Global Predictions in Aggregation, from Pure Monomer to Coarsening

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Examples of Aggregation
Clusters in a uniform bath of monomers

\[ (k) + (1) \leftrightarrow (k + 1) \]

Detailed balance leads to Becker-Döring equation:

\[ k_t = \omega \left( \eta k^{2/3} - \sigma k^{1/3} \right) \]

where, \( \eta \equiv \frac{\rho_1 - \rho_s}{\rho_s} \), and \( \rho_s \) is the saturation density.
The Becker-Doring model is used to derive the Zeldovich nucleation rate.

Small clusters “climb” up the free energy barrier due to fluctuations. The rate at which they cross is exponentially small in the height of the barrier.

\[ j \propto e^{-\frac{g^*}{k_B T}} \]
Motivation and Models
Aggregation Kinetics
Conclusions
Examples
Two Models of Aggregation
Combined Model

Macroscopic Model

Monomers move according to diffusion equation

\[ \eta \text{ on the boundary adjusts to make cluster “critical”} \]

\[ k_t \propto D \left( \eta k^\frac{1}{3} - \sigma \right) \]
Supersaturation on boundary adjusts to make both expressions for $k_t$ agree

\[ k_t = \frac{\omega (\eta k^{\frac{2}{3}} - \sigma k^{\frac{1}{3}})}{1 + \left( \frac{k}{k_*} \right)^{\frac{1}{3}}} \]

\[ k_* \propto \left( \frac{D}{\omega \nu^{\frac{2}{3}}} \right)^3 \rho_s^3 \]

$k \ll k_* \Rightarrow \text{BD}$

$k \gg k_* \Rightarrow \text{LS}$
Upshot of New Model

- It makes physical sense
- Can use Zeldovich nucleation rate — Small clusters
- Can use Lipshitz-Slyozov kinetics for cluster growth — Large clusters

One model for the whole process
Cluster size kinetics $\Rightarrow$ Advection PDE for cluster density, $\rho(k, t)$

Zeldovich nucleation rate $\Rightarrow$ Effective source term as $k \to 0^+$

Super-saturation determined from conservation of particles

Signaling problem has three distinguished limits corresponding to the three eras.
Non-Linear Advection PDE

\[ \partial_t \rho + \partial_k \left( (k^{1/3} \eta - s) \rho \right) = 0 \]

\[ k^{1/3} \rho \rightarrow j = e^{\delta \eta} \quad \text{as } k \rightarrow 0^+ \]

\[ \int_{0}^{\infty} k \rho(k, t) \, dk = -\delta \eta \]

\[ \rho(k, 0) = 0 \]

<table>
<thead>
<tr>
<th>Variable</th>
<th>( \eta )</th>
<th>( k )</th>
<th>( t )</th>
<th>( \delta \eta )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td>( \varepsilon )</td>
<td>( \left( \frac{d \varepsilon^4}{\Omega \sigma^4} \right)^{3/5} ) ( \gamma^{3/10} )</td>
<td>( \left( \frac{\varepsilon}{d \sigma^2 \Omega^2} \right)^{3/5} ) ( \gamma^{1/5} )</td>
<td>( \frac{\varepsilon^2}{\sigma^3} )</td>
<td>( \rho_s \left( \frac{\Omega^2 \sigma}{d^2 \varepsilon^3} \right)^{3/5} \gamma^{-3/5} )</td>
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<tr>
<td>( \gamma )</td>
<td>( \equiv e^{\sigma^3/\varepsilon^2} )</td>
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Global Predictions in Aggregation
The $\varepsilon \rightarrow 0$ limit of PDE has nice characteristics

Resulting in an integral equation for $\delta \eta$

$$\delta \eta(t) = - \int_0^t \left( \frac{2}{3} (t - \nu) \right)^{\frac{3}{2}} e^{\delta \eta(\nu)} d\nu$$
Cluster density is reconstructed from $\delta \eta$

$$\rho(k, t) = k^{-\frac{1}{3}} e^{\delta \eta (t - \frac{3}{2} k^{\frac{2}{3}})}$$

At $t = O(1)$ nucleation is effectively over...
By following the front location, $K$, and the width of the distribution, $a$, the PDE simplifies resulting in an ODE for $K$

$$K_t = K^{\frac{1}{3}} (1 - K) \quad a \propto K^{\frac{1}{3}}$$
The solution is a curve describing the location of the front.

Implicit solution

\[ t = \sum_{j=0}^{2} r_j \log \left( 1 + r_j K^{\frac{1}{3}} \right) \]

\[ r_j = e^{\frac{2j+1}{3} i\pi} \]
Combining with the nucleation era, we have the distribution during the growth era.
Coarsening Era

Scaling yields a parameter-free advection PDE for $\rho$

$$\rho_t + (w\rho)_k = 0$$

where $w$ depends on moments of $\rho$.
Initial conditions are found by “numerical matching”

Numerical Solution
Problem: The $\epsilon \to 0$ limit of the tail end of the growth era is singularly narrow and tall, while the coarsening era can only be solved numerically...

Solution: An asymptotic solution for narrow distributions is found, and the numerical solution takes the widened solution as initial conditions.

Result: Numerical solution is “global”, $\epsilon$ causes small shift in time-variable
The numerical solution “takes” the solution from one asymptotic solution to another.
The PDE has a family of similarity solutions.

Numerical solution asymptotes to discontinuous similarity solution as $t \to \infty$. 
BD and LS are limits of combined model
Signaling problem has three distinguished limits
A particular (discontinuous!) similarity solution is selected
Numerical matching to connect to analytic solutions
Lifshitz and Slyozov had good insight

From the 1959 J. Phys. Chem. Solid (19),

A good sketch of the growth and coarsening eras
Possible Future Directions

- Compare predicted size and time scales with experimental data
- Successor to Zeldovich
- Theory for 2D clusters
- Effect of *ignition transient*
- Spatially inhomogeneous supersaturation

