Late Stage Coarsening: Theoretical and Computational Developments

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• Coarsening Introduction

• Late Stage Scaling and Universality

• Simulation of Cahn-Hilliard Equation
  ◦ Eyre’s Theorem and von Neumann Stability
  ◦ Accuracy Requirements
Phase Separation Dynamics

Two-phase systems:

- binary alloys
- polymer blends
- uniaxial magnets
- binary fluids

Rapid temperature quench leads to . . .
... nearly equilibrated domains separated by thin interface

\[ F - F_{eq} \propto \text{amount of interface} \]

\[ \dot{F} < 0 \implies \text{reduction of interface} \implies \text{coarsening!} \]
Sharp Interfaces: interface width $\xi(T)$ constant, so domain size $L(t) \gg \xi$ asymptotically

Self-Similarity: correlation function
$C(r, t) = f\left(\frac{r}{L(t)}\right)$

Power-law Growth: $L \sim A t^{1/3}$ and Universality!
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Theoretical Picture

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- Chemical potential \( \mu(x) = \frac{\delta F}{\delta \mu(x)} \)
- Free energy: \( F = \int d^dx \left\{ \frac{1}{2} \kappa (\nabla \phi)^2 + V(\phi) \right\} \)
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$\Rightarrow$ Cahn-Hilliard eq: $\partial_t \phi = \nabla^2 [V'(\phi) - \nabla^2 \phi]$
Equilibrium interface

\[ \mu = V'(\phi) - \nabla^2 \phi = 0 \implies \phi(z) \sim \tanh(z/2\xi) \]

plug into \[ F[\phi] \] to find surface tension \( \sigma \).
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In bulk, near equilibrium

\[ \mu \approx V''(\phi_{eq})(\phi - \phi_{eq}) \]
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Near interfaces \( \mu \sim \kappa \)

Gibbs-Thomson: \( \mu(x) = \frac{\sigma}{\Delta \phi_{eq}} \kappa(x) \)
Interface dynamics

- Gibbs-Thomson gives $\mu$ at the interface
- quasistatic: $\nabla^2 \mu = 0$ gives $\mu(x)$ everywhere!
- interface velocity: $v(x) \sim [\hat{n} \cdot \nabla \mu]$
Assume scaling with domain size $L$

- $\mu \sim \kappa \sim 1/L$ so $\mu(x) \sim 1/L$ everywhere
- $\mathbf{j} = \nabla \mu \sim 1/L^2$
- $\dot{L} \sim v = [\mathbf{n} \cdot \mathbf{j}]$
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- $\mathbf{j} = \nabla \mu \sim 1/L^2$
- $\dot{L} \sim v = [\mathbf{n} \cdot \mathbf{j}] \sim 1/L^2$
- implies $L \sim t^{1/3}$ growth law
Universality: assume asymptotic domain wall trajectories determine asymptotic structure

Implies $C(r, t) = f(r/L)$ depends on

- volume fraction
- dimension of system
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Implies $C(r, t) = f(r/L)$ depends on

- volume fraction
- dimension of system
- surface tension anisotropy $\sigma(\hat{n})/\sigma_0$
- ratio of equilibrium mobilities: $M(\phi_1)/M(\phi_2)$
- and nothing else! Needs to be tested . . .
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Cahn-Hilliard simulation [Rogers, Elder, Desai ’88]:

Take $V(\phi) = (1 - \phi^2)^2$ and use Euler step

$$\phi_{t+\Delta t} = \phi_t + \Delta t \nabla^2 \mu_t$$

but this has a lattice instability for $\Delta t \geq \text{const.} \Delta x^4$

Severely constrains simulations

while $\nu \sim 1/L^2 \sim 1/t^{2/3}$, $\Delta t$ remains fixed
If simulation were **accuracy** limited instead of **stability** limited:

A fixed number of steps to resolve passing of interface gives $\Delta t \sim 1/v \sim t^{2/3}$
If simulation were accuracy limited instead of stability limited:

A fixed number of steps to resolve passing of interface gives $\Delta t \sim 1/\nu \sim t^{2/3}$

$$\Delta t = \frac{dt}{dn} \sim t^{2/3} \Rightarrow t \sim n^3 \text{ rather than } t \sim n$$
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Eyre’s Theorem ['98] proves stable steps exist. Split $F = F^C + F^E$ and use e.o.m.

$$
\phi_{t+\Delta t} - \Delta t \nabla^2 \mu_{t+\Delta t}^C = \phi_t + \Delta t \nabla^2 \mu_t^E
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$$

Necessary splitting conditions: for curvature matrix $M_{i,j} = \frac{\delta^2 F}{\delta \phi_i \delta \phi_j}$ and similarly $M^E$ and $M^C$

- $M^C$ must have strictly non-negative eigenvalues
- $M^E$ must have strictly non-positive eigenvalues
- $\lambda^E_{max} \leq \frac{1}{2} \lambda_{min}$
von Neumann Stability [BV-L and Rutenberg, in prep]

Start with CH eq: \( \dot{\phi} = -\nabla^2 \phi - \nabla^4 \phi - \nabla^2 \phi^3 \)

Take \( \phi(x) = c + \eta(x) \) and linearize CH equation

Write general splitting in Fourier space:

\[
[1 + L_k \Delta t] \eta_{t+\Delta t} = [1 + R_k \Delta t] \eta_t
\]

vN stability for all \( \Delta t \) requires \( L_k > |R_k| \)
Example: consider splitting with r.h.s.:

\[ \phi_t - a_1 \Delta t \nabla^2 \phi_t - a_2 \Delta t \nabla^4 \phi_t + \Delta t \nabla^2 \phi^3_t \]

where \( a_1 = a_2 = 1 \) implies the Euler step.
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Exact step:

$$\phi_{t+\Delta t} = \phi_t + \Delta t \nabla^2 \mu_t + \frac{\Delta t^2}{2!} \nabla^2 \dot{\mu}_t + \frac{\Delta t^3}{2!} \nabla^2 \ddot{\mu}_t + \ldots$$

For $\Delta t \sim t^{2/3}$ we need $O(\Delta t^n)$ coefficient to decay sufficiently fast.
Can show $\partial_t^n \phi = \partial_t^{n-1} \nabla^2 \mu \sim t^{-2n/3}$ at interface

- If splitting gives terms proportional to $\partial_t^{n-1} \nabla^2 \mu$ at order $O(\Delta t^n)$, we’re okay
- If not, then at some order $O(\Delta t^p)$, the error terms no longer decay as fast
- This is rate limiting and gives $\Delta t \sim t^{2(p-1)/3p}$
- Eyre/vN give $p = 2$, so $\Delta t \sim t^{1/3}$
Summary

• New predictions for coarsening universality classes
• Stable numerical methods available (may have more general application)
• More improvement possible, going to $p = 3, 4 \ldots$