( \zeta \) kept finite, we simplify the generating function:

\[ G = \frac{c_2(0)}{\tau} \frac{1}{1+(2+r)\zeta}. \]  

This form of the generating function implies that

\[ c_k = \frac{c_2(0)}{(2+r)\tau^2} \exp \left[ -\frac{1}{2+r} \frac{k}{\tau} \right]. \]  

Since \( \gamma = 2 \) and \( (2+r)R(0) = 2c_2(0) + c_1(0) = 1 \) for the bi-disperse initial conditions \( R(0) = c_2(0) \) and the mass density is always set equal to one), the above scaling form reduces to the anticipated scaling form of Eq. (19).

[1] E. M. Hendriks and M. H. Ernst, J. Colloid Interface Sci. 97, 176 (1984)
[2] R. W. Samsel and A. S. Perelson, Biophys. J. 37, 493 (1982); A. S. Perelson and R. W. Samsel, in: Kinetics of Aggregation and Gelation, eds. F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).
[3] P. G. J. van Dongen and M. H. Ernst, J. Phys. A 16 L327 (1983); P. G. J. van Dongen and M. H. Ernst, Phys. Rev. Lett. 54, 1396 (1985).
[4] F. Leyvraz and S. Redner, Phys. Rev. Lett. 57, 163 (1986);
[5] F. Leyvraz and S. Redner, Phys. Rev. A 36, 4033 (1987).
[6] F. Calogero and F. Leyvraz, J. Phys. A 33, 5619 (2000).
[7] F. Calogero and F. Leyvraz, J. Phys. A 32, 7697 (1999).
[8] See, e.g., S. K. Friedlander, Smoke, Dust and Haze: Fundamentals of Aerosol Behavior (Wiley, New-York, 1977); M. H. Ernst, in: Fundamental Problems in Statistical Physics VI, ed. E. G. D. Cohen (Elsevier, New York, 1985).
[9] S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).