Late Stage Coarsening: Theoretical and Computational Developments

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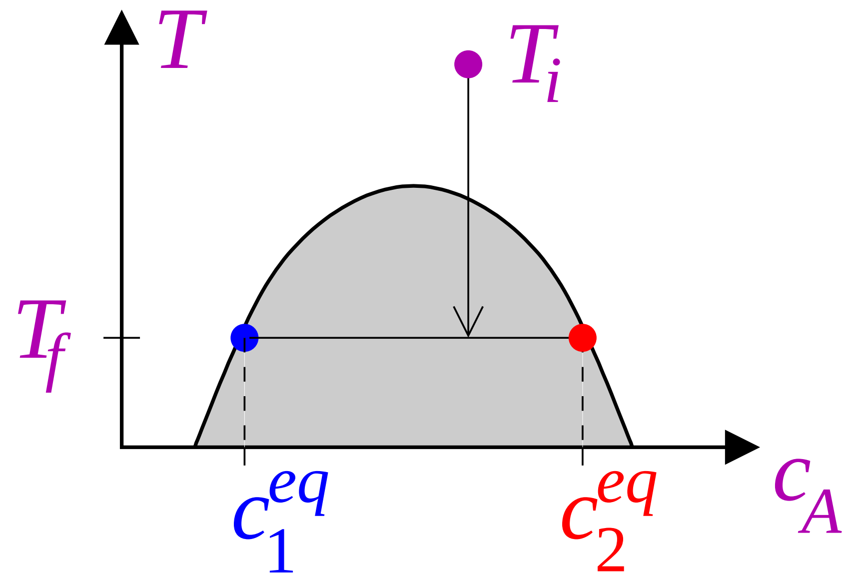
- Coarsening Introduction
- Late Stage Scaling and Universality
- Simulation of Cahn-Hilliard Equation
  - ◇ Eyre's Theorem and von Neumann Stability
  - ◇ Accuracy Requirements

Phase Separation Dynamics

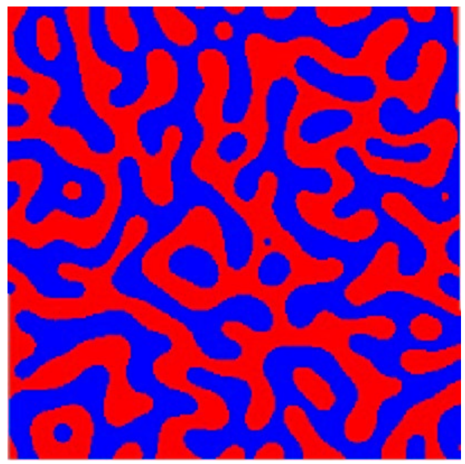
Two-phase systems:

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



Rapid temperature quench leads to . . .

. . . nearly equilibrated domains separated by thin interface

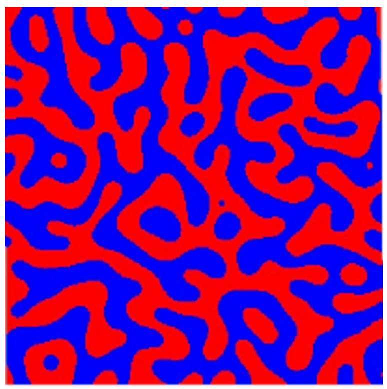
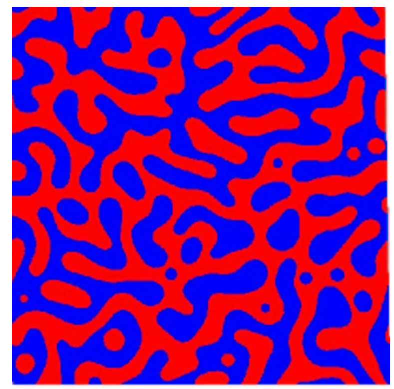


$$F - F_{eq} \propto \text{amount of interface}$$

$$\dot{F} < 0 \;\Rightarrow\; \text{reduction of interface} \Rightarrow \text{coarsening!}$$

Sharp Interfaces: interface width $\xi(T)$ constant, so domain size $L(t) \gg \xi$ asymptotically

Self-Similarity: correlation function $C(\mathbf{r}, t) = f\big(\mathbf{r}/L(t)\big)$

$t = t_0$  $t = 8t_0$ 

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

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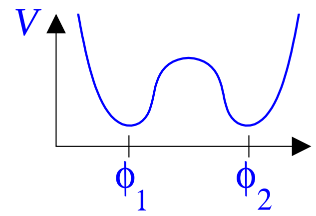
- chemical potential $\mu(\mathbf{x}) = \frac{\delta F}{\delta \mu(\mathbf{x})}$
- Free energy: $F = \int d^d x \left\{ \frac{1}{2}\kappa(\nabla\phi)^2 + V(\phi) \right\}$



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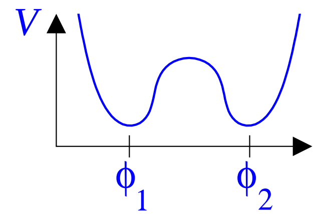

$\Rightarrow$ Cahn-Hilliard eq: $\partial_t \phi = \nabla^2[V'(\phi) - \nabla^2\phi]$

Equilibrium interface

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plug into $F[\phi]$ to find surface tension σ.

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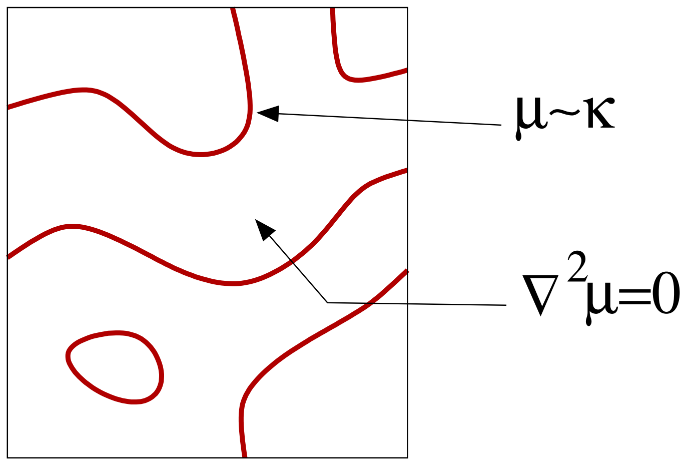
Near interfaces $\mu \sim \kappa$

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

Interface dynamics



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

Assume scaling with domain size L

- $\mu \sim \kappa \sim 1/L$ so $\mu(\mathbf{x}) \sim 1/L$ everywhere
- $\mathbf{j} = \nabla\mu \sim 1/L^2$
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- $\mathbf{j} = \nabla\mu \sim 1/L^2$
- $\dot{L} \sim v = [\hat{\mathbf{n}} \cdot \mathbf{j}] \sim 1/L^2$
- implies $L \sim t^{1/3}$ growth law

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Implies $C(\mathbf{r}, t) = f(\mathbf{r}/L)$ depends on

- volume fraction
- dimension of system
- surface tension anisotropy $\sigma(\hat{\mathbf{n}})/\sigma_0$
- 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

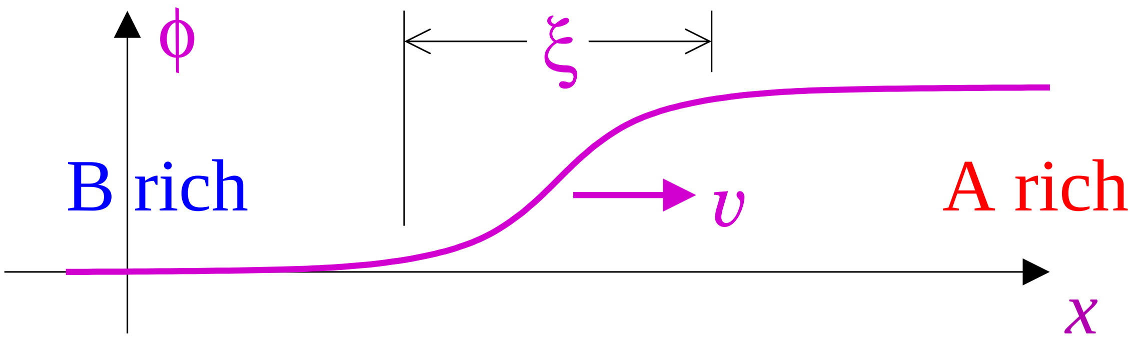
$$\phi_{t+\Delta t} = \phi_t + \Delta t \nabla^2 \mu_t$$

but this has a lattice instability for
$\Delta t \geq$ const. Δx^4

Severely constrains simulations

while $v \sim 1/L^2 \sim 1/t^{2/3}$, Δt remains fixed

If simulation were accuracy limited instead of stability limited:



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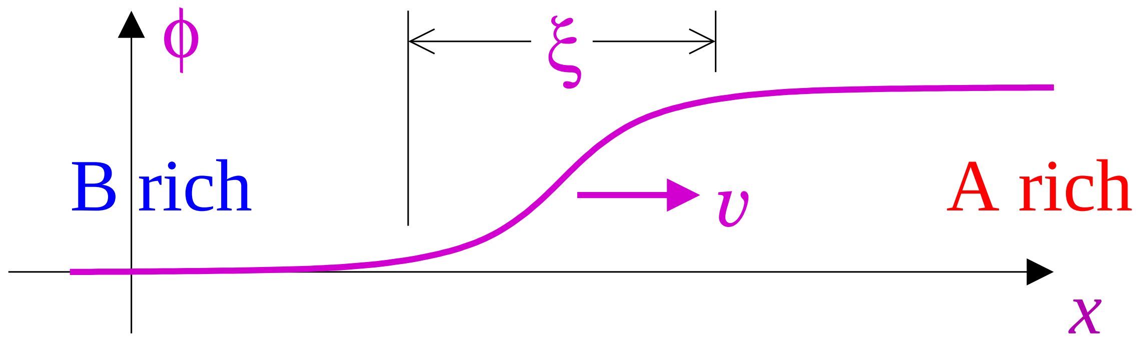

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$\Delta t = \frac{dt}{dn} \sim t^{2/3} \Rightarrow t \sim n^3$ rather than $t \sim n$

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Eyre's Theorem ['98] proves stable steps exist.

Split $F = F^C + F^E$ and use e.o.m.

$$\phi_{t+\Delta t} - \Delta t \nabla^2 \mu^C_{t+\Delta t} = \phi_t + \Delta t \nabla^2 \mu^E_t$$

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Necessary splitting conditions: for curvature matrix $M_{ij} = \frac{\delta^2 F}{\delta\phi_i \delta\phi_j}$ 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 $\phi(\mathbf{x}) = c + \eta(\mathbf{x})$ and linearize CH equation

Write general splitting in Fourier space:

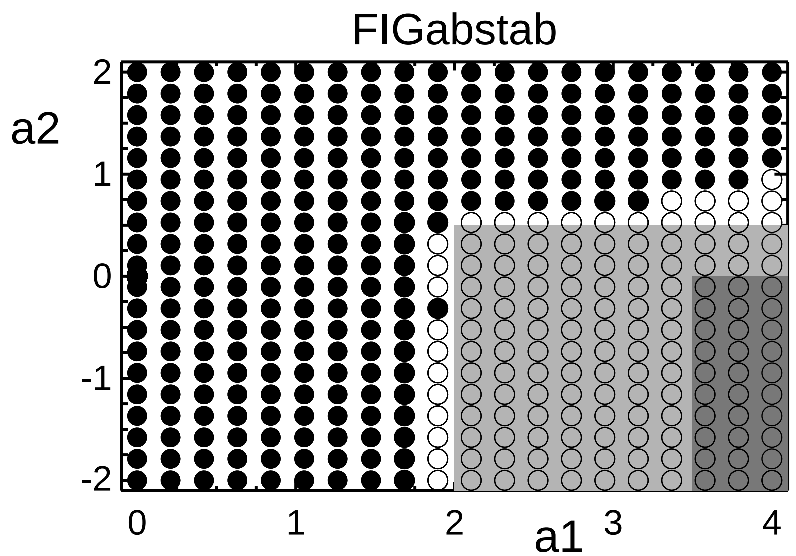
$$[1 + \mathcal{L}_{\mathbf{k}}\Delta t]\eta_{t+\Delta t} = [1 + \mathcal{R}_{\mathbf{k}}\Delta t]\eta_t$$

vN stability for all Δt requires $\mathcal{L}_{\mathbf{k}} > |\mathcal{R}_{\mathbf{k}}|$

Example: consider splitting with r.h.s.:

$$\phi_t - a_1 \Delta t \nabla^2 \phi_t - a_2 \Delta t \nabla^4 \phi_t + \Delta t \nabla^2 \phi_t^3$$

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 $p = 3, 4 \ldots$