Domain Growth in Binary Mixtures

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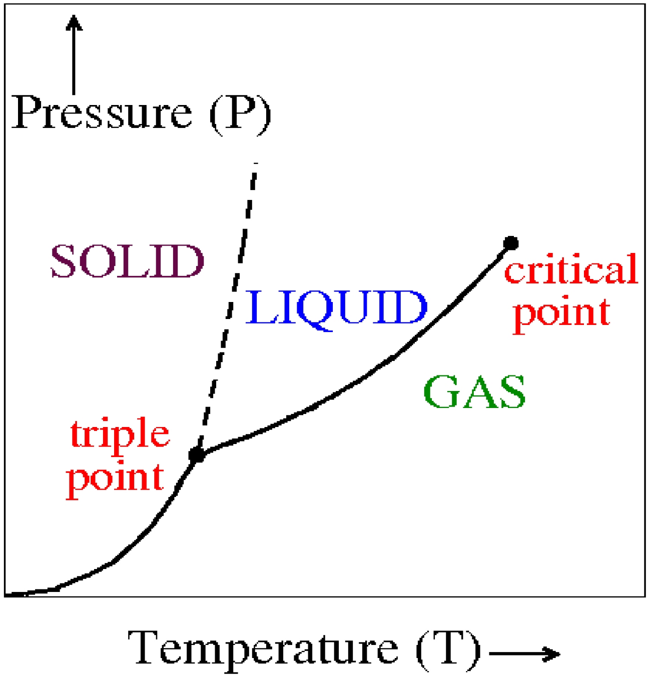
- Introduction to phase separation

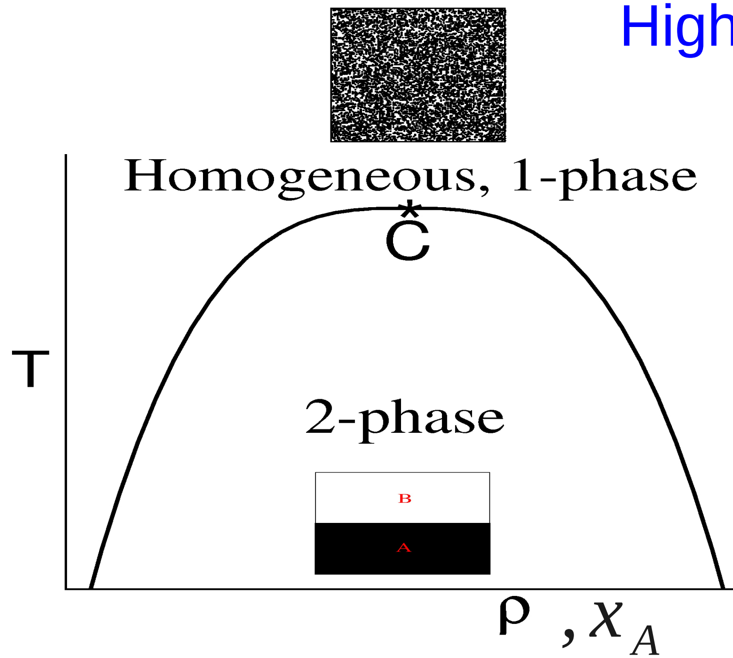
- Kinetics of Phase Separation in Binary Mixtures
  -- review of history for Ising Model

- Finite-size scaling for domain coarsening
  -- effect of system size, scaling law,
  corrections to scaling

- Conclusion

Introduction: Phase Behavior of a chemical system

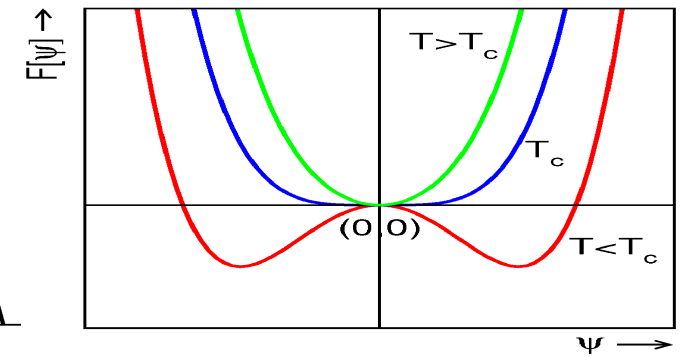




Order parameter $\psi = x_A - x_B$

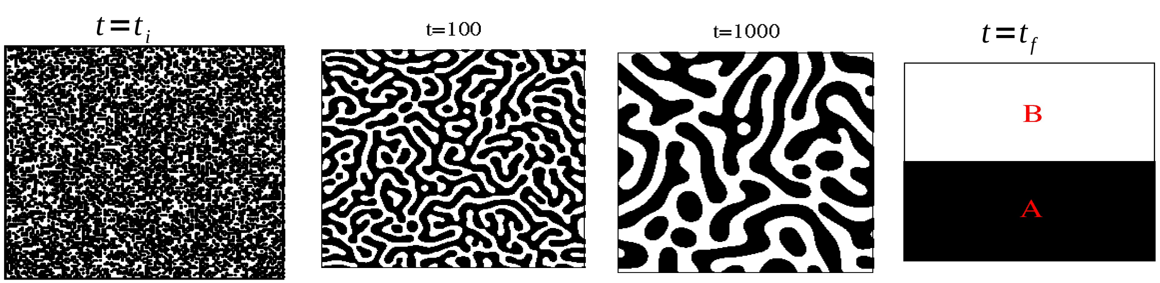
High T, $\psi = 0$; Low T, $\psi \neq 0$

Free energy minima at <u>equilibrium</u> values of ψ



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

--Landau Free energy.



Self-Similar Structure

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

Growth exponent depends upon transport mechanism.

<u>Solid Mixtures</u>: Diffusive mechanism

$$\frac{d\ell(t)}{dt} \sim |\nabla \mu| \sim \frac{\gamma}{\ell(t)^2} \rightarrow \alpha = 1/3$$

--Lifshitz-Slyozov (1961).

Monte Carlo Simulation of Ising Model

$$H = -J\sum_{\langle ij\rangle} S_i S_j; \quad S_i = \pm 1$$ A B

50:50 composition in d=2

Till 1985: $\alpha \simeq 0.2$ Lebowitz, Grest

$\ell(t) \sim \ln t\,?$ Mazenko

1986: Huse

$$\frac{d\ell(t)}{dt} = \frac{C_1}{\ell(t)^2} + \frac{C_2}{\ell(t)^3}$$

$$\ell(t) = \frac{C_2}{2C_1} + (3C_2 t)^{1/3}$$

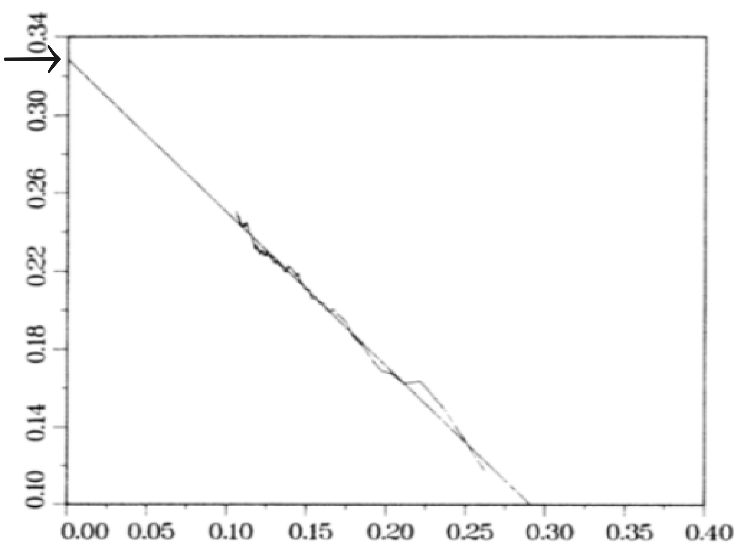
$$\alpha(t) = \frac{d[\ln \ell(t)]}{d[\ln t]}$$

$$\alpha(t) = \frac{1}{3}\left[1 - \frac{C_2}{2C_1}\frac{1}{\ell(t)}\right]$$

$$\alpha(\infty) = \frac{1}{3}$$

$1/3 \rightarrow$

$\alpha(t)$



$1/\ell(t)$

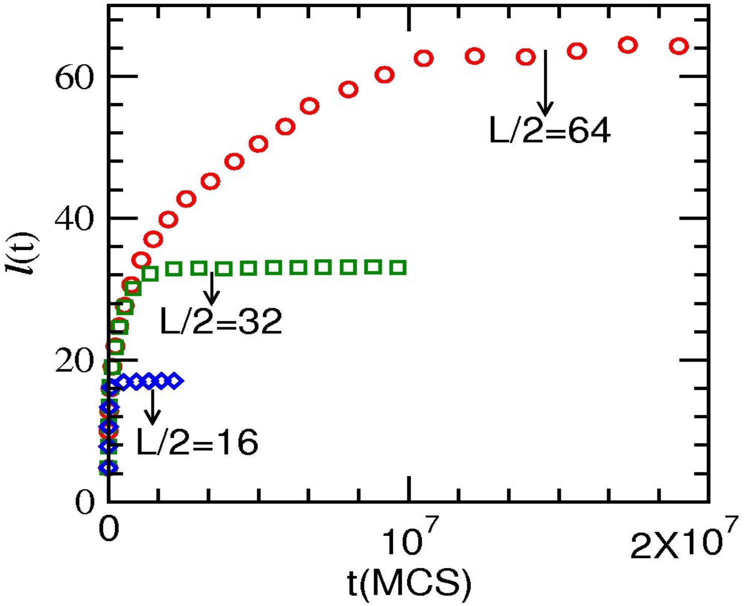
Amar *et al.* (1988)

$\alpha \simeq 0.33$

$L^2 = 512^2$

Finite-size Effect?

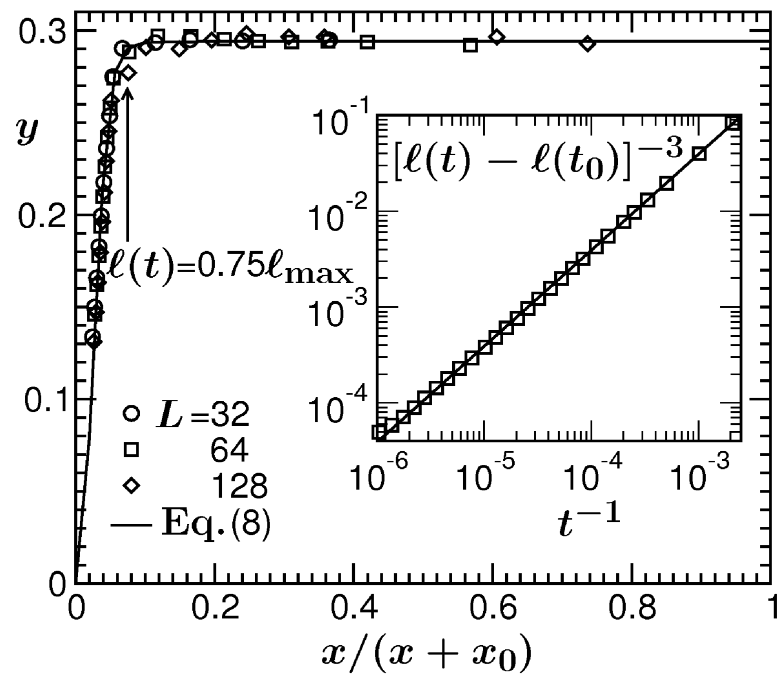
Monte Carlo Simulation of 2-d Ising Model



$$L=\infty: \quad \ell(t)-\ell(t_0)=At^{\alpha}$$

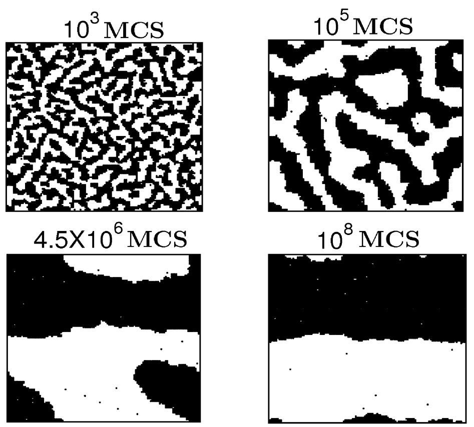
$$L<\infty(\ell_{max}<\infty): \quad \ell(t)-\ell(t_0)=y(x)t^{\alpha}$$

$$x=(\ell_{max}-\ell(t_0))/t^{\alpha}$$



$$\alpha=0.334$$

$$\ell(t_0=20)=3.6$$



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

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

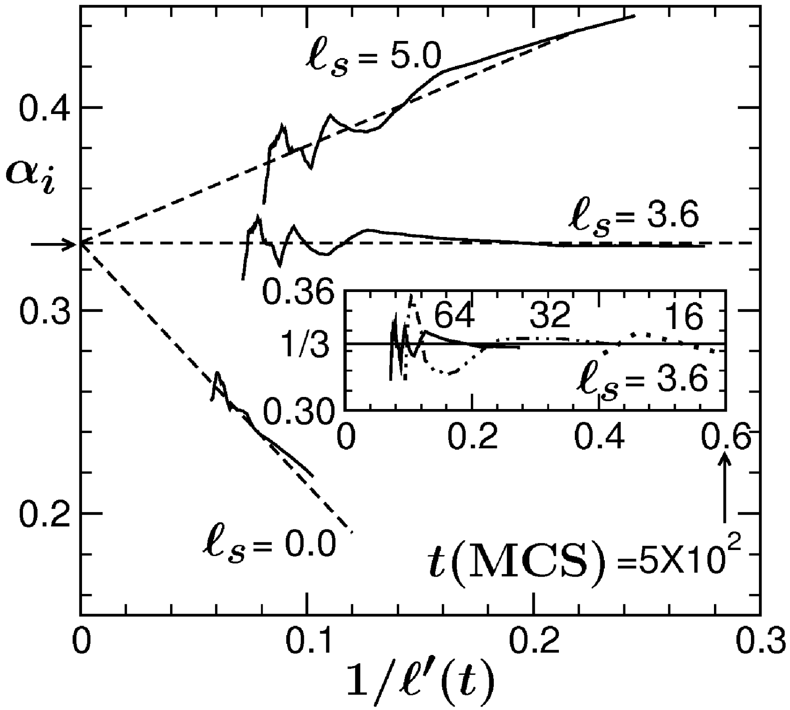
$$y(x)=\frac{Ax}{x+B/(E+Cx^{D})};y(x\to\infty)\approx A[1-px^{-(D+1)}]=A[1-px^{-n}];n\approx 5$$

Size effect is very small and correction to scaling is negligible!

Monte Carlo Simulation of 2-d Ising Model: How big is too big?

$$\ell(t) = \ell(t_0) + At^{\alpha} \quad \ell'(t) = \ell(t) - \ell_s = [\ell(t_0) - \ell_s] + At^{\alpha}$$

$$\alpha_i = \frac{d[\ln \ell'(t)]}{d[\ln t]} \qquad \alpha_i = \alpha + m\frac{1}{\ell'(t)}; \quad m = \alpha[\ell_s - \ell(t_0)]$$



$$\frac{d\ell(t)}{dt} \sim \frac{\gamma}{\ell(t)^2}$$

$$\gamma(\ell) = \frac{\gamma}{1+2\delta/\ell} \qquad \delta \rightarrow \text{Tolman Length}$$

Huse: $$\frac{d\ell(t)}{dt} = \frac{C_1}{\ell(t)^2} + \frac{C_2}{\ell(t)^3}$$

Negligible correction to scaling: $\delta \simeq 0$

$L^2 \simeq 10^{-3}.512^2$ big enough

Corrections are of higher order

S. Majumder and SKD, PRE Rapid Comm. (2010)

Kinetics of Phase Separation in *Fluids: MD study*

• **Fluid Mixtures:** Diffusive, Viscous (?) & Inertial (?) hydrodynamic

Viscous growth: surface energy density = viscous stress

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

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

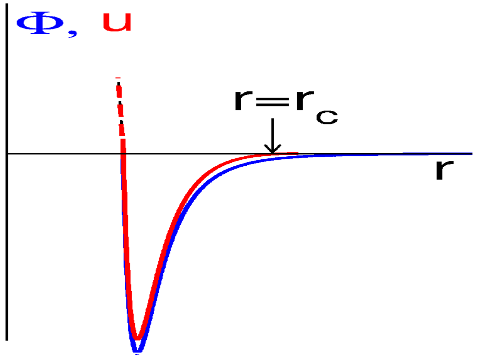
Inertial growth: surface energy density = kinetic energy density

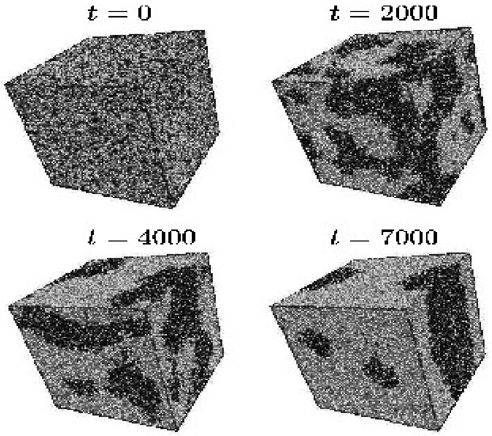
$$\frac{\gamma}{\ell} = n v^2 \rightarrow \frac{d\ell}{dt} \sim \frac{1}{\ell^{1/2}} \rightarrow \alpha = 2/3$$

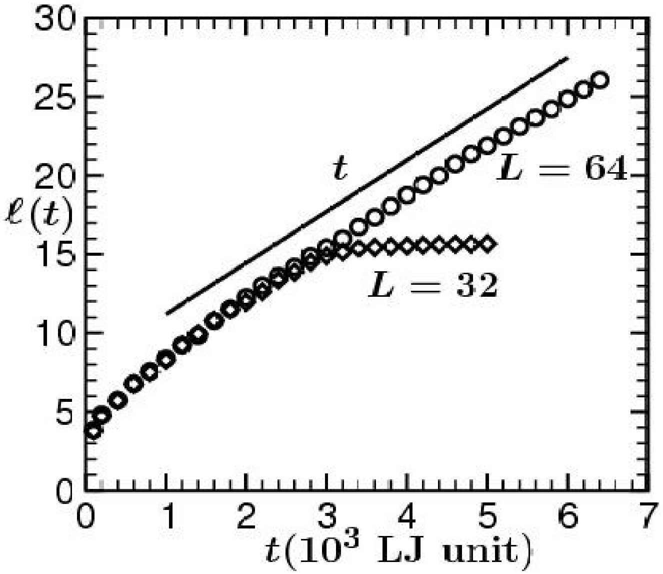
A 2-fluid (A+B) model for phase separation

$$\phi(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$$



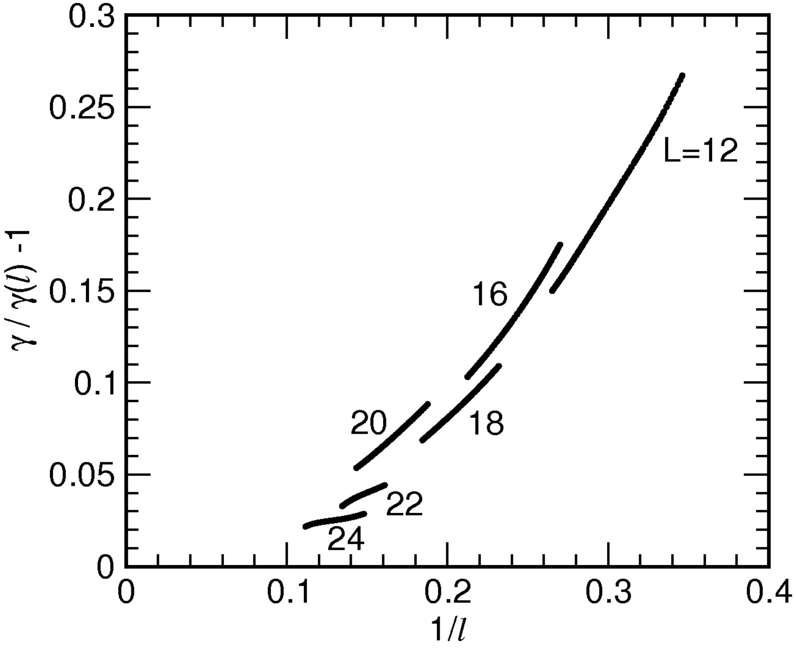




S. Ahmad and SKD (2010)

SKD, M.E. Fisher *et al.*, PRL (2006) S. Ahmad, SKD & S. Puri (2010)

Nucleation in a Binary Fluid



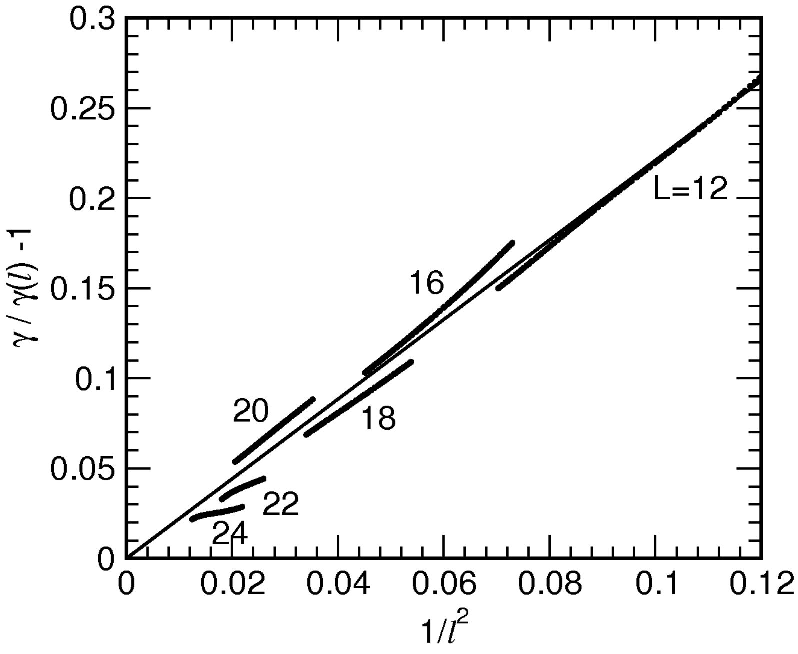
Classical Nucleation Theory:

$$F_s = 4\pi\ell^2\gamma \qquad \gamma = \text{constant}$$

In reality: $\gamma = \gamma(\ell)$

R.C. Tolman (1949): $$\gamma(\ell) = \frac{\gamma}{1 + 2\delta/\ell}$$

$$\frac{\gamma}{\gamma(\ell)} - 1 = 2\delta/\ell$$



Leading order correction is of quadratic order:

$$\gamma(R) = \frac{\gamma}{1 + 2(\xi/\ell)^2} \,?$$

B.J. Block, SKD, M. Oettel, P. Virnau & K. Binder, submitted (JCP)

Conclusion

- Finite-Size effect in domain-coarsening is small
- Correction to scaling in the growth law is negligible for critical quench
- Tolman length in symmetric model seems to be absent

Thank You