

# Kinetics of Phase Ordering, Domain Growth and Coarsening II: Some Applications

by  
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# Overview

- (a) Introduction
- (b) Phase Separation and Wetting at Surfaces
- (c) Segregation in Granular Materials
- (d) Conclusion

# (a) Introduction

We have discussed problems of phase ordering kinetics or domain growth or coarsening.

## Modeling:

- Kinetic Ising Models (spin dynamics)
- Coarse-grained or Phenomenological Models (order parameter fields and velocity fields)
- Molecular-level Models (direct solution of equations of motion, naturally incorporate hydrodynamics)
- Etc.

# Bulk phase separation

- Microscopic level

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j, \quad S_i = \pm 1$$

Ising model

- + Kawasaki spin-exchange kinetics

- Phenomenological level

$$\mathcal{F}[\psi] = \int d\vec{r} \left[ -\frac{1}{2} k_B (T_c - T) \psi^2 + \frac{k_B T}{12} \psi^4 + \frac{J}{2} (\vec{\nabla} \psi)^2 \right]$$

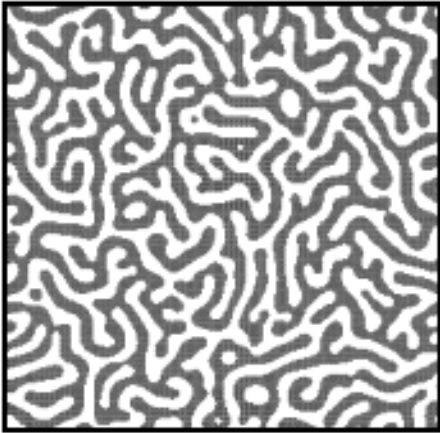
$$\begin{aligned} \frac{\partial \psi}{\partial t} &= -\vec{\nabla} \cdot \vec{J} \\ &= \vec{\nabla} \cdot [D \vec{\nabla} \mu + \vec{\theta}] \\ &= \vec{\nabla} \cdot \left[ D \vec{\nabla} \left( \frac{\delta \mathcal{F}}{\delta \psi} \right) + \vec{\theta} \right] \end{aligned}$$

Cahn-Hilliard-Cook (CHC) model or Model B

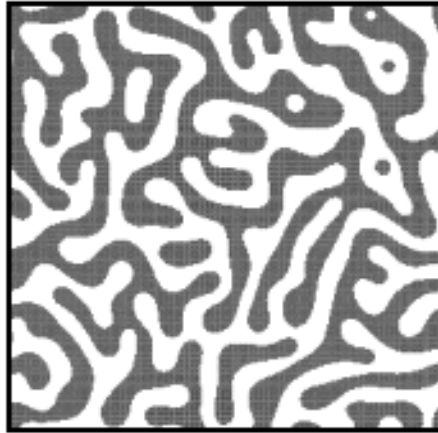
Hydrodynamics is incorporated through velocity field (Model H)

## Critical Mixture (50% A and 50% B)

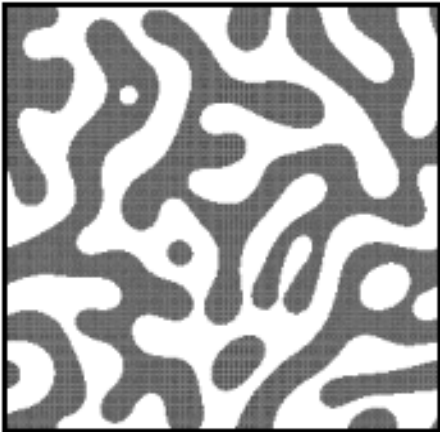
t=100



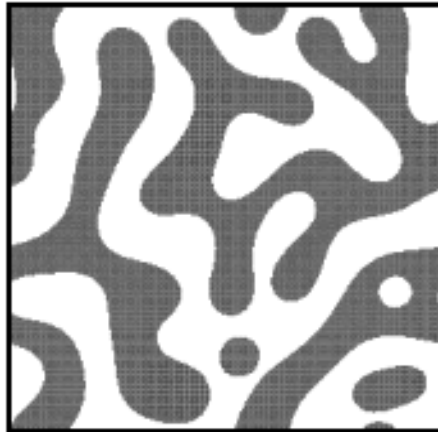
t=500



t=2000



t=5000



- 1) Phase separation is driven by interfaces (defects).
- 2) Composition must be conserved during evolution.
- 3) 
$$\frac{dL}{dt} = \frac{\sigma}{L} \times \frac{1}{L} \Rightarrow L(t) \sim (\sigma t)^{1/3}$$

Lifshitz-Slyozov growth law

- 4) System shows dynamical scaling. However, there is still no complete understanding of the correlation function or structure factor.

- We now apply these concepts to study some current and topical problems of phase-separation kinetics.

## (b) Phase Separation and Wetting at Surfaces

- Consider unstable binary mixtures ( $T < T_c$ ) in contact with a surface which prefers one of the components.

S. Puri, J. Phys. Condensed Matter 17, R101 (2005).

Phase separation in bulk + wetting at surface

Partially wet (PW) morphology

Completely wet (CW) morphology

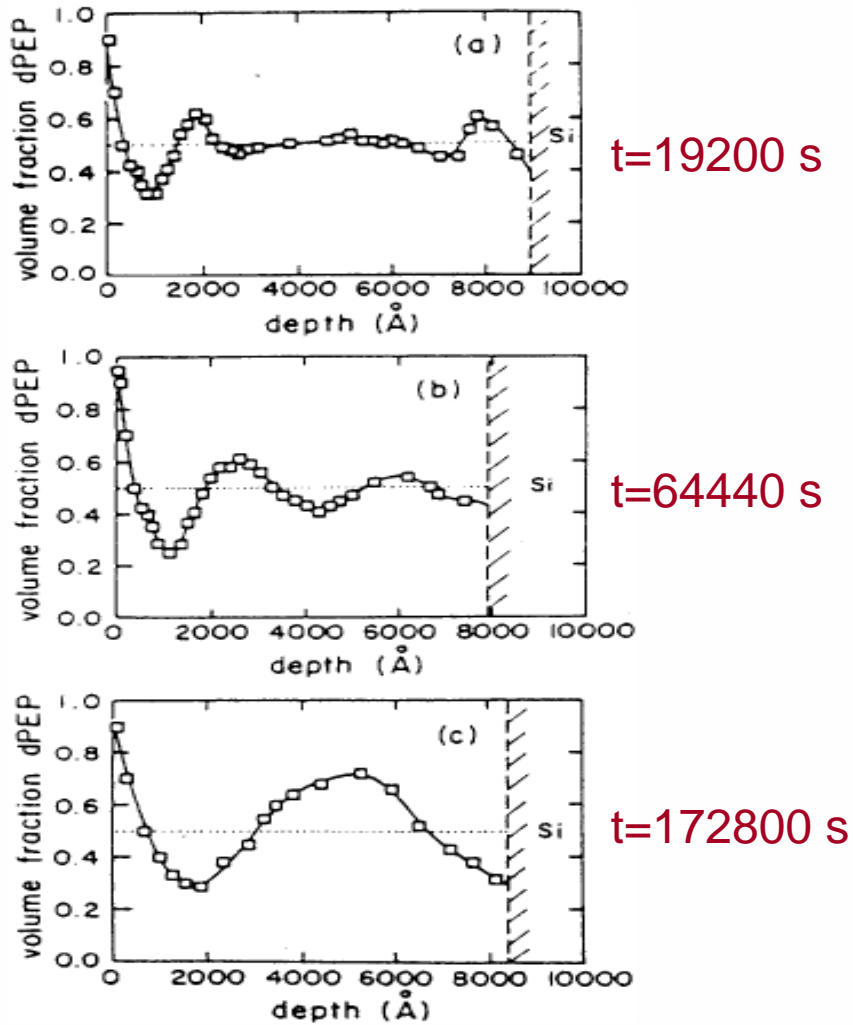
- Kinetic interplay of phase separation and wetting =  
Surface-directed spinodal decomposition (SDSD)

Experiments:

R.A.L. Jones et al, Phys. Rev. Lett. 66, 1326 (1991);

M. Geoghegan and G. Krausch, Prog. Poly. Sci. 28, 261 (2003).

## SDSD in mixtures of PEP and d-PEP



**Figure 1.** Evolution of laterally averaged profiles for an unstable polymer mixture (PEP and dPEP) in contact with an open surface which prefers dPEP [16]. The frames show the depth-dependence of the average density of dPEP at (a) 19 200 s, (b) 64 440 s and (c) 172 800 s after the quench. The average composition of the mixture is denoted by a dotted line.



# Modeling of SDSD

- Model for binary mixtures near surfaces  
S. Puri, J. Phys. Condensed Matter 17,  
R101 (2005).

# Microscopic level

## Semi-infinite Ising model

$$\begin{aligned}\mathcal{H} = & -J \sum_{\langle ij \rangle \in \text{B}} S_i S_j \\ & -J_s \sum_{\langle ij \rangle \in \text{S}} S_i S_j \\ & + \sum_i V(z_i) S_i, \quad V(z) \sim z^{-n}\end{aligned}$$

Bulk exchange

Surface exchange

Surface potential,  
prefers A

+ Kawasaki spin-exchange kinetics

# Phenomenological model

## Free-energy functional

$$\begin{aligned}\mathcal{F}[\psi] &= \mathcal{F}_b + \mathcal{F}_s \\ &\simeq \int d\vec{r} \left[ -\frac{1}{2}k_B(T_c - T)\psi^2 + \frac{k_B T}{12}\psi^4 + \frac{J}{2}(\vec{\nabla}\psi)^2 + V(z)\psi \right] \\ &\quad + \int d\vec{\rho} \left\{ -\frac{1}{2}[(q-2)J_s + J - k_B T]\psi(\vec{\rho}, 0)^2 + V(0)\psi(\vec{\rho}, 0) \right. \\ &\quad \left. + \frac{J_s}{2}[\vec{\nabla}_{\parallel}\psi(\vec{\rho}, 0)]^2 - \frac{J}{2}\psi(\vec{\rho}, 0)\frac{\partial\psi}{\partial z}\Big|_{z=0} \right\}\end{aligned}$$

Bulk

Surface

## Dynamical model

CHC Equation

$$\frac{\partial\psi}{\partial t} = \vec{\nabla} \cdot \left[ D\vec{\nabla} \left( \frac{\delta\mathcal{F}}{\delta\psi} \right) + \vec{\theta} \right]$$

+ Two boundary conditions

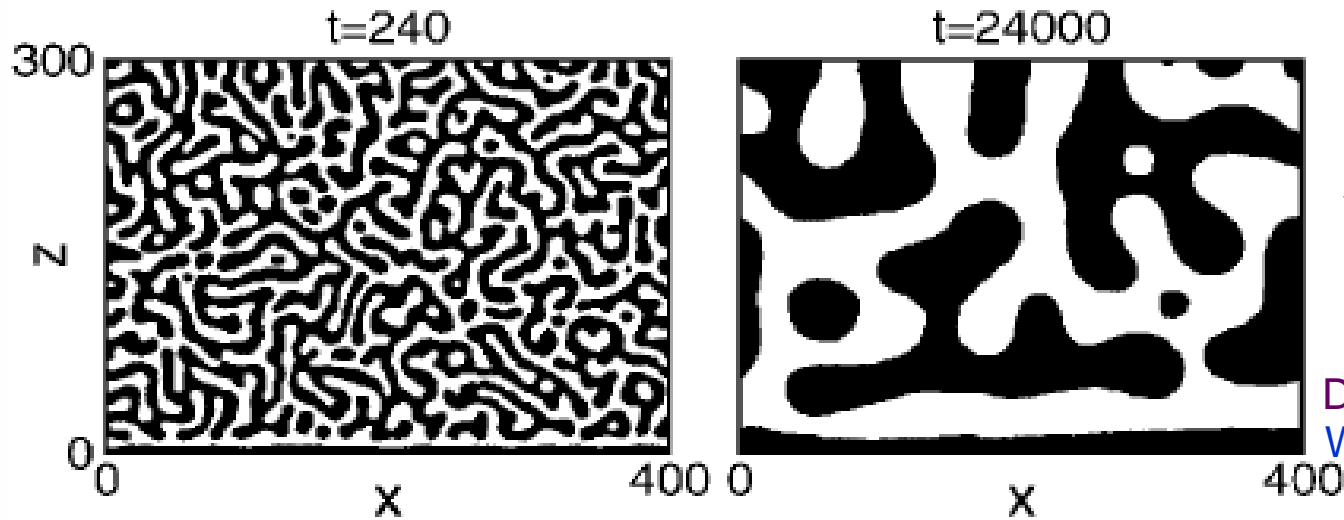
Relaxational kinetics

$$\lambda^{-1} \frac{\partial}{\partial t} \psi(\vec{\rho}, 0, t) = - \frac{\delta\mathcal{F}}{\delta\psi(\vec{\rho}, 0, t)}$$

Zero current

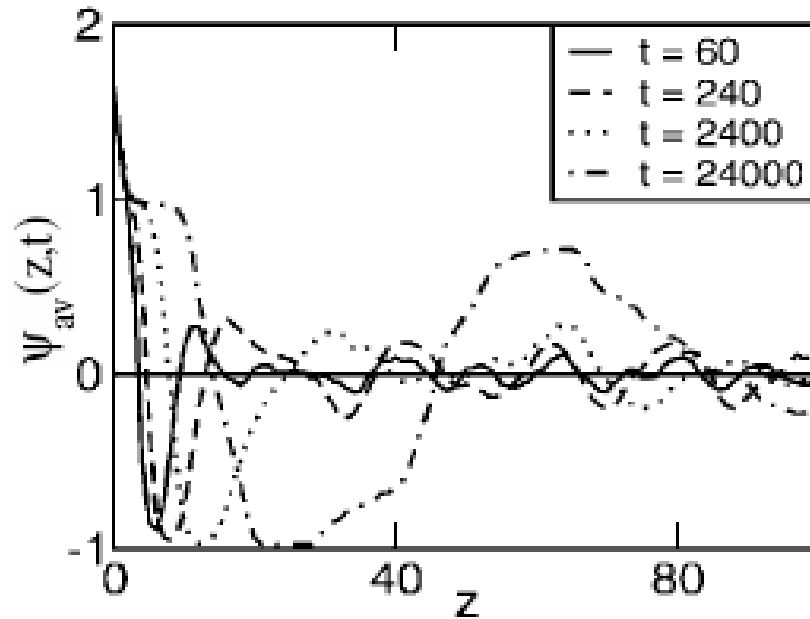
$$0 = \left[ D \frac{\partial}{\partial z} \left( \frac{\delta\mathcal{F}}{\delta\psi} \right) + \theta_z \right]_{z=0}$$

# SDSD in Critical Mixtures (50%A and 50%B)



$$V(z) = -h_1 \left( \frac{\sigma}{z} \right)^4$$

Depletion layer  
Wetting layer



Depletion layer thickness

$$h(t) = R_2(t) - R_1(t)$$

- We want to understand the kinetics of wetting and phase separation in the vicinity of the wetting layer.

S. Puri and K. Binder,

Phys. Rev. Lett. 86, 1797 (2003);

Phys. Rev. E 66, 061602 (2004).

S.K. Das, S. Puri et al.,

Phys. Rev. Lett. 96, 016107 (2007);

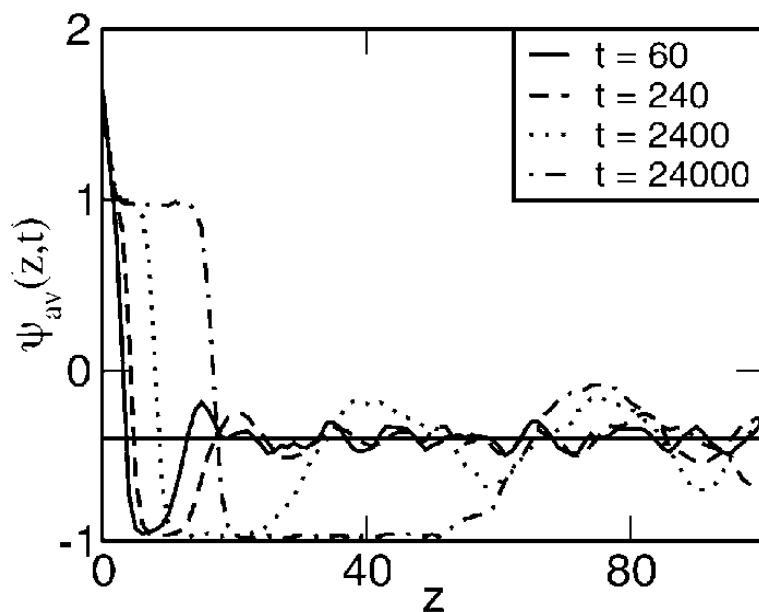
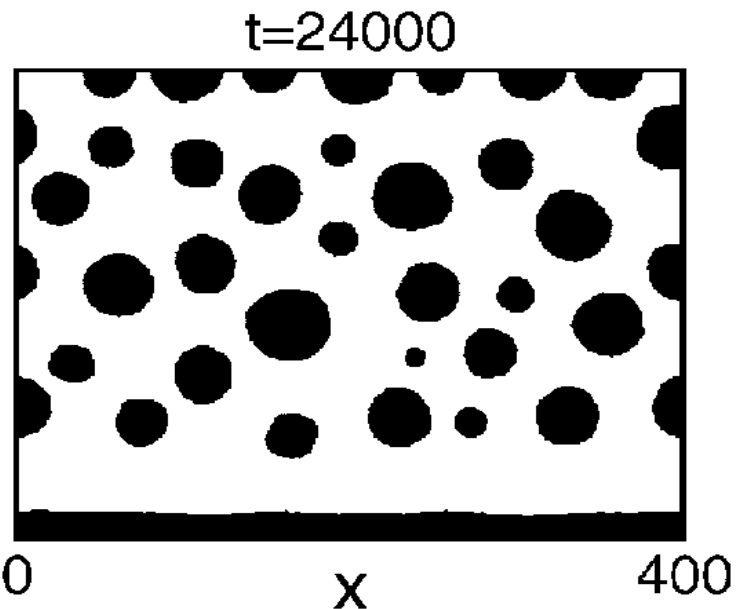
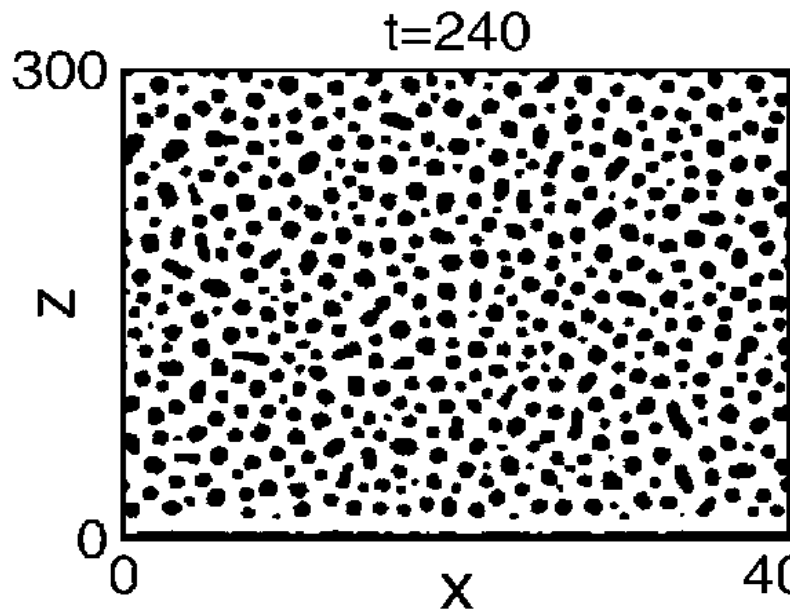
Phys. Rev. E 73, 031604 (2008).

Consider the general case of off-critical mixtures with

minority component wetting

majority component wetting

# Minority component wets (30% A and 70%B)



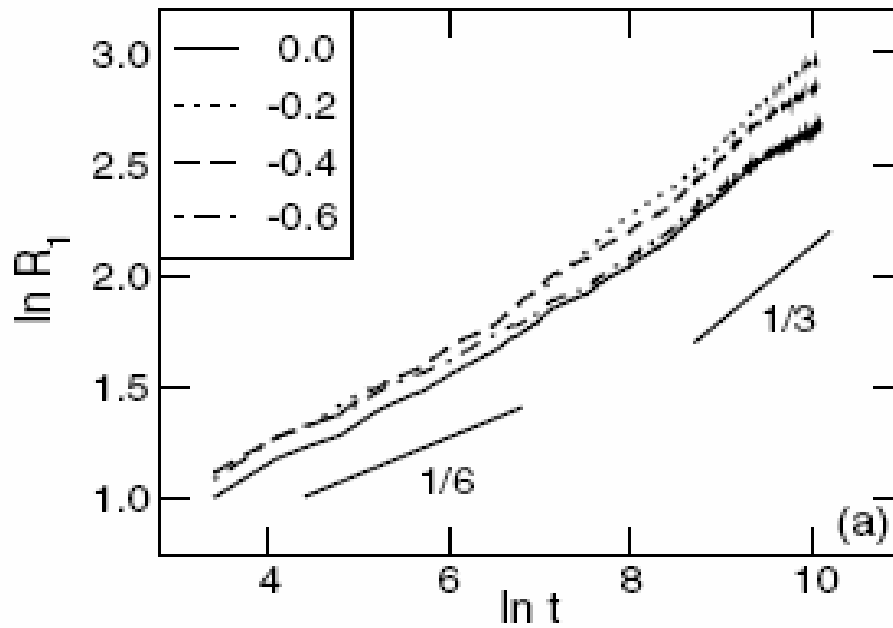
$$\frac{dR_1}{dt} = -J_z = \left. \frac{dV(z)}{dz} \right|_{z=R_1} + \frac{\sigma}{Lh}$$

$$R_2(t) \simeq \frac{2}{1 + \psi_0} R_1(t), \quad h(t) \simeq \frac{1 - \psi_0}{1 + \psi_0} R_1(t)$$

$$\frac{dR_1}{dt} = \frac{nh_1}{R_1^{n+1}} + \frac{\sigma}{LR_1} \left( \frac{1 + \psi_0}{1 - \psi_0} \right)$$

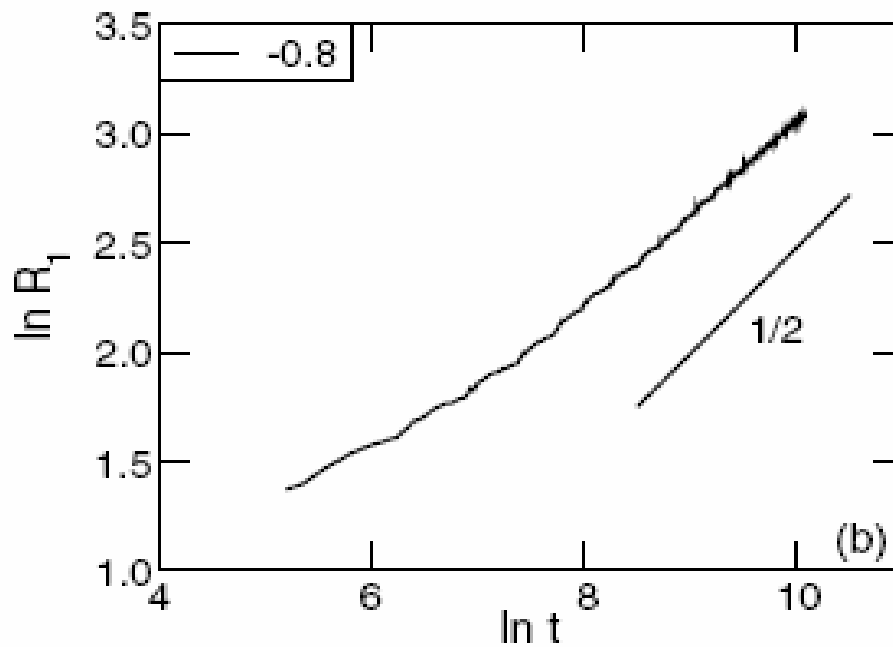
$$R_1(t) \sim (h_1 t)^{1/(n+2)}, \quad t \ll t_c,$$

$$\sim \sqrt{\frac{(1 + \psi_0)}{f(\psi_0)(1 - \psi_0)}} (\sigma t)^{1/3}, \quad t \gg t_c$$



Bulk segregation

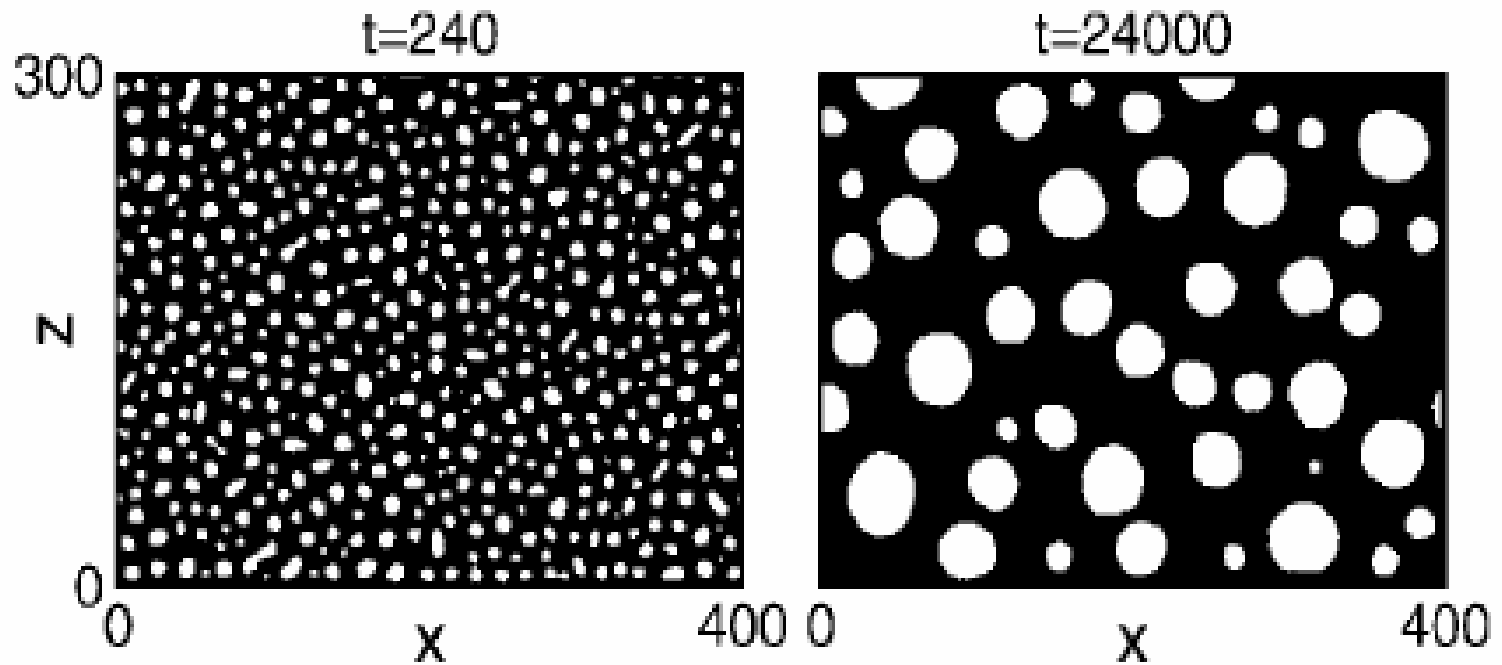
$$\psi_0 < 0$$



No bulk segregation

$$\psi_0 \ll 0$$

Majority component wets (70%A and 30% B)

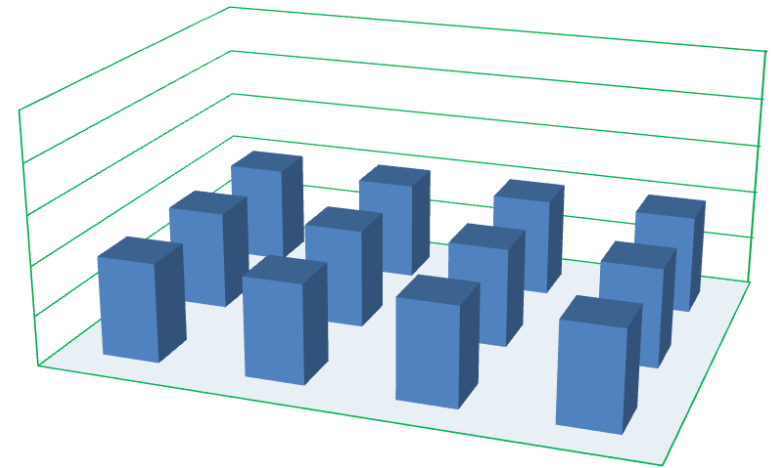
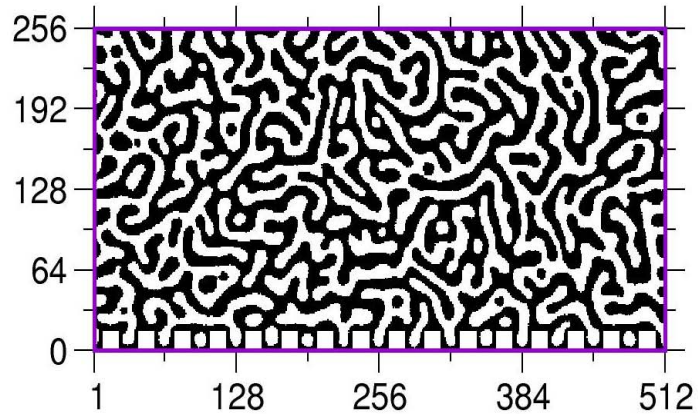


Bulk droplets compete with wetting layer for component A

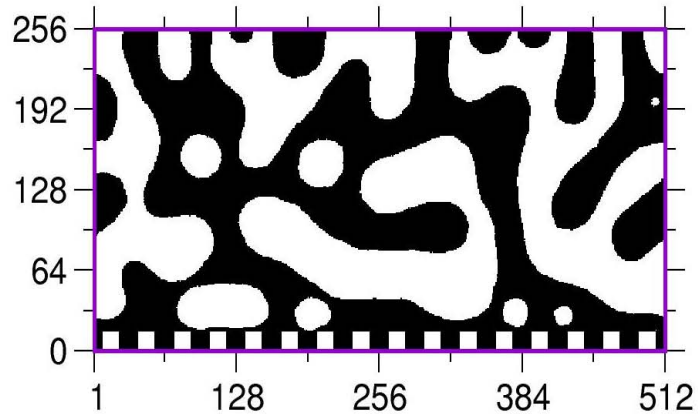


# SDSD on Physically Patterned Surfaces

$t = 300$



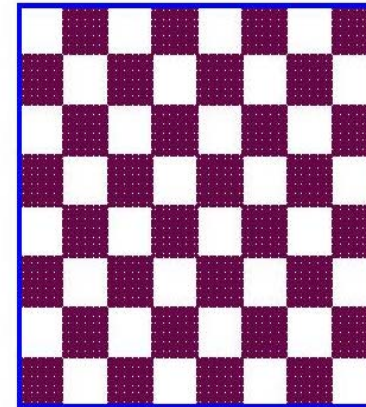
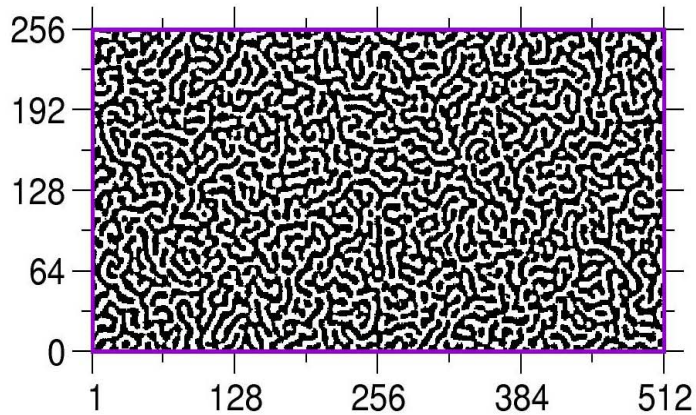
$t = 24000$



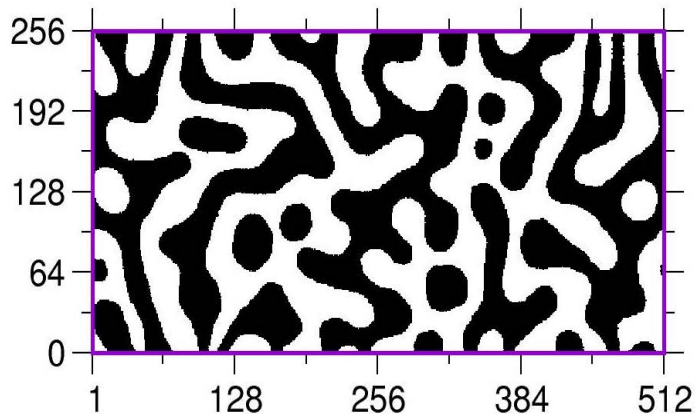
P.K. Jaiswal and S. Puri (2010)

# SDSD on Chemically Patterned Surfaces

$t = 30$

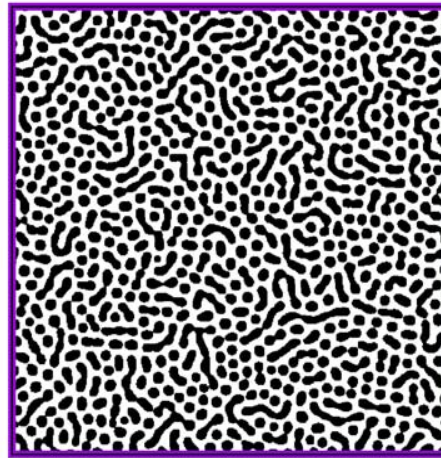
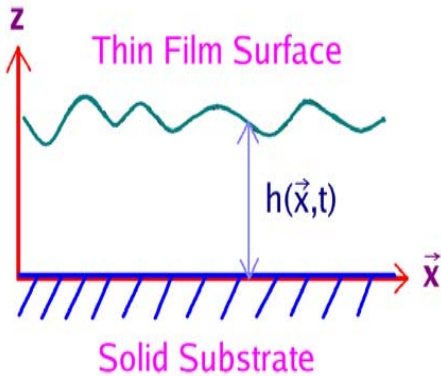


$t = 6000$

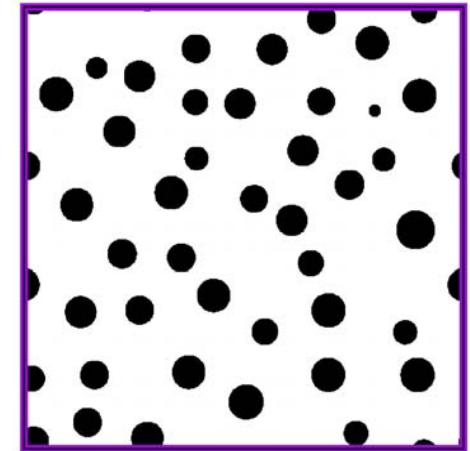


P.K. Jaiswal and S. Puri (2010)

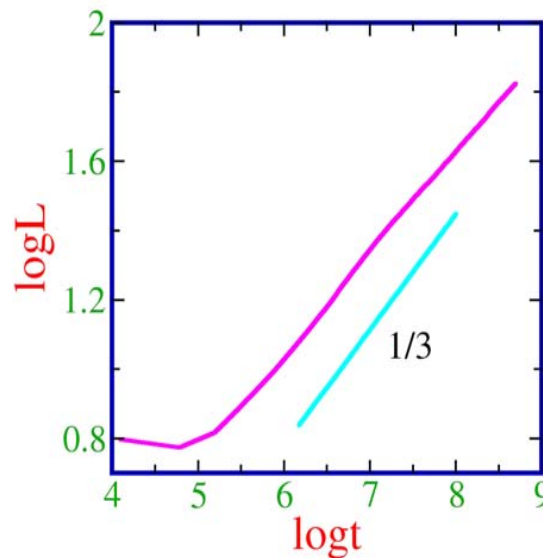
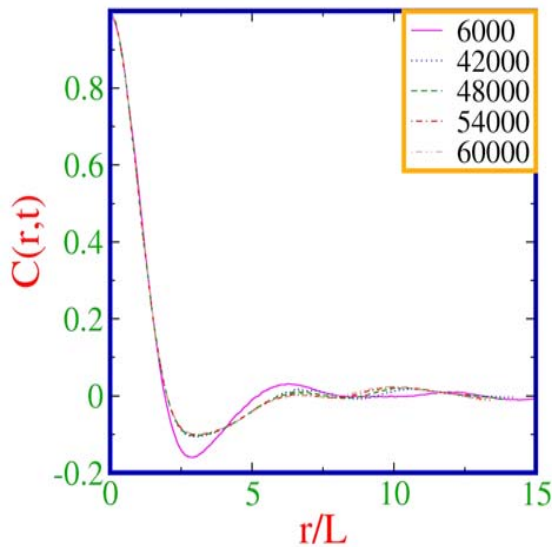
# Spinodal Dewetting of Thin Films



$t = 300$



$t = 30000$

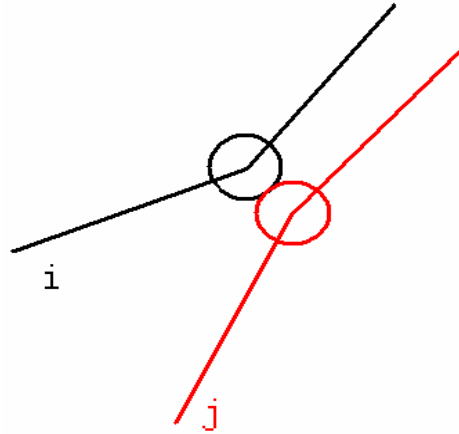


- Chemical Potential,  $\mu \sim \sigma/L$
- Current,  $J \sim |\nabla \mu| \sim \sigma/L^2$
- Interface velocity,  $v \sim dL/dt \sim \sigma/L^2$
- Characteristic Length,  $L(t) \sim (\sigma t)^{1/3}$

R. Khanna, S. Puri, A. Sharma et al. (2010)

# (c) Segregation in Granular Materials

Granular collisions



$$\vec{v}'_i = \vec{v}_i - \frac{(1+e)}{2} \left[ \hat{n} \cdot (\vec{v}_i - \vec{v}_j) \right] \hat{n}$$
$$\vec{v}'_j = \vec{v}_j + \frac{(1+e)}{2} \left[ \hat{n} \cdot (\vec{v}_i - \vec{v}_j) \right] \hat{n}$$

Restitution coefficient  $e=1$  (elastic)  
 $e<1$  (inelastic)

- Density and momentum are conserved during collision.
- Magnitude of normal velocity is reduced for  $e<1$ .
  - Loss of energy (cooling)
  - Parallelization of velocities (correlations build up)

Fraction of energy lost per collision

$$= \frac{1 - e^2}{d} = \frac{\varepsilon}{d}$$

Temperature  $T = \frac{2E}{d}$  and

$$\frac{dT}{dt} = -\frac{\varepsilon}{d} \omega(T) T$$

Collision frequency

$$\begin{aligned} \omega(T) &\propto n \chi(n) \sigma^{d-1} \sqrt{T} \\ &= \omega(T_0) \sqrt{\frac{T}{T_0}} \end{aligned}$$

Haff's cooling law

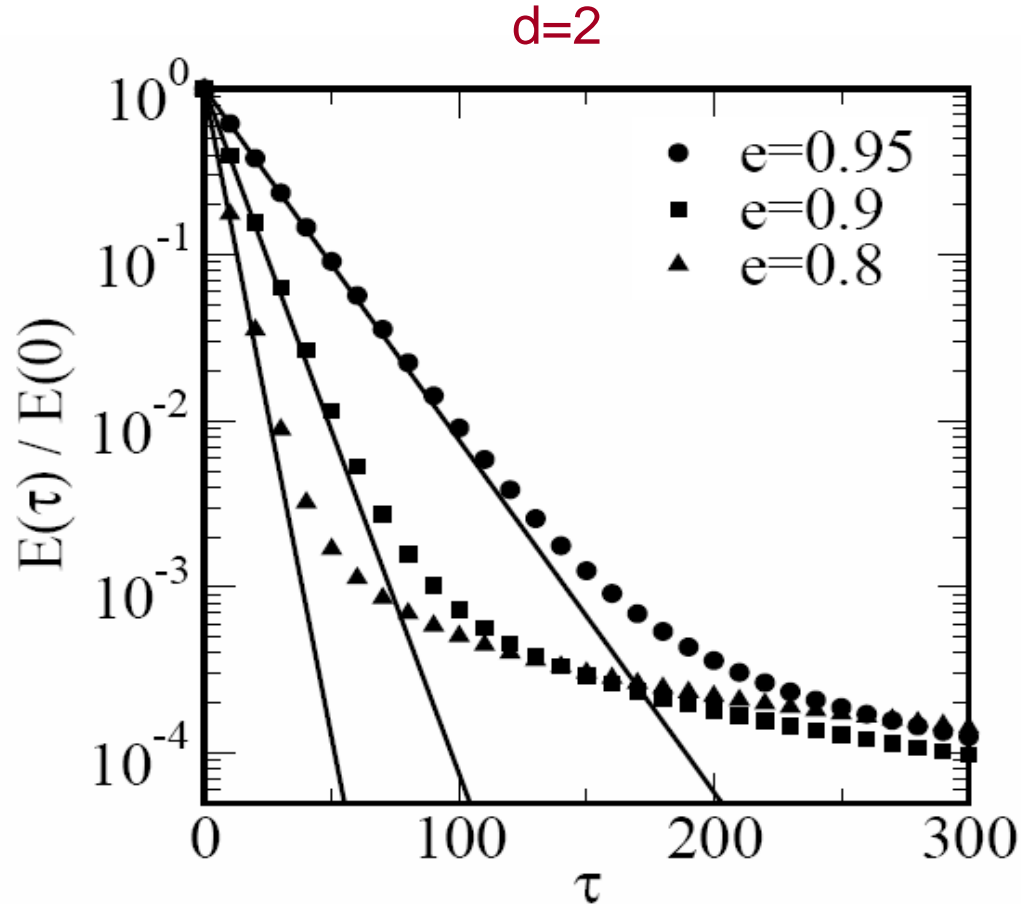
$$T(t) = \frac{T_0}{\left[1 + \varepsilon \omega(T_0) t / 2d\right]^2}$$

Collision time

$$\begin{aligned} \tau(t) &= \int_0^t dt' \omega(t') \\ &= \frac{2d}{\varepsilon} \ln \left[ 1 + \frac{\varepsilon \omega(T_0)}{2d} t \right] \end{aligned}$$

$$T(\tau) = T_0 \exp\left(-\frac{\varepsilon}{d} \tau\right)$$

Event-driven simulations in  $d=2,3$   
 $N=10^6$ , number fraction=0.2



S.R. Ahmad and S. Puri, Europhys. Lett. 75, 56 (2006);  
Phys. Rev. E 75, 031302 (2008).

- The homogeneous cooling state (HCS) is unstable to density fluctuations, due to more rapid cooling in regions of higher density.

I. Goldhirsch and G. Zanetti, Phys. Rev. Lett. 70, 1619 (1993).

Linear instabilities are due to

Shear mode  $\xi_{\perp} \approx l_0 \sqrt{\frac{2d}{\varepsilon}}$

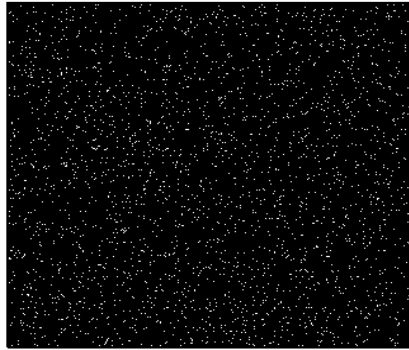
Heat mode  $\xi_{\parallel} \approx l_0 \frac{2d}{\varepsilon}$

$$l_0 = \frac{\sqrt{2T}}{\omega(T)} = \frac{\sigma^{1-d}}{n\chi(n)}$$

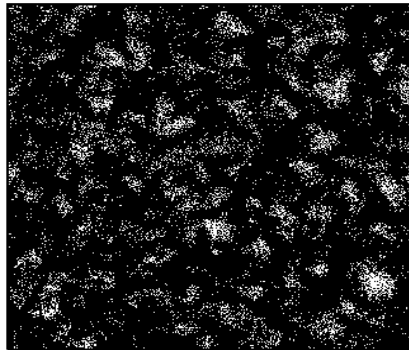
- After a crossover time, the granular gas goes from the HCS to an inhomogeneous cooling state (ICS).

# Density field

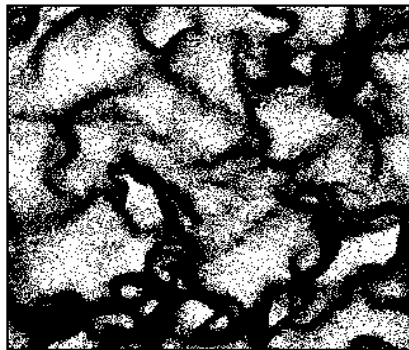
$\tau=10$



$\tau=100$

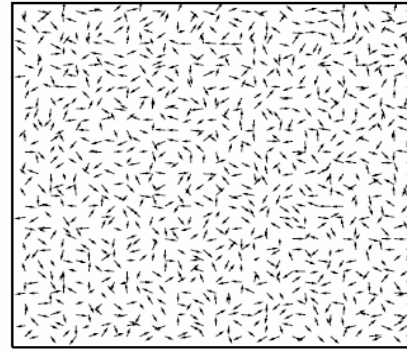


$\tau=1000$

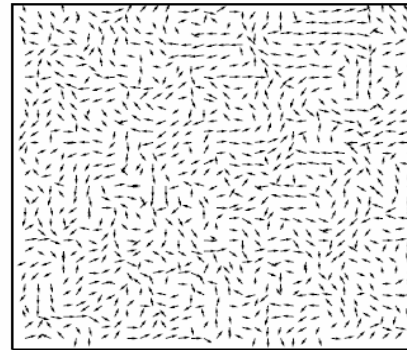


# Velocity field

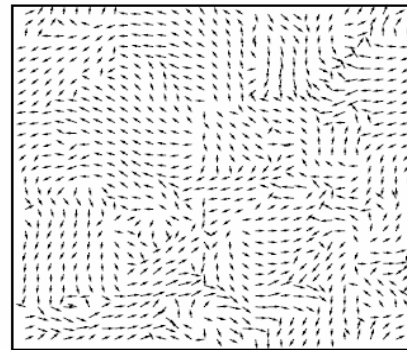
$\tau=10$



$\tau=100$



$\tau=1000$



$e=0.9$   
 $n=0.2$



## (d) Conclusion

- We have discussed the modeling and analytical understanding of domain growth problems.
- We have extended these simple ideas to study the problem of surface-directed spinodal decomposition or phase separation in confined geometries.
- The concepts of phase ordering kinetics are of wide applicability. For example, granular materials undergo segregation due to collision-induced correlations. This has many features in common with usual phase separation.