Kinetics of Phase Separation in Binary Mixtures

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Plan:

- **Introduction:** (a) Equilibrium Description of Phase Separation
  (b) Kinetics of Phase Separation
  (c) Modeling at Atomistic and Coarse-grained levels

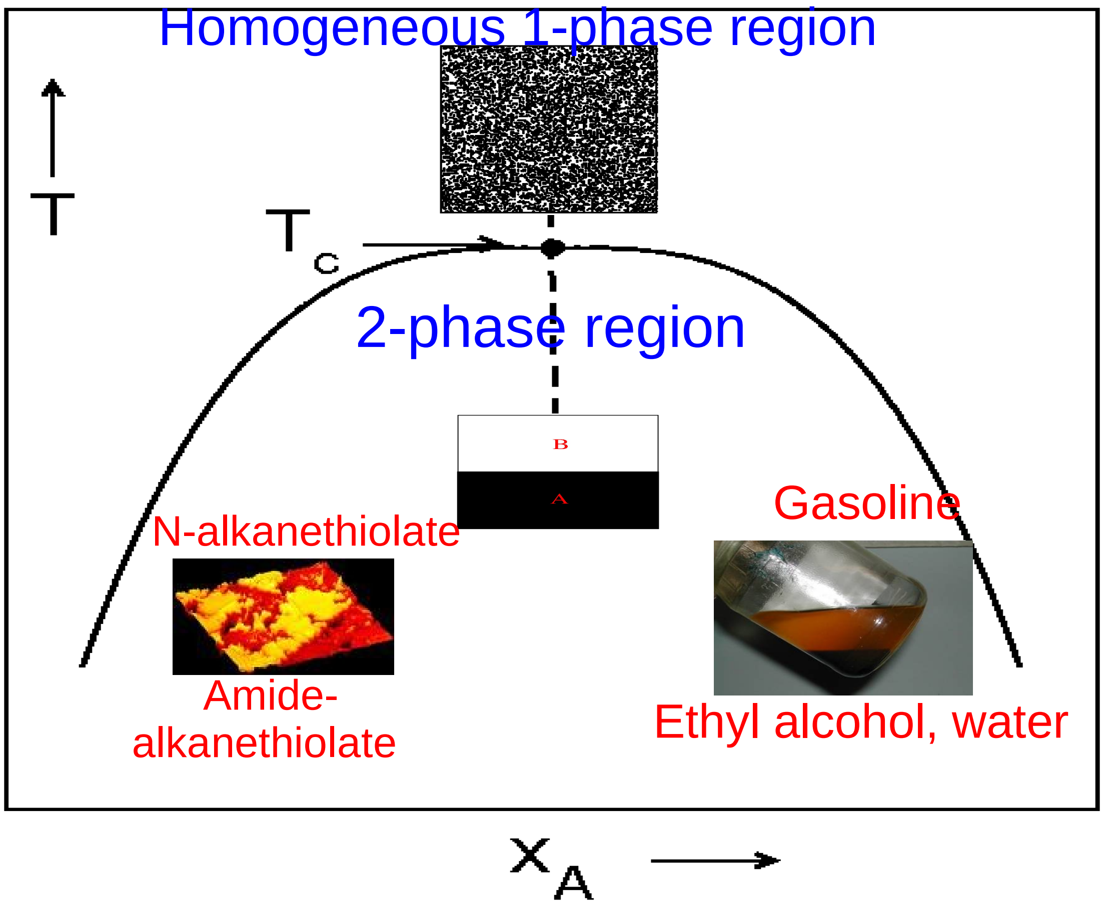
- **Kinetics of Phase Separation in Solids:** Atomistic or Coarse-grained?
  (a) Bulk Systems
  (b) Confined Systems

- **Kinetics of Phase Separation in Fluids:** Need for Multi-Scale Modeling?

- **Conclusion**

Phase Separation: INTRODUCTION

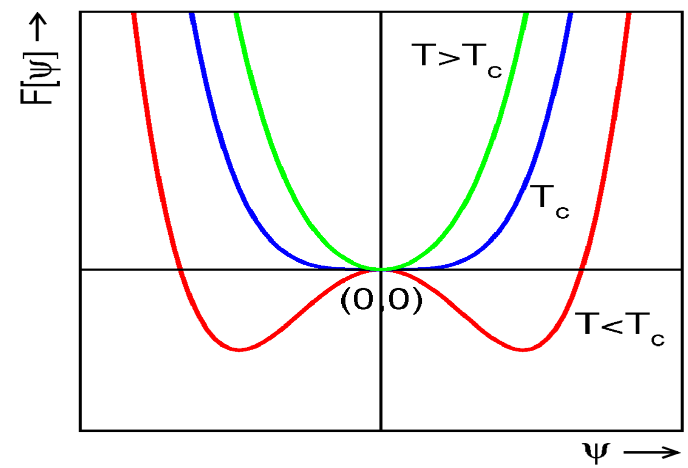
Binary Mixture A+B



Order parameter $\psi = x_A - x_B$

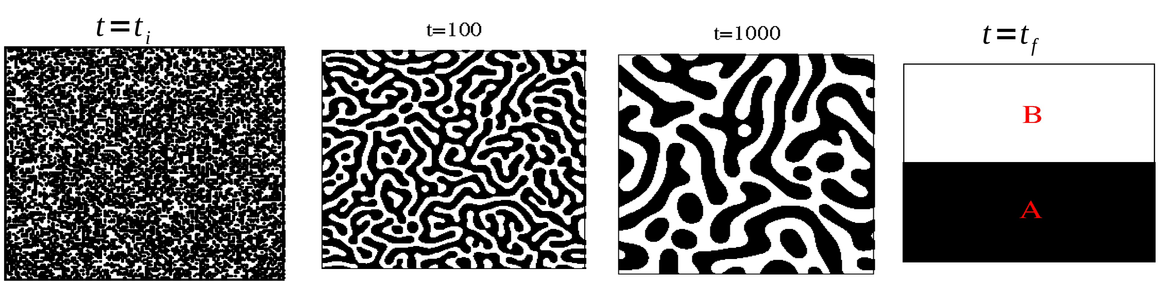
High T, $\psi = 0$; Low T, $\psi \neq 0$

Free energy minima at equilibrium values of ψ



$$F(\psi) = (T - T_c)\psi^2 + \psi^4$$

--Landau Free energy.



Self-Similar Structure

Domains grow via curvature driven motion of boundary:

$$L(t) \propto t^{\alpha}$$

Growth exponent depends upon transport mechanism.

Kinetics of Phase Separation in *BULK*

- **Solid Mixtures**: Diffusive mechanism

Rate of growth $\frac{d\ell(t)}{dt} \sim |\nabla\mu| \sim \frac{1}{\ell(t)^2} \rightarrow \alpha = 1/3$ --**Lifshitz-Slyozov**, 1961

Methods:

➔Monte Carlo Simulation of Ising Model $H = -J\sum_{\langle ij\rangle} S_i S_j;\ \ S_i = \pm 1$ A B

➔Coarse-grained continuum dynamical equations

Landau Free energy $F(\psi) = (T - T_c)\psi^2 + \psi^4$

Ginzburg-Landau Free energy $F[\psi(\vec{r},t)] = \int d\vec{r}\,[\frac{-\psi^2}{2} + \frac{\psi^4}{4} + (\vec{\nabla}\psi)^2]$

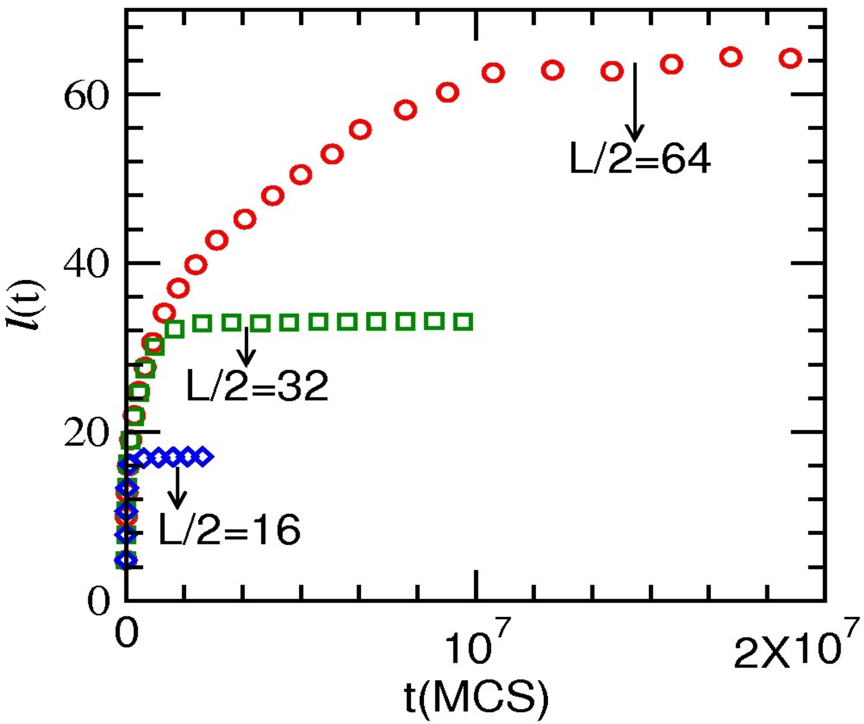
$$\psi = \frac{1}{V}\sum_i S_i;\psi \epsilon [1,-1] \quad \mu(\vec{r},t) = \delta F/\delta\psi(\vec{r},t) \quad \vec{J}(\vec{r},t) = -\vec{\nabla}\mu(\vec{r},t)$$

$$\frac{\partial}{\partial t}\psi(\vec{r},t) = -\vec{\nabla}\cdot\vec{J}(\vec{r},t) = -\nabla^2[\psi + \nabla^2\psi - \psi^3]$$

--- Cahn-Hilliard Equation; solve them on lattice.

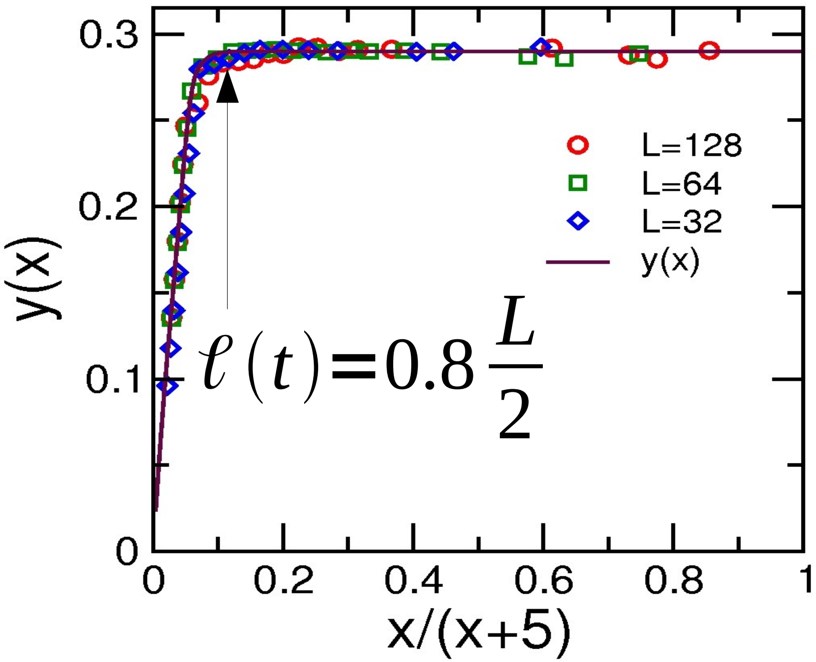
Kinetics of Phase Separation in *BULK*

2-d Monte Carlo results of Ising model: S.Majumder and SKD (2009)



$$L=\infty: \quad \ell(t)-\ell(0)=At^{\alpha}$$

$$L<\infty: \quad \ell(t)-\ell(0)=y(x)t^{\alpha}; \quad x\propto L/t^{\alpha}$$



$$\alpha=0.336$$

$$x\to 0\,(L<\infty): \quad y(x)\sim x$$

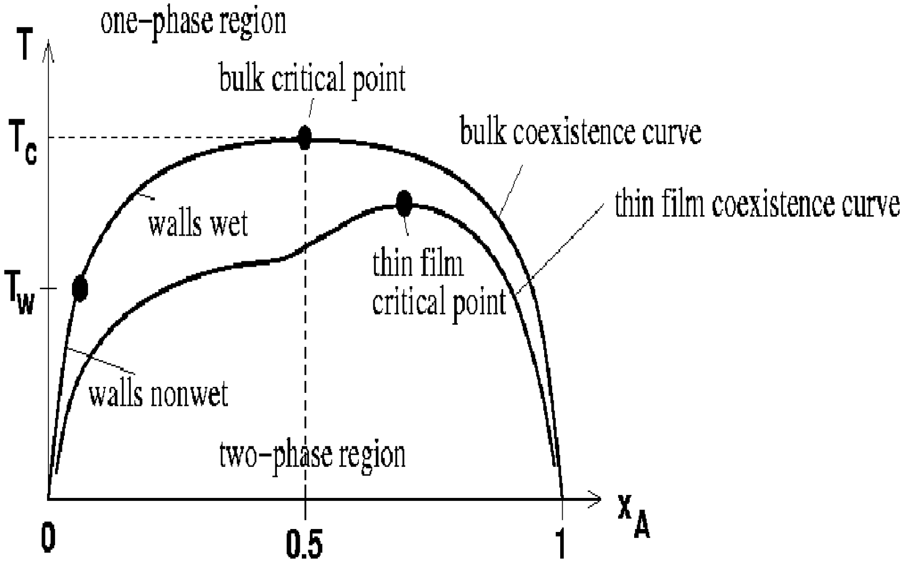
$$x\to\infty\,(L\to\infty): \quad y(x)\sim A$$

$$y(x)=\frac{Ax}{x+B/(E+Cx^{D})}; y(x\to\infty)\approx A\left[1-px^{-(D+1)}\right]=A\left[1-px^{-n}\right]; n\approx 6$$

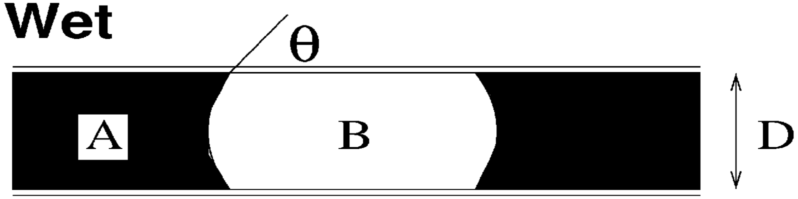
Dynamic Critical Phenomena (SKD, M.E. Fisher, et al.): $n\approx 3$

Kinetics of Phase Separation: *Thin Film*

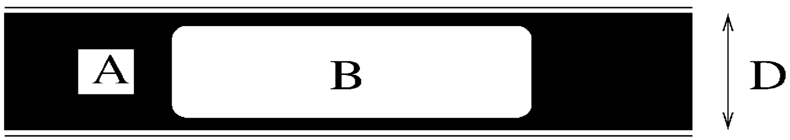
- ***Binary mixture A+B confined between two parallel walls that prefer A***



Partially Wet



Completely Wet



Young's equation: $\gamma_{AB}\cos\theta = \gamma_{BW} - \gamma_{AW}$

$T < T_W, \theta \neq 0$

$T \to T_W^-, \theta \to 0$

Methods to study Kinetics in Solid Film:

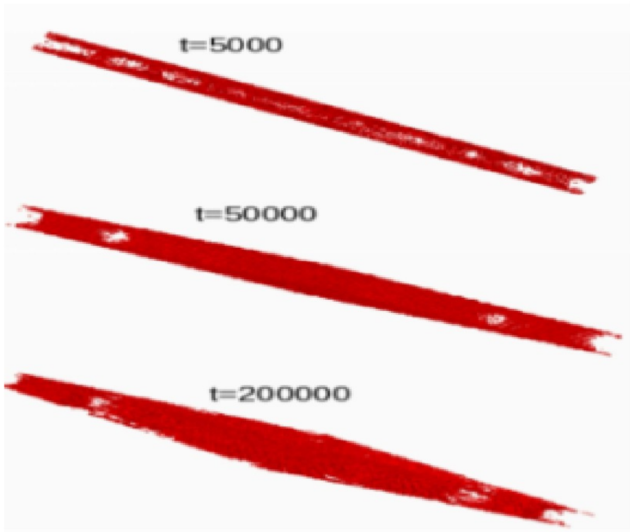
Ising Model: $$H = -J\sum_{\langle ij\rangle^b} S_i S_j - J_s \sum_{\langle ij\rangle^{s_1,s_2}} S_i S_j - H_{S_1}\sum_{S_1} S_i - H_{S_2}\sum_{S_2} S_i$$

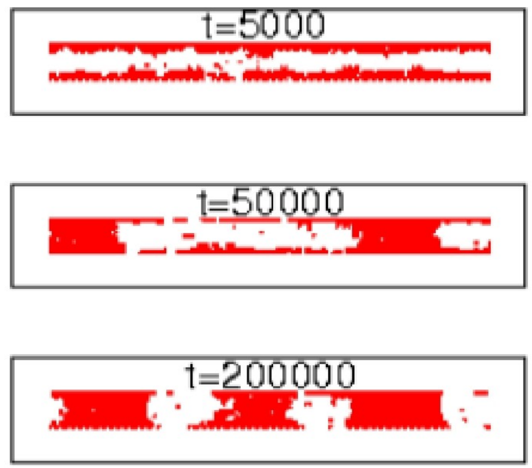
Corresponding Exact Mean-Field Dynamical Equations: Binder and Frisch

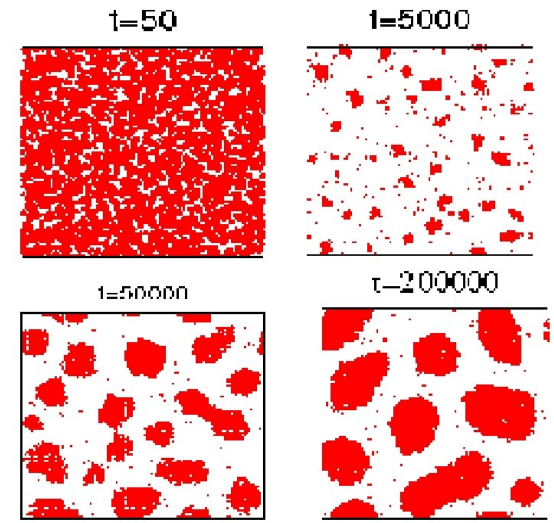
Ginzburg-Landau Model: $$F[\psi(\vec{r})] = F_b[\psi(\vec{r})] + F_{S_1}[\psi(\vec{r})] + F_{S_2}[\psi(\vec{r})]$$

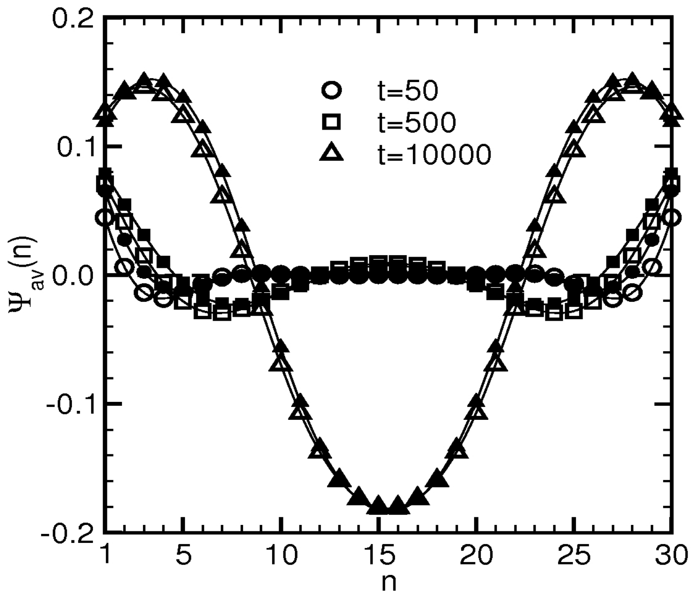
+ appropriate boundary conditions: Puri and Binder (1992)

Kinetics of Phase Separation: *Thin Film*





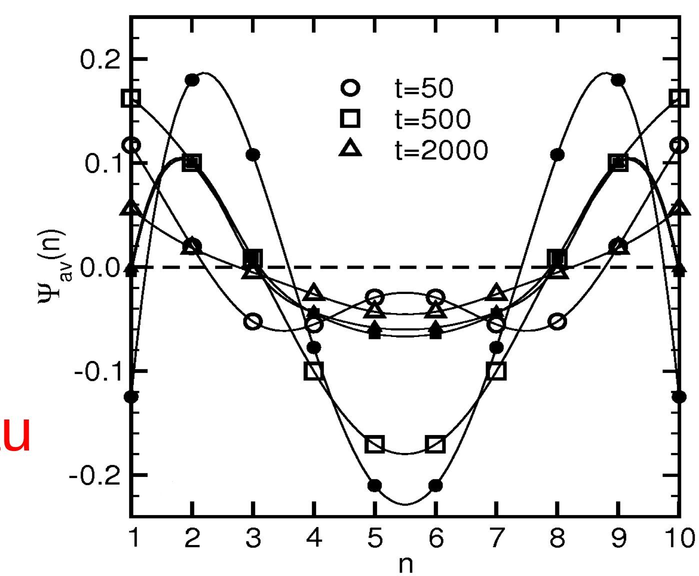




$T = 0.98T_c$

Open Symbols: Ising

Filled Symbols: Ginzburg-Landau



$T = 0.66T_c$

SKD, J. Horbach, K. Binder (2009)

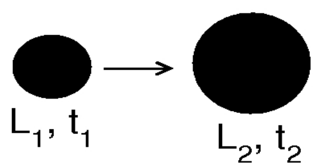
Kinetics of Phase Separation in *BULK*

- **Fluid Mixtures:** • Hydrodynamics important -- Advective transport
  - 3 regimes of growth:

Diffusive, Viscous hydrodynamic (?), Inertial hydrodynamic (?)

Viscous growth: surface energy density = viscous stress

$$\frac{\gamma}{L} = 6\pi\eta\frac{v}{L}$$



Interface velocity $v = \frac{dL}{dt} \sim \frac{\gamma}{\eta} \rightarrow \alpha = 1$

Inertial growth: surface energy density = kinetic energy density

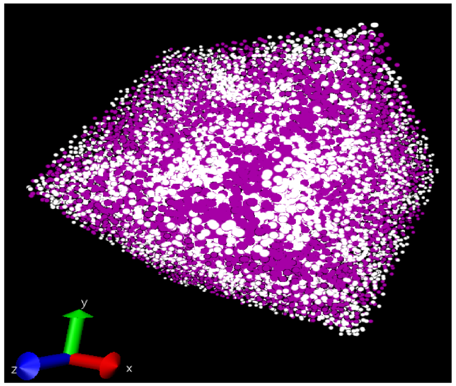
$$\frac{\gamma}{L} = n v^2 \rightarrow \frac{dL}{dt} \sim \frac{1}{L^{1/2}} \rightarrow \alpha = 2/3$$

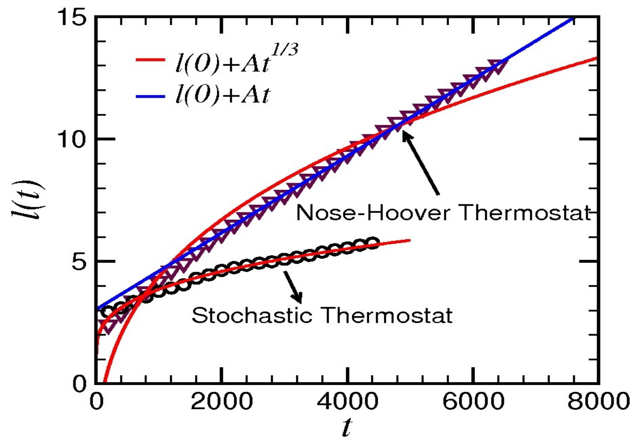
- Methods:
  - Continuum dynamical equations – Model H
  - ***Molecular Dynamics (MD) of off-Lattice continuous potential models***

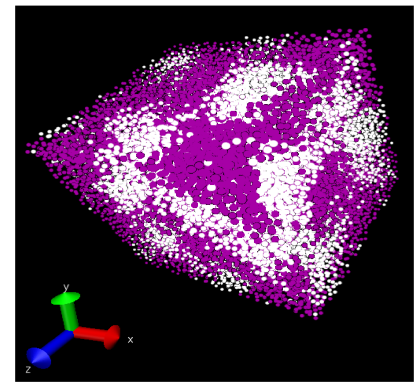
Kinetics of Phase Separation in *Fluid*

MD simulation at $k_B T < k_B T_c$

for a phase separating binary Lennard-Jones fluid. SKD, M.E. Fisher *et al.*(2006)







Prominent linear viscous growth:

S. Ahmad, SKD, S. Puri (2009)

Coarse-grained -- Model-H

Recall: $F[\psi(\vec{r})] = \int d\vec{r}\,[\frac{-\psi^2}{2} + \frac{\psi^4}{4} + (\vec{\nabla}\psi)^2]$

$\mu(\vec{r},t) = \delta F / \delta \psi(\vec{r},t)$

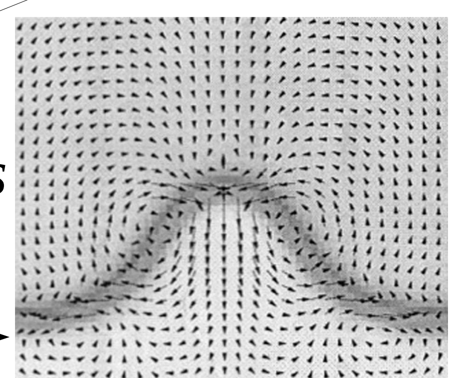
Density field: $\vec{J}(\vec{r},t) = -\vec{\nabla}\mu(\vec{r},t) - \psi\vec{v}$

$\frac{\partial}{\partial t}\psi(\vec{r},t) = -\vec{\nabla}\cdot\vec{J}(\vec{r},t)$

Velocity field:
Navier-Stokes equation

$\frac{\partial}{\partial t}\vec{v}(\vec{r},t) = -\psi\vec{\nabla}\mu + usual\,terms$

Kendon et al.



Is this velocity ordering real?

Molecular Dynamics is not suggestive!!

Conclusion:

- Appropriate application of Finite-Size Scaling Theory in domain coarsening phenomena.

- Ginzburg-Landau is not a good description far away from critical point.

- Multi-Scale modeling is needed if the smallest value of the characteristic length is very large.

Students and Collaborators:

Suman Majumder
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Sanjay Puri
Juergen Horbach

Thank You