II. Paradigms for coarsening dynamics

Modeling hierarchy in 1D
- Phase-space geometry of relaxation
- 1D bubble bath - mean-field model

Modeling hierarchy in 3D
- Lifshitz-Slyozov-Wagner mean-field model
  - Well-posedness & Wasserstein metric
  - Non-universality of self-similar behavior
What can one predict about the "typical" patterns that emerge on intermediate time scales?

Case study: 1D

\[ u_t = \varepsilon^2 u_{xx} - f(u) \]

\[ f = u^3 - u \]

\[ u \]

\[ h_i, h_i(t), h_{i+1} \]

\[ x \]
J.B. Hamon et al.: Surface self diffusion by vacancy motion
Island ripening on Cu(001)

Phys Rev Lett 79 1997 2506
Ostwald ripening of two-dimensional islands on Si(001)
Modeling domain coarsening in 1D

\[ u_t = \varepsilon^2 u_{xx} + u - u^3 \]

Front migration law

\[ h_j = \varepsilon \left( e^{-A(h_{j+1} - h_j)/\varepsilon} - e^{-A(h_j - h_{j-1})/\varepsilon} \right) \]

Geometric model - 1D bubble bath

\[ l_1, l_2, l_3 \]

\[ l_1 + l_2 + l_3 \]

Statistical mean-field model of coagulation

\[ f(l, t) \, dl \quad \text{Probability domain length is in } (l, l+dl) \]

\[ \frac{\partial f(l, t)}{\partial t} = \frac{1}{\#} \int_0^l f(y, t) f(l-y, \text{bin}(x), t) \, dy \]
\( u_t = \varepsilon^2 u_{xx} - f(u) \quad 0 < x < 1 \quad t > 0 \)
\( u_x = 0 \quad x = 0, 1 \)
\( u(x,0) = u_0(x) \)

\[ I(u) = \int_0^1 F(u) + \frac{1}{2} \varepsilon^2 u_x^2 \]

\( f = F' \)

Gradient flow for \( I(u) \)
Figure 1. Initial data at time $t = 0$. 
Figure 2. Solution at time $t = 100$.

$f(u) = \frac{1}{2} (u^3 - u)$
Phase space geometry for nonlinear relaxation

"Punctuated equilibrium"

Fusco-Hale
Carr-Pego
Sudden collapse of smallest domains

Geometric Model

1) Partition a line

2) Collapse smallest domain

3) Repeat thousands of times

Statistics: Distribution of domain sizes

\[ n(x,t) \, dx = \# \text{ of domains with length in } (x,x+dx], \text{ per unit length} \]

\[ N(t) = \int_0^\infty n(x,t) \, dx = \text{total \# of domains, per unit length} \]

\[ u(x,t) \, dx = \frac{n(x,t) \, dx}{N(t)} = \text{probability a domain has length in } (x,x+dx) \]
"Mean field" model of sudden collapse

\[ \bar{x}(t) \quad \text{length of smallest domain remaining} \]

\[ \frac{dN}{dt} = -2 \quad \text{"Time" defined so events occur at constant rate} \]

\[ \text{Process} \quad \text{Rate} \left( \frac{2n(x,t)}{\sigma^t} \right) \]

1) Destroy \( x \)

\[ x, x, y \rightarrow x + x + y : -2u(x,t) \]

2) Create \( x \)

\[ y, x, x-y-z \rightarrow x : \int_0^\infty u(y)u(x-y-z)dy \]

* Coagulation equations

- \[ N(t) \frac{d}{dt} u(x,t) = \int_0^\infty u(y,t)u(x-y-z,t)dy, \]

- \[ N(t) \frac{d}{dt} \bar{x}(t) - u(\bar{x}(t)) = 1, \text{ with } u = 0 \text{ for } x < \bar{x}(t). \]
An amazing solution procedure

Scale time so \( \mathcal{X}(t) = t \):

\[
\frac{\partial u}{\partial t}(x,t) + u(t) \int_0^x u(y,t) u(x-y-t,t) \, dy = 0
\]

Expand coordinates with time for self-similarity:

\[
\frac{x}{t} = y \quad n(y,t) = tu(ty,t) \\
\frac{3}{t} \frac{\partial n}{\partial t} = \frac{2}{3y}(yn) + \frac{3}{2} \int_0^x n(y,t) \int_0^{y-2} \frac{\partial n}{\partial t} \int_0^{y-1} \frac{\partial n}{\partial t} \, dy \\
\]

Let \( \mathcal{F} \) denote the Fourier transform in \( y \):

\[
\mathcal{F}(\mathcal{F}n)(\xi) = \int_{-\infty}^{\infty} n(y) e^{-i\xi y} \, dy
\]

Let

\[
\omega(y,t) = \mathcal{F}^{-1}(\frac{1}{2\sqrt{t}} \ln \frac{1+t}{t}) \circ \mathcal{F}n
\]

Then

\[
\frac{2}{3t} \omega = \frac{2}{3y}(y\omega)
\]

The solution

\[
w(y,t) = t \omega_0(ty)
\]
Modeling domain coarsening in 3D

Stochastic Ising model - atomic level

Cahn-Hilliard PDE \[ \frac{\partial u}{\partial t} = \Delta (-u + u^3 - \epsilon^2 \Delta u) \]

Mullins-Sekerka sharp interface motion

\[ \Delta u = 0 \text{ in } \Omega(t) \]
\[ u = k \text{ on } \Gamma(t) \]
\[ v = \frac{\partial u}{\partial n} \text{ on } \Gamma(t) \]

Monopole model - Voorhees + others

Lifshitz-Slyozov-Wagner mean field theory

\[ f(v,t) = \text{Expected # of domains of volume } v \]

\[ \frac{3f}{\Delta t} + \frac{2}{3v} \left((v^{3/2} \theta(t) - 1)f \right) = 0 \]
I.S.W model of domain coarsening

1) Particles evolve by diffusional exchange of heat or mass

\[ \Delta u = 0 \quad \text{in} \ \Omega(t) \quad \text{(Quasi-steady diffusion)} \]
\[ u = \kappa \quad \text{on} \ \partial \Omega(t) \quad \text{(Gibbs-Thomson)} \]
\[ V = \frac{\partial u}{\partial n} \quad \text{on} \ \partial \Omega(t) \quad \text{(flux drives motion)} \]

2) Dilute approximation: particles are spherical and interact only via mean field \( u \approx u_\infty(t) \)

Denote particle radius by \( R(t) \)

\[ u = \frac{1}{r} + u_\infty(t) \left( 1 - \frac{R(t)}{r} \right) \]

\[ \frac{dR}{dt} = \frac{1}{R^2} (Ru_\infty(t) - 1) \]

Conservation of total volume \( \Rightarrow u_\infty(t) = 1/R_{av}(t) \).
Evolution of the particle size distribution (PSD)

Let \( n(R, t) \) be the number density of particles of size \( R \):

\[
\int_{R}^{\infty} n(x, t) \, dx = \frac{\text{# of particles with radius } \geq R}{\text{initial # of particles}}
\]

This is constant if \( R(t) \) is a particle size:

\[
0 = \frac{d}{dt} \int_{\infty}^{R} n = \int_{\infty}^{R} \frac{\partial n}{\partial t} \, dx + n(R, t) \frac{dR}{dt}
\]

so (taking \( \partial/\partial R \)) a smooth PSD evolves according to the Fokker-Planck equation

\[
\frac{\partial n}{\partial t} + \frac{\partial}{\partial R} \left( n \frac{1}{R^2} \left( \frac{R}{R_c(t)} - 1 \right) \right) = 0
\]

We take the critical radius \( R_c(t) \) equal to the average radius \( R_{av}(t) = \langle R \rangle \).
Analysis of Lifshitz and Slyozov (1961)

Rescale by critical radius $R_\text{c}(t)$. Put

$$\rho = \frac{R}{R_\text{c}}, \quad \tau = 3 \log \left( \frac{R_\text{c}(t)}{R_\text{c}(0)} \right), \quad \gamma = \frac{1}{R_\text{c}' R_\text{c}^2}.$$

$$\frac{d\rho}{dt} = \frac{1}{R_\text{c}} \frac{dR_t}{dt} - \frac{R}{R_\text{c}^2} \frac{dR_\text{c}}{dt} \Rightarrow$$

$$\frac{d\rho^3}{d\tau} = \gamma (\rho - 1) - \rho^3.$$

Claim: As $\tau \to \infty$, $\gamma \to \gamma_\text{c} = \frac{27}{4}$.

Argument:

$\gamma > \gamma_\text{c}$ $\Rightarrow$ $\rho \to \rho_2$ if $\rho > \rho_1$ $\Rightarrow$ Volume $\to \infty$

$\gamma < \gamma_\text{c}$ $\Rightarrow$ $\rho \to 0$ in finite time $\Rightarrow$ Volume $\to 0$
Predicted self-similar regime

- Critical radius grows like a power of time, with a particular exponent and rate constant:

$$\frac{d}{dt} \frac{R_c^3}{3} = \frac{4}{27} \Rightarrow R_c \sim \left( R_c^3 + \frac{4}{9} t \right)^{1/3}$$

- The particle size distribution approaches an explicit self-similar form for most initial data

Problems

(see review articles by P. W. Voorhees)

- Observed PSD's are much broader than predicted
- Rate constants are difficult to measure
- FP equation valid only in extremely dilute systems (system size $\ll$ Debye screening length)
- Time scale for convergence to SSS not explained
- There is a whole family of SSS corresponding to $\gamma > \frac{27}{7}$. Thus there is a selection problem: which solutions converge to the predicted form?
Mean-field model of Ostwald ripening for 2D islands on Si(001)
NC Bartelt et al Phys Rev B 54 1996
Attachment-limited kinetics ⇒ $V = \kappa - \langle \kappa \rangle$

With circular islands, radii $R_j(t)$ satisfy

$$\frac{dR_j}{dt} = -\frac{1}{R_j} + \frac{1}{R_c(t)}$$

Conservation of total area ⇒ $R_c(t) = \langle R \rangle$.

Self-similar solution of $\partial_t n + \partial_R (n \dot{R}) = 0$: $n(r, t) = \frac{\rho}{2} \left( \frac{2}{2 - \rho} \right)^4 \exp \left( \frac{-2\rho}{2 - \rho} \right)$, $\rho < 2$

$$\rho = \frac{R}{R_c(t)}, \quad R_c(t) = \left( R_0^2 + \frac{t}{2} \right)^{1/2}$$
FIG. A. Normalized experimental distributions of island sizes at 50 s, 100 s, and 420 s compared with the predictions of mean-field theories of Oswald ripening. The dotted lines correspond to blow-off average ripening limited by diffusion in the substrate sea surrounding the islands. The solid line which shows much better agreement with the data, is the distribution for attachment limited kinetics [Eq. (A3)].

The rate of change of island area $A$ is given by

$$\frac{dA}{dt} = -C \Gamma (\mu - \mu_A).$$  \hspace{1cm} (4.1)

We have checked this relationship over a wide temperature range. Figure 5 shows the time dependence of islands on a 480°C substrate from 820°C. Also plotted for 570°C is the decay rate of small islands. The linear behavior persists. Equation (4.3) and clearly inconsistent with the attachment-limited diffusion limit discussed in Secs. V and VI. The $A$ parameter of the steps is the overall ripening rate, as well as the width-observed capillary wave moti

V. RELATIONSHIP BETWEEN DISSOLUTION AND OVERALL COMPARISON WITH MEAN N

The (experimentally) determined