1) 2)

Phase separation dynamics in a two-dimensional magnetic mixture

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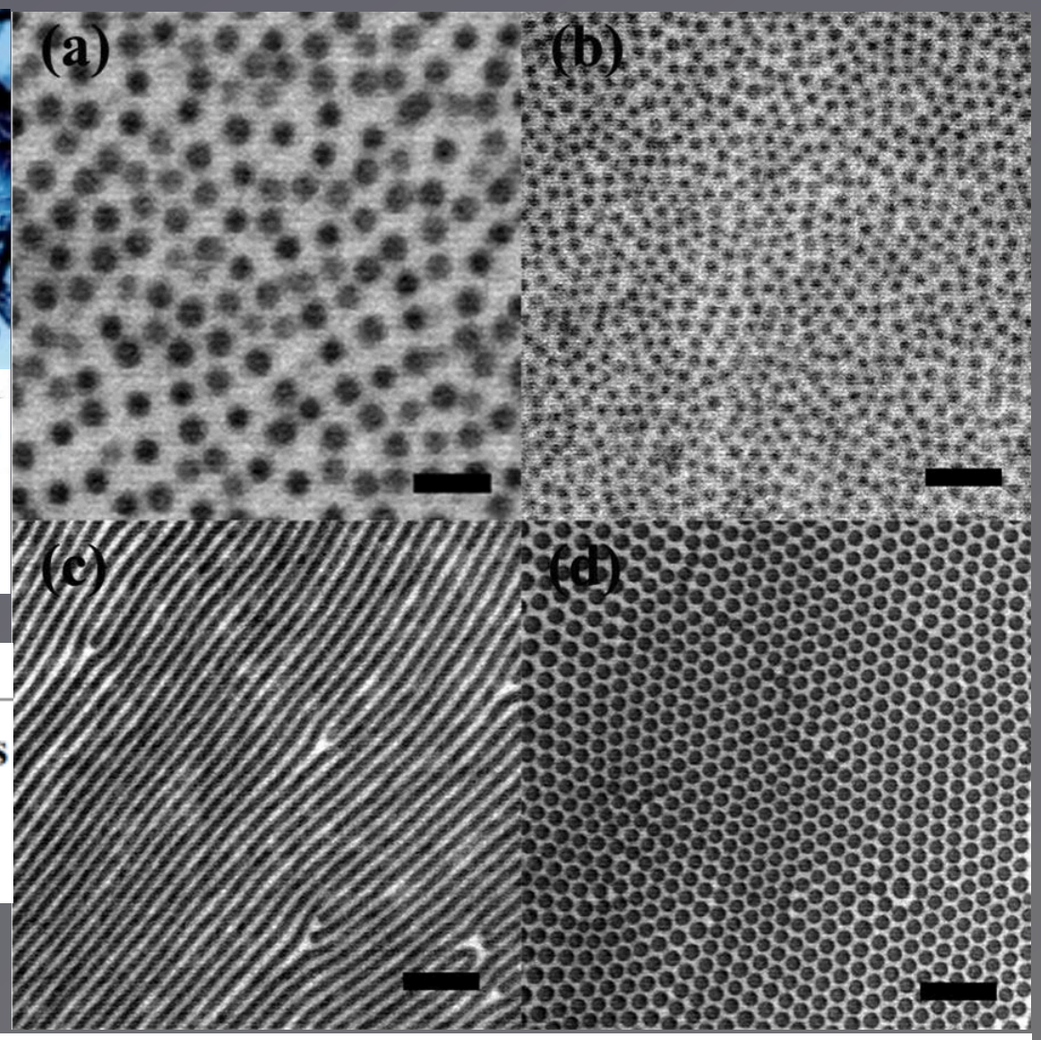
DPG Berlin, Talk CPP 10.8
Fachverband Chemische Physik und Polymerphysik

March 27th, 2012

Motivation



more examples:

Rev. Mod. Phys. 65, 851–1112 (1993)

Pattern formation outside of equilibrium

M. C. Cross P. C. Hohenberg

www.rsc.org/softmatter

Pattern formation by dewetting and evaporating sedimenting suspensions

Mehdi Habibi,[a] Peder Moller,[b] Abdoulaye Fall,[c] Salima Rafai[d] and Daniel Bonn[bc]

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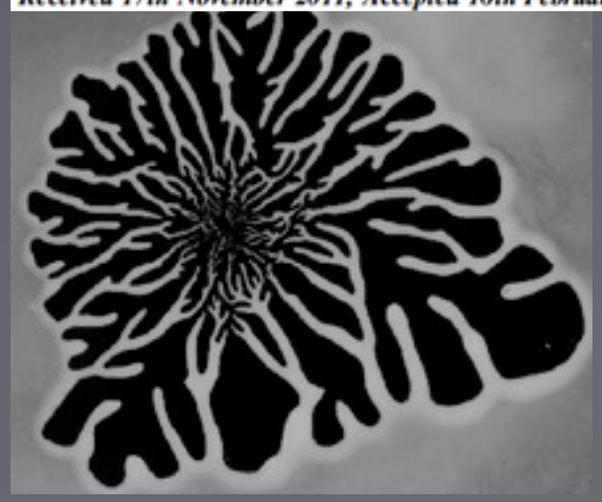
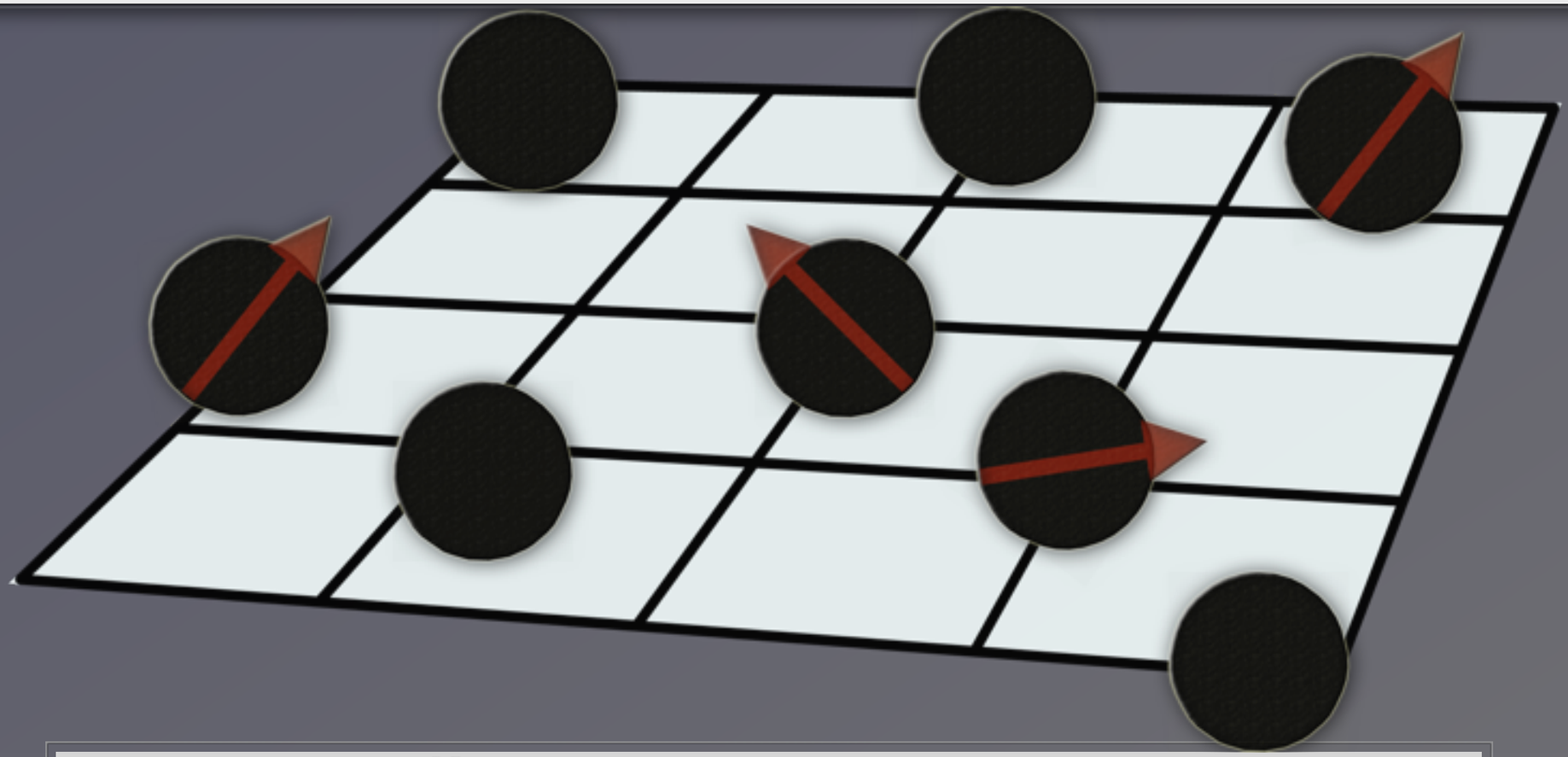


PRL **104,** 255703 (2010) PHYSICAL REVIEW LETTERS week ending 25 JUNE 2010

Magnetically Induced Pattern Formation in Phase Separating Polymer-Solvent–Nanoparticle Mixtures

Rakchanok Rungsawang,[1] Joakim da Silva,[1] Cheng-Pei Wu,[1] Easan Sivaniah,[1,*] Adrian Ionescu,[2] Crispin H. W. Barnes,[2] and Nicholas J. Darton[3]

A simple model: Heisenberg mixture

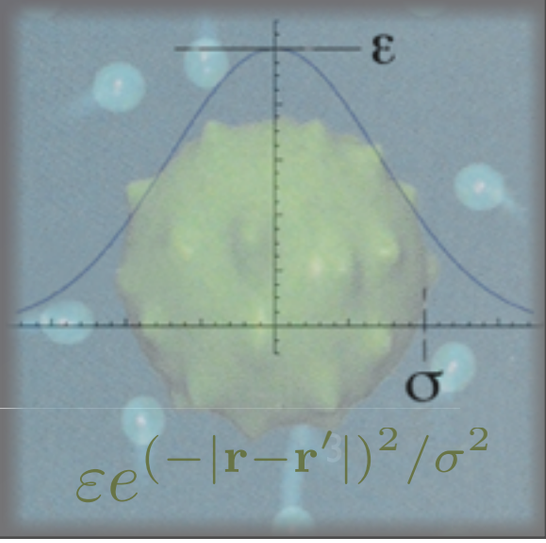


$$\mathcal{H}^{\text{int}} = \frac{1}{2}\sum_{\alpha,\beta}\sum_{\substack{i,j=1\\ i\neq j}}^{N} V^{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{s}_i,\mathbf{s}_j)\ ,\ \text{where}\ \ \alpha,\beta=\{A,B\}$$

Interaction potential

$$V_{\text{core}}(\mathbf{r}_i,\mathbf{r}_j)+V_{\text{mag}}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{s}_i,\mathbf{s}_j)\delta_{\alpha,B}\delta_{\beta,B}$$

$$V_{\text{mag}}(\mathbf{r},\mathbf{r}',\mathbf{s}_1,\mathbf{s}_2) = -J\frac{e^{-(|\mathbf{r}-\mathbf{r}'|/\sigma-1)}}{|\mathbf{r}-\mathbf{r}'|/\sigma}\mathbf{s}_1\cdot\mathbf{s}_2$$



Part I: Equilibrium Theory

Density functional theory

Central quantity: $\rho_\alpha(\mathbf{r},\omega) = \rho_\alpha(\mathbf{r}) h_\alpha(\mathbf{r},\omega)$

Classical grand potential :

$$\Omega[\{\rho_\alpha\}] = \mathcal{F}[\{\rho_\alpha\}] - \sum_\alpha \int d\omega \int d\mathbf{r} \Big[\mu_\alpha - V_{\text{ext}}(\mathbf{r},\omega)\Big] \rho_\alpha(\mathbf{r},\omega)$$

$$\mathcal{F}[\{\rho_\alpha\}] = \quad \mathcal{F}_{\text{id}}[\{\rho_\alpha\}] + \mathcal{F}_{\text{ex}}[\{\rho_\alpha\}]$$

$$\mu_\alpha = \frac{\delta \mathcal{F}[\{\rho_\alpha\}]}{\delta \rho_\alpha}$$

Excess free energy:

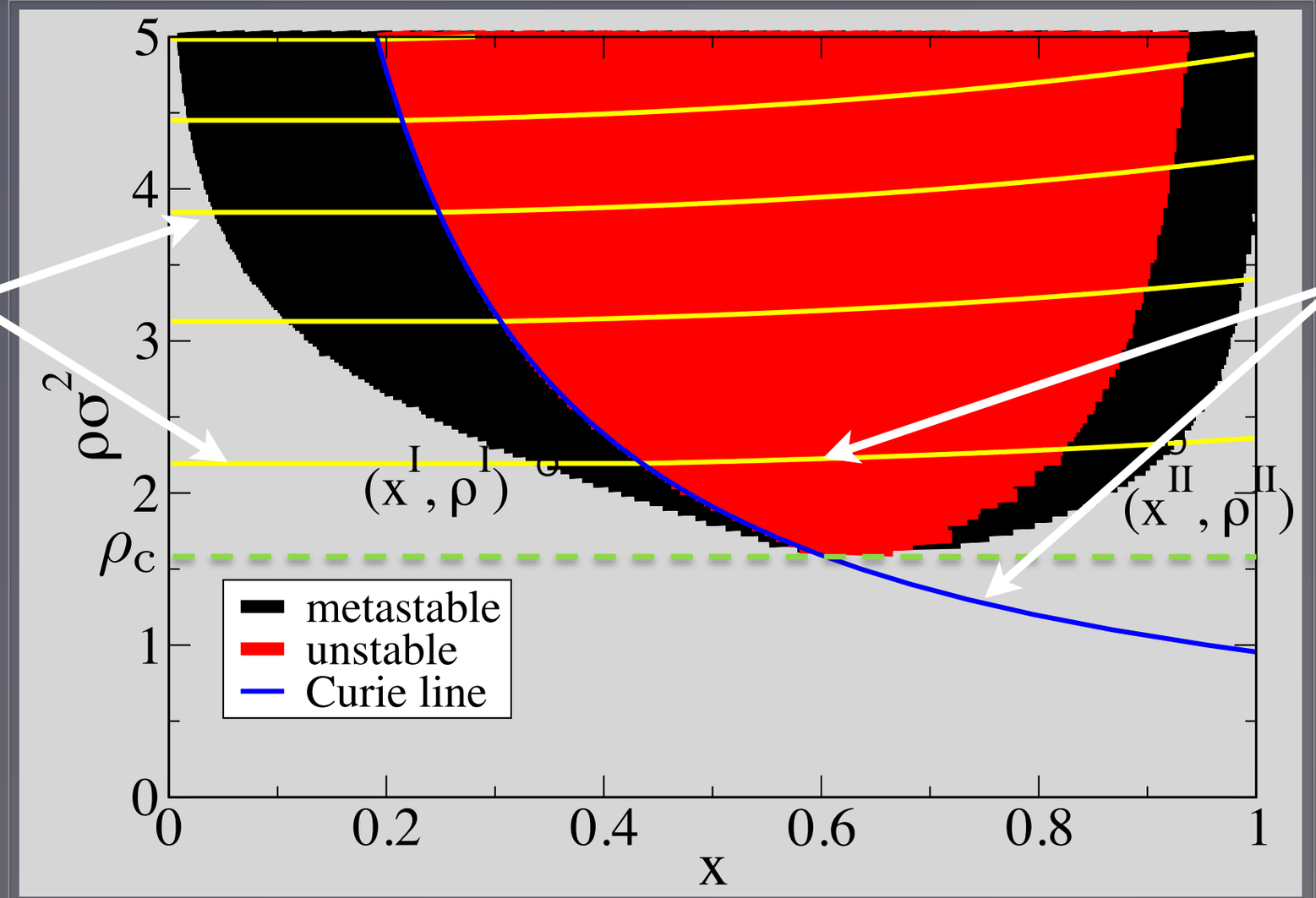
$$\mathcal{F}_{\text{ex}}[\{\rho_i\}] = \frac{1}{2} \sum_{\alpha,\beta} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \int d\omega \int d\omega' \, \rho^{(2)}_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega,\omega';\lambda) V^{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|,\omega,\omega')$$

Equilibrium density is given by:

$$\left.\frac{\delta \Omega[\rho_\alpha, h]}{\delta \rho_\alpha(\mathbf{r})}\right|_{\rho^{(0)}_\alpha(\mathbf{r})} = 0 \quad \text{, and} \quad \left.\frac{\delta \Omega[\rho_\alpha, h]}{\delta h_\alpha(\mathbf{r},\omega)}\right|_{h^{(0)}_\alpha(\mathbf{r},\omega)} = 0$$

Phase diagram

Isobars

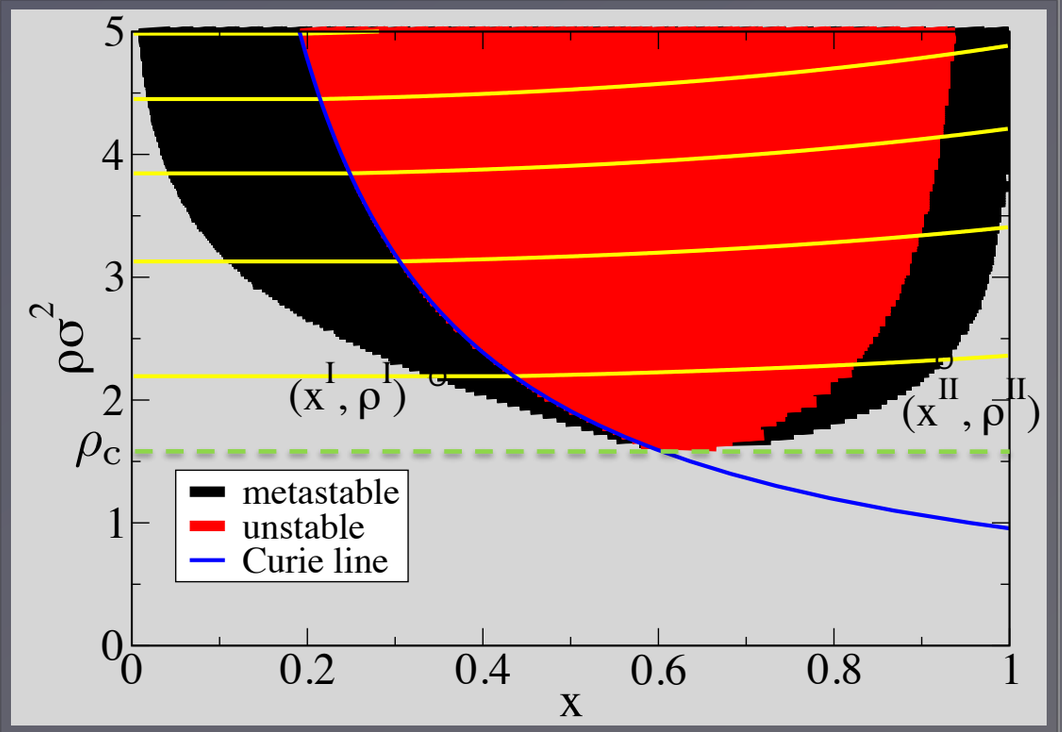


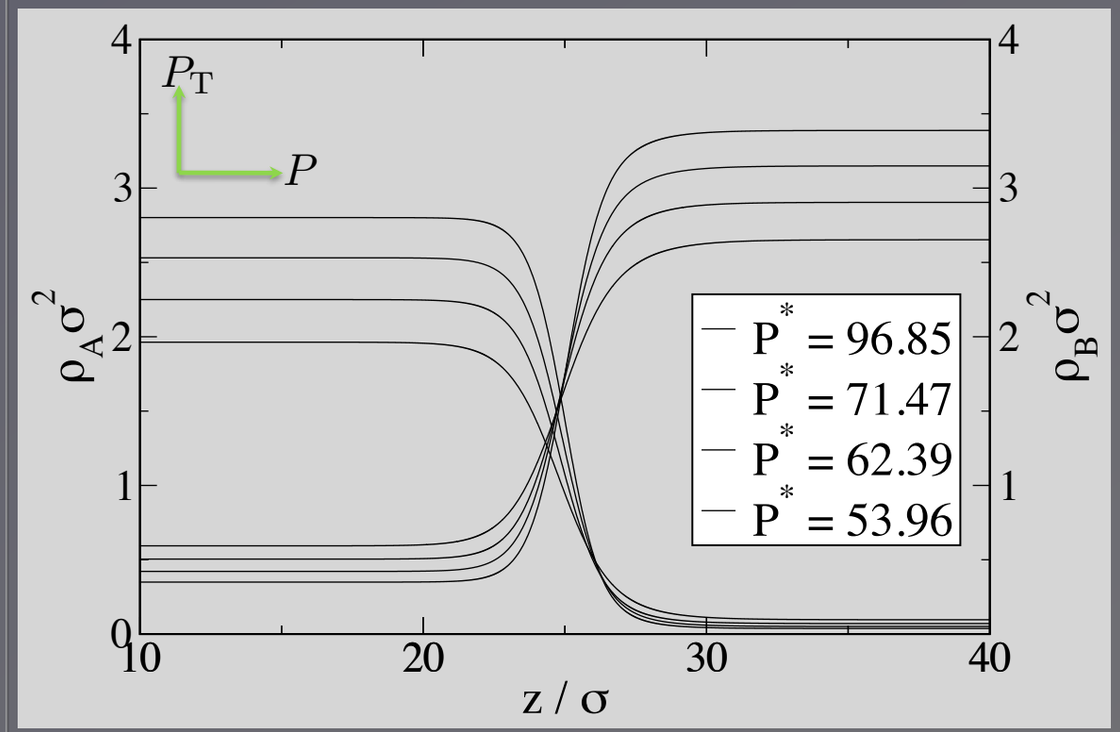
Phase transitions

- First order demixing transition
- Second order transition for the magnetization

- Coexisting states with $\mu_\alpha^{\mathrm{I}} = \mu_\alpha^{\mathrm{II}}, \quad P^{\mathrm{I}} = P^{\mathrm{II}}$ and $T^{\mathrm{I}} = T^{\mathrm{II}}$
- Tricritical point with stable states for r < r_c

Inhomogeneous densities





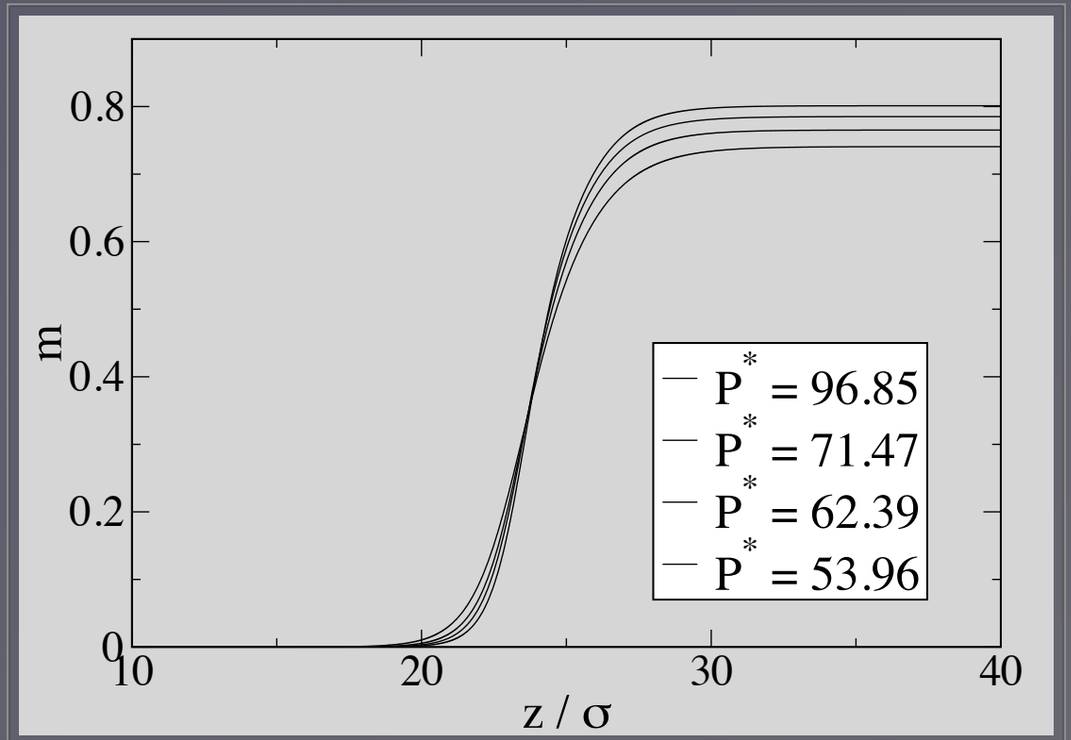
- Minimize: $\left.\frac{\delta\Omega[\rho_\alpha, h]}{\delta\rho_\alpha(\mathbf{r})}\right|_{\rho_\alpha^{(0)}(\mathbf{r})} = 0$, and $\left.\frac{\delta\Omega[\rho_\alpha, h]}{\delta h_\alpha(\mathbf{r},\omega)}\right|_{h_\alpha^{(0)}(\mathbf{r},\omega)} = 0$

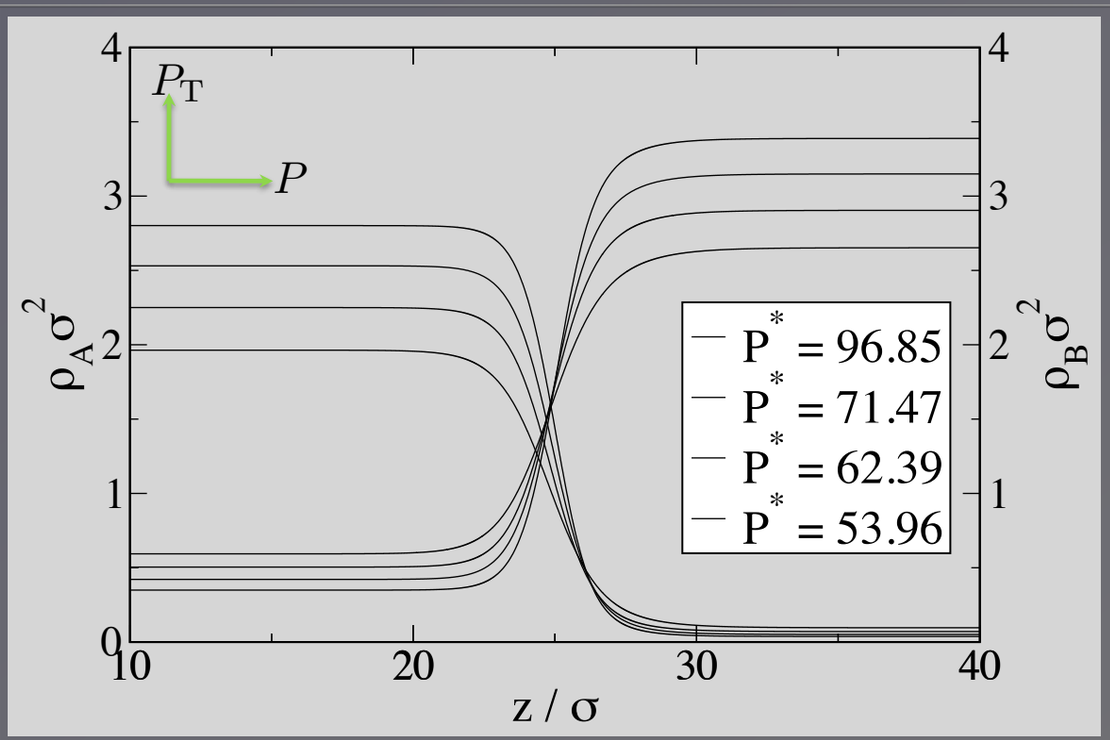
→ System completely equilibrated

- Full information of system after phase separation

→ Coexisting bulk densities and bulk magnetizations

Magnetization





- Inhomogeneous magnetization profile for species B
- No magnetization in phase I
- Softening of the interface can also be seen in the magnetization

Part II: Out of equilibrium

Dynamical density functional theory

One-body Smoluchowski equation for a binary mixture:

$$\Gamma^{-1}\frac{\partial\rho_\alpha(\mathbf{r},t)}{\partial t} = k_BT\nabla^2_\alpha\rho_\alpha(\mathbf{r},t) + \nabla_\alpha\left[\rho_\alpha(\mathbf{r},t)\nabla_\alpha V_{\rm ext}(\mathbf{r},t)\right] + \\ +\frac{1}{2}\nabla_\alpha\sum_{\alpha\beta}\int d\mathbf{r}'\,\rho^{(2)}_{\alpha\beta}(\mathbf{r},\mathbf{r}',t)\nabla_\alpha v_2(\mathbf{r},\mathbf{r}')$$

Adiabatic approximation and sum rule:

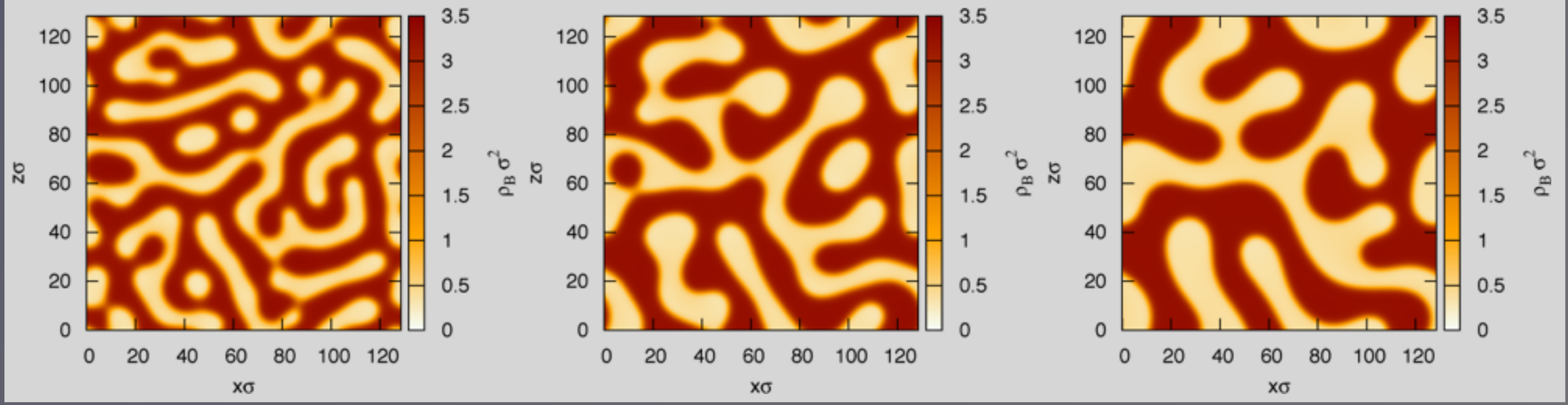
$$\int d\mathbf{r}'\,\rho^{(2)}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\nabla v_2(\mathbf{r},\mathbf{r}') \;=\; \rho_\alpha(\mathbf{r})\nabla\frac{\delta F_{\rm ex}[\rho_\alpha(\mathbf{r}),\rho_\beta(\mathbf{r})]}{\delta\rho_\alpha(\mathbf{r})}$$

DDFT key equation:

$$\Gamma^{-1}_\alpha\frac{\partial\rho_\alpha(\mathbf{r},t)}{\partial t} = \nabla\cdot\left[\rho_\alpha(\mathbf{r},t)\nabla\frac{\delta\mathcal{F}[\rho_A(\mathbf{r},t),\rho_B(\mathbf{r},t)]}{\delta\rho_\alpha(\mathbf{r},t)}\right]$$

U. Marconi, P. Tarazona, JCP **110** 8032, 1999

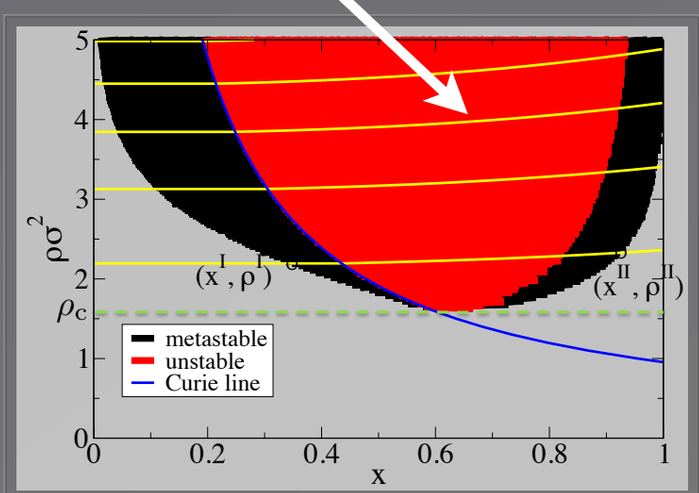
Spinodal decomposition



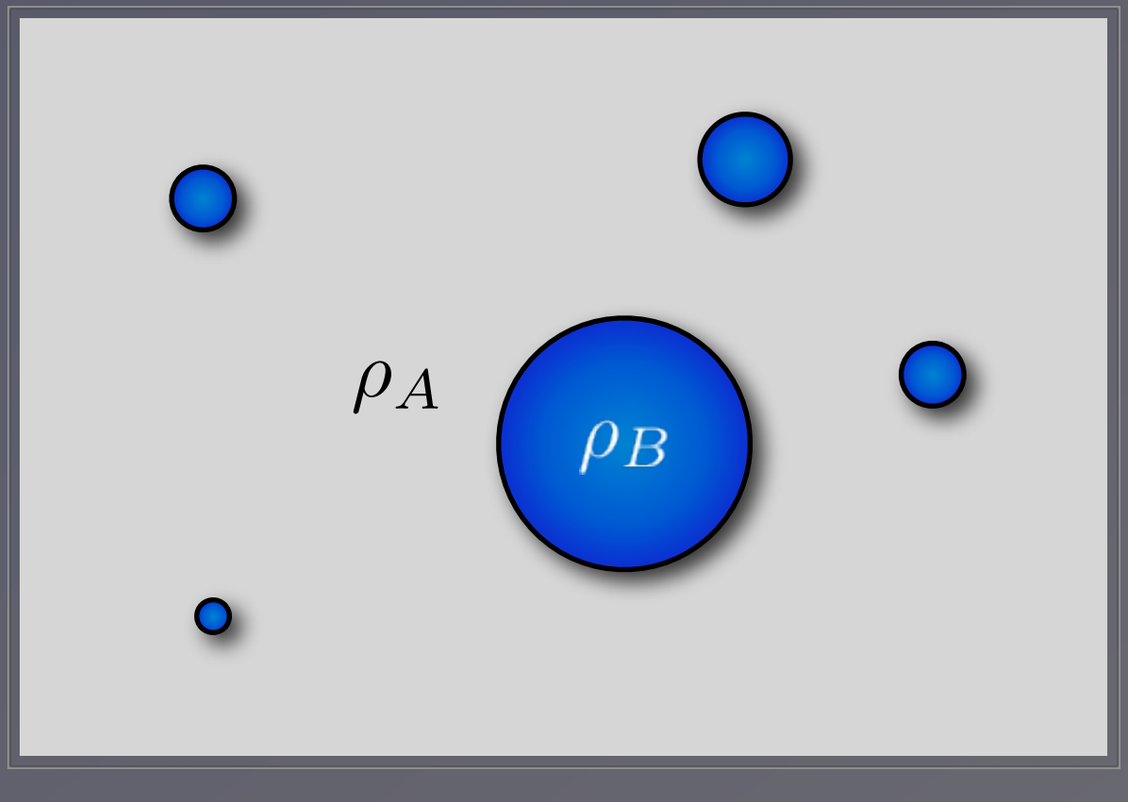
- Study states where dynamics is linearly unstable

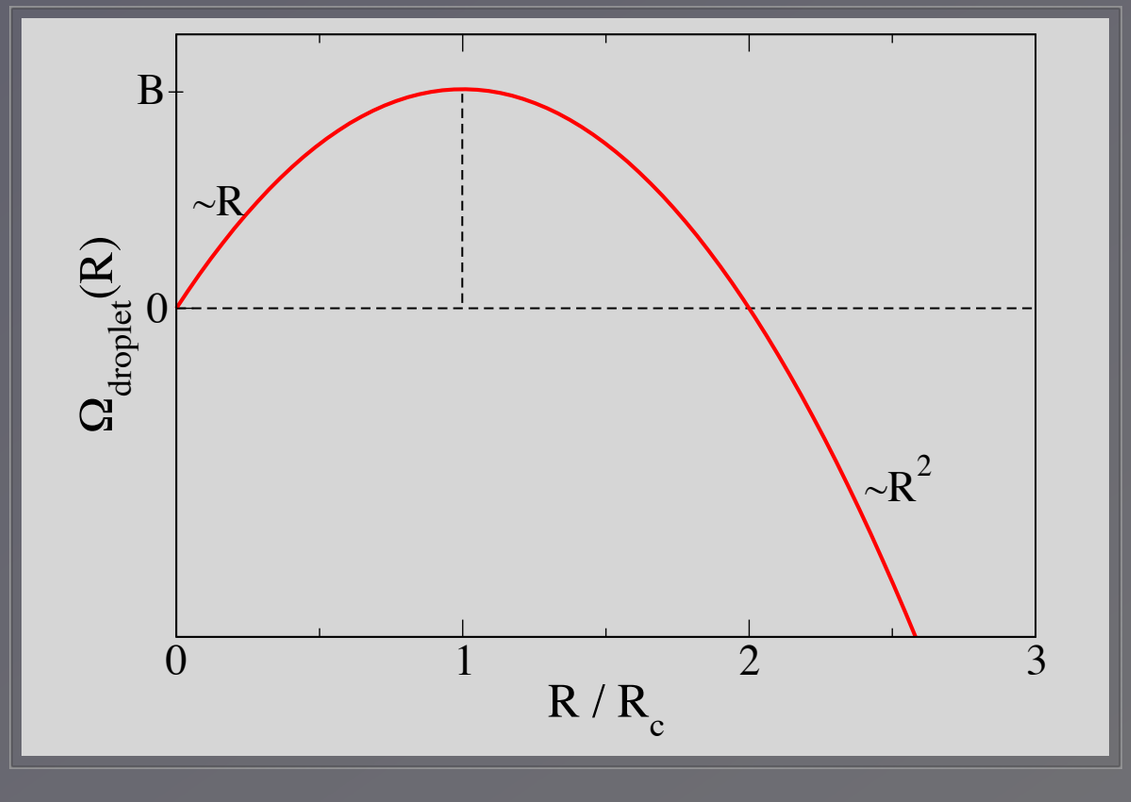
→ Density variations grow slowly over time

$$\rho_\alpha(\mathbf{r},t) = \rho_\alpha^{\text{bulk}} + \delta\rho_\alpha(\mathbf{r},t)$$
$$\delta\rho_\alpha(\mathbf{r},t) \sim \sin(\mathbf{k}\cdot\mathbf{r})$$



Nucleation (2d)



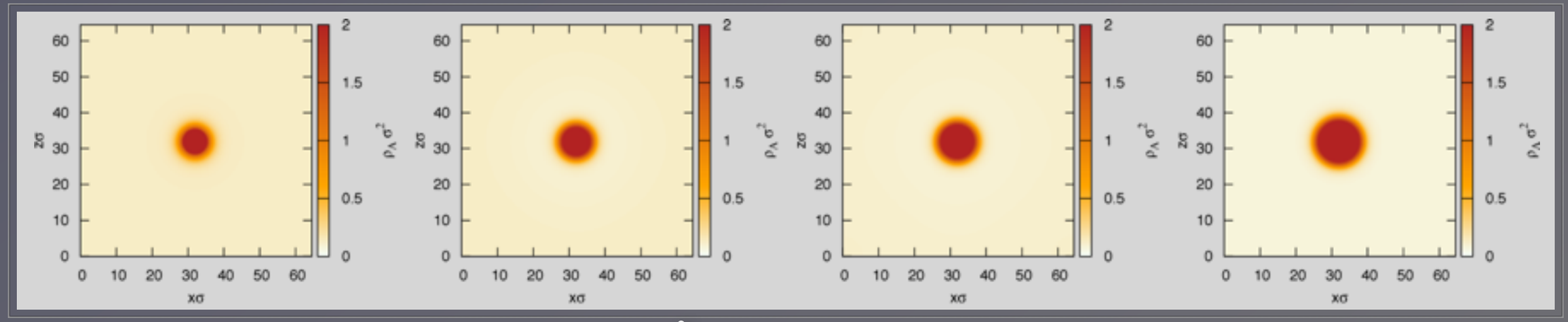


- Exchange of energy, volume or particles such that:

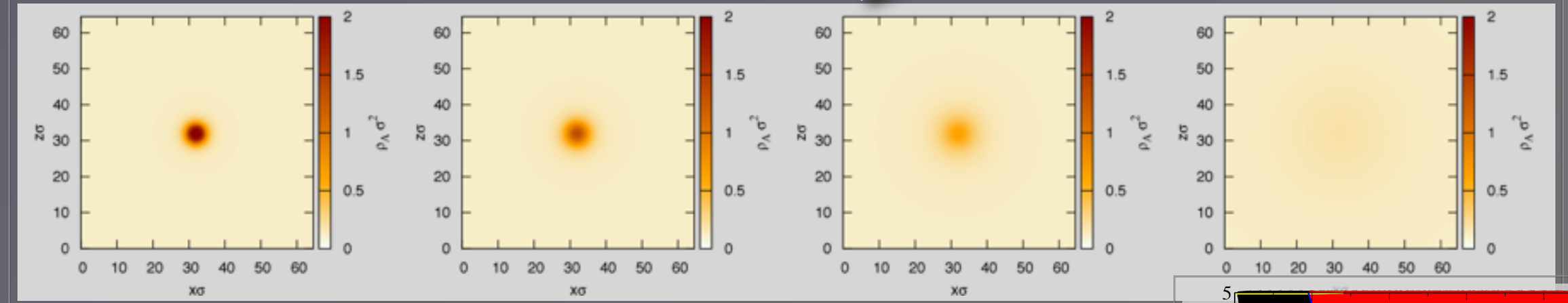
$$T_A = T_B, \quad P_A = P_B, \quad \mu_A = \mu_B$$

- Surface tension impedes the formation of droplets
- Supercritical nuclei for R > Rc

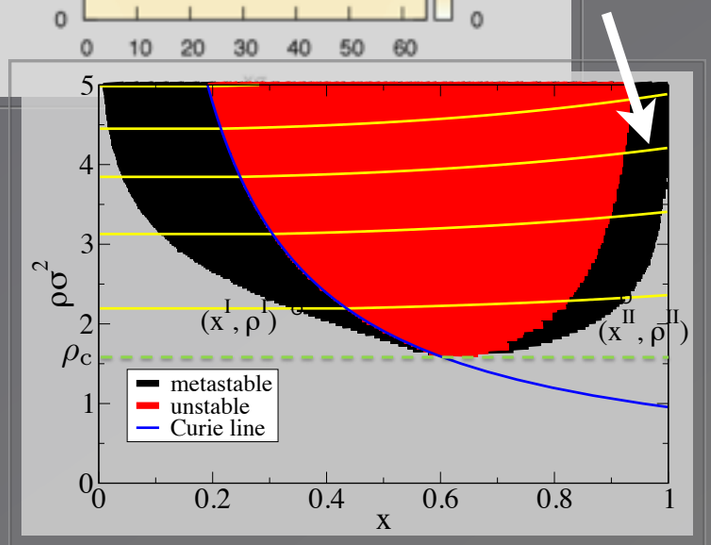
Nucleation dynamics



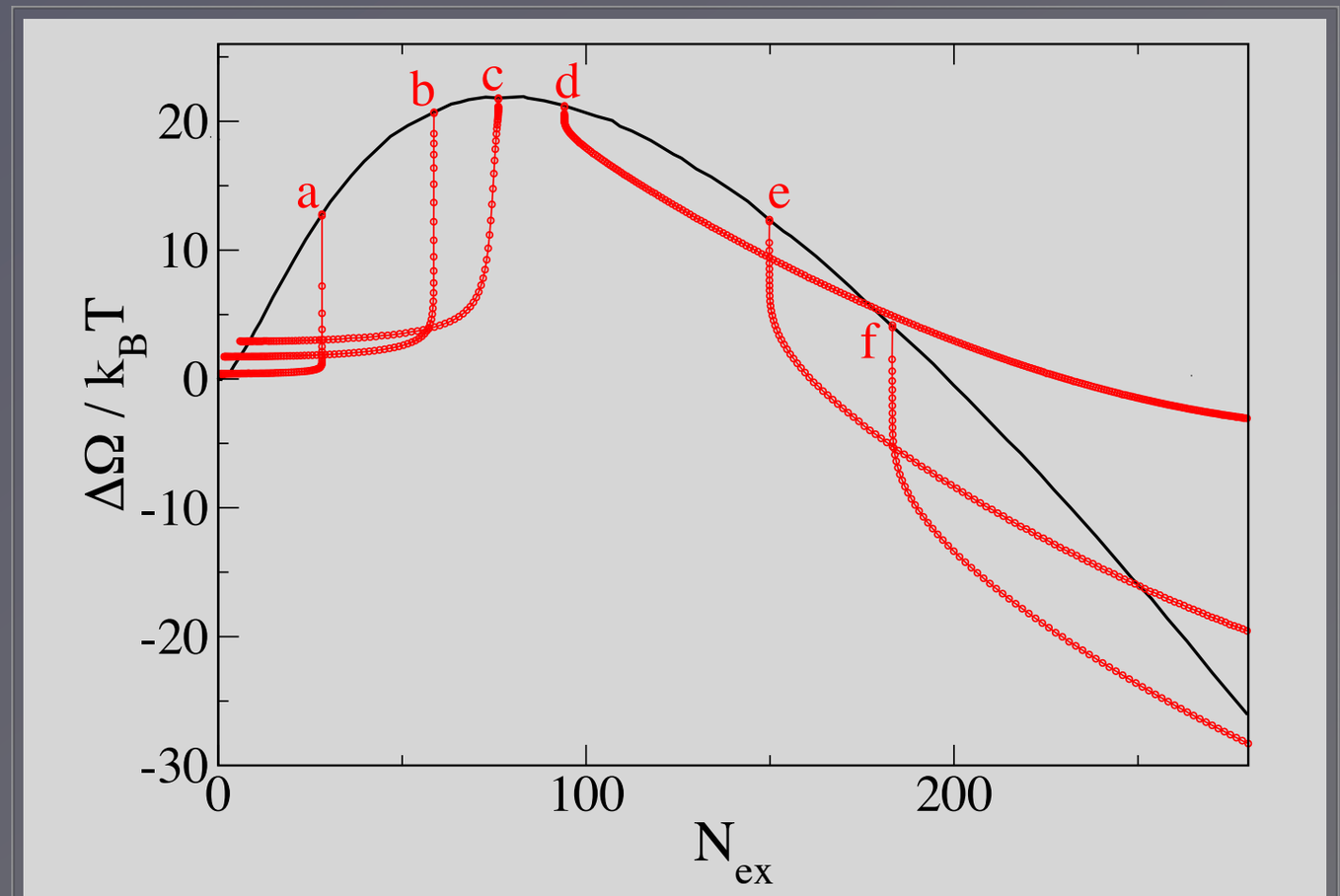
time



- Isotropic particles in the sea of magn. particles
- Pathways for supercritical and subcritical nuclei



DDFT free energy pathway

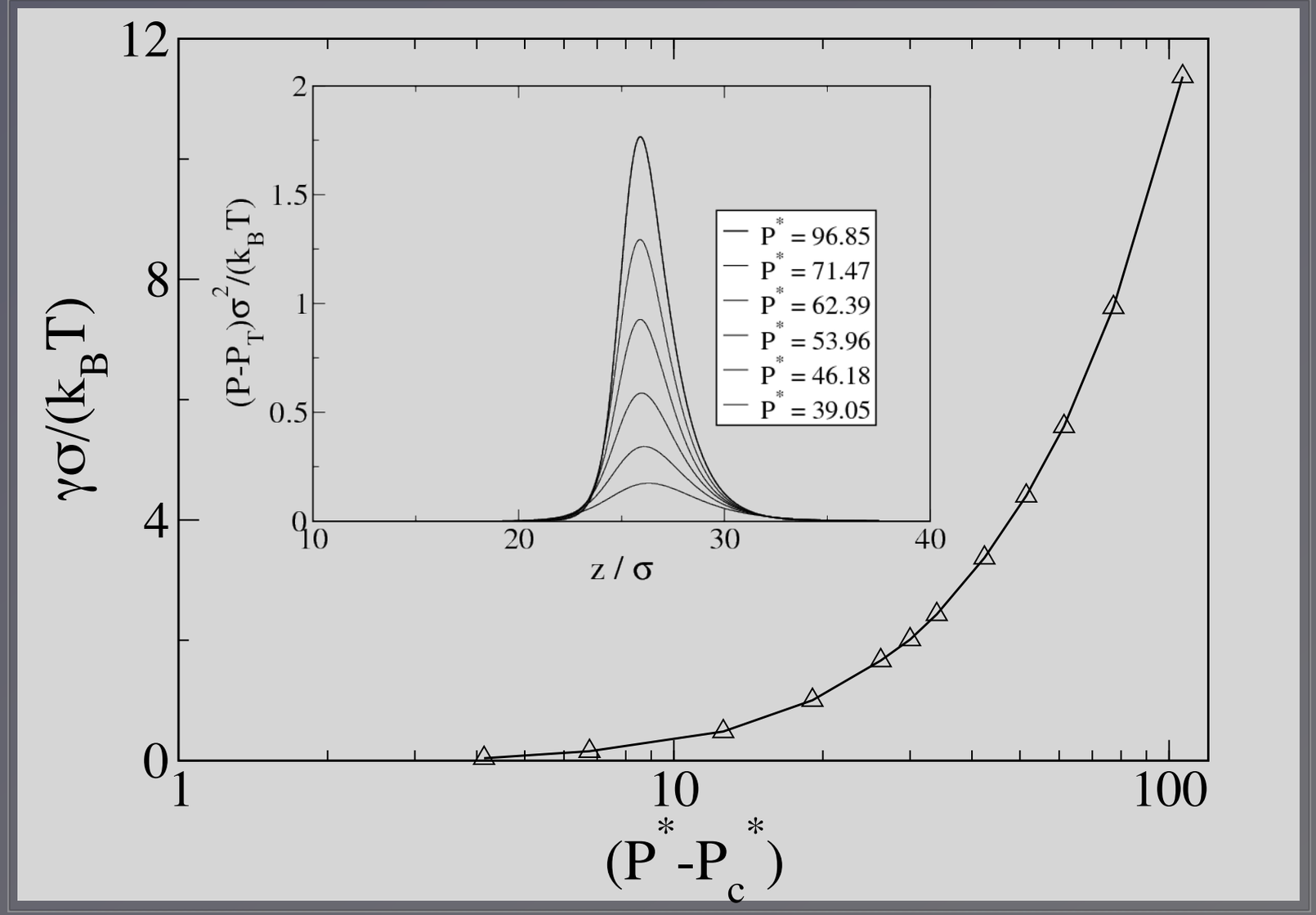


- EDFT and DDFT consistent in predicting nucleus growth or shrinking, but: free energy pathways are different!
- Recall that EDFT works in (T,V,μ) ensemble and DDFT in (T,V,N) ensemble, respectively

Summary

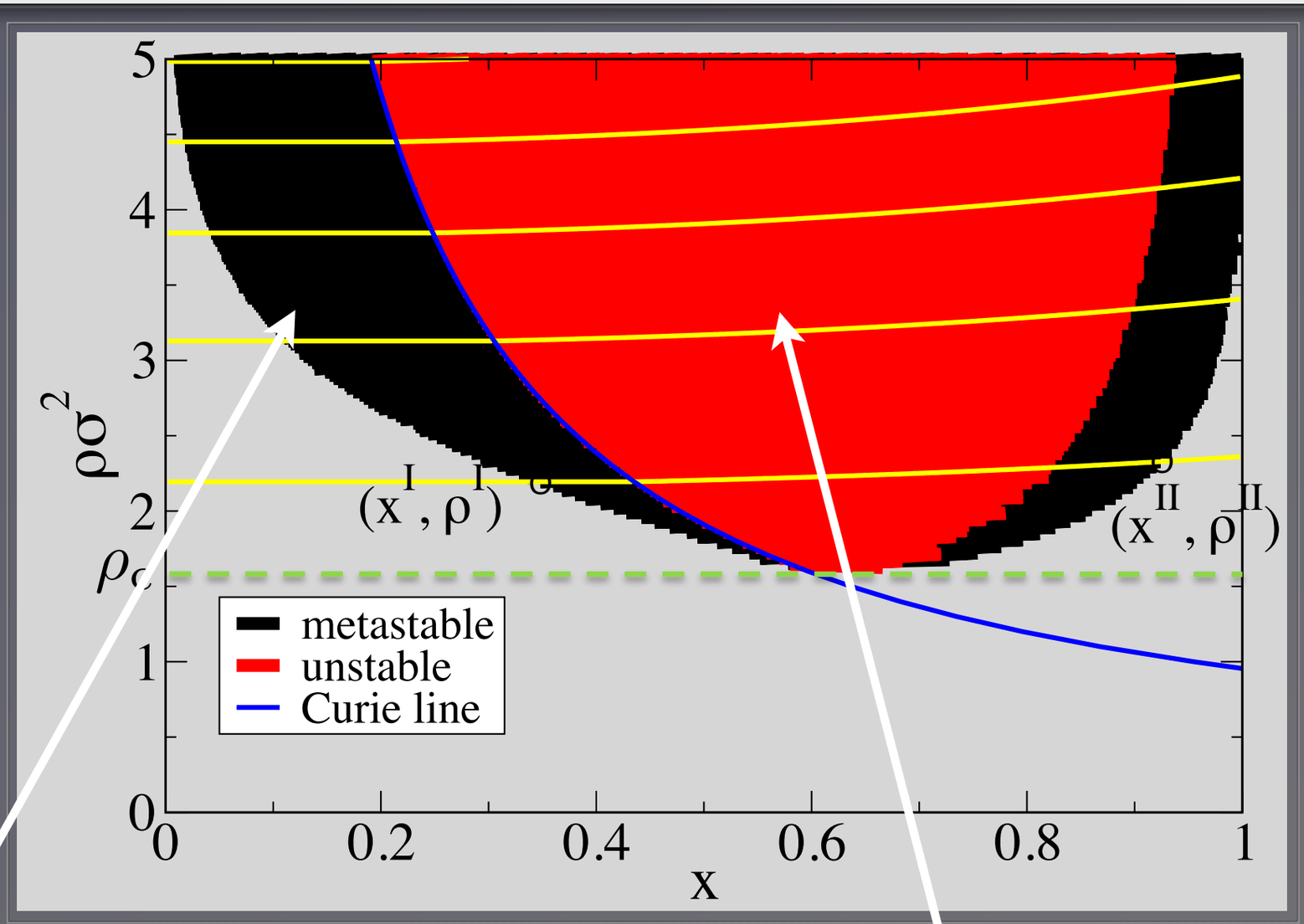
- Model for a binary colloidal mixture
- Phase diagram and equilibrium (EDFT) results of the free interface
- DDFT study with consistent results
- Free energy pathways of EDFT and DDFT

Surface tension



- Pressure $\mathbf{P} = P_T(z)\hat{e}_x\hat{e}_x + P_N(z)\hat{e}_z\hat{e}_z$
- Line tension $\gamma = \int_{-\infty}^{\infty} dz\,(P - P_T(z))$

Phase separation dynamics



Can we study nucleation with DDFT?

or unstable states (spinodal decomposition)?

What about the orientational degree of freedom?

Time-evolution of the pdf

$$\frac{\partial}{\partial t}P(\mathbf{r}^N,\hat{\omega}^N,t) = \mathcal{L}_S P(\mathbf{r}^N,\hat{\omega}^N,t)$$

$$\mathcal{L}_S(\dots) = \sum_{i=1}^{N}\Big\{\nabla_{\mathbf{r}_i}\mathbf{\Gamma}(\hat{\omega}_i)\left[k_BT\nabla_{\mathbf{r}_i} + \nabla_{\mathbf{r}_j}U(\mathbf{r}^N,\hat{\omega}^N,t)\right] + \Gamma_r\hat{R}_i\left[k_BT\hat{R}_i + \hat{R}_iU(\mathbf{r}^N,\hat{\omega}^N,t)\right]\Big\}(\dots)$$

$$\hat{R}_i = \hat{\omega}_i \times \nabla_{\hat{\omega}_i}$$

Total force and torque:

$$\rho^{(n)}(\mathbf{r}^n,\hat{\omega}^n,t) = \frac{N!}{(N-n)!}\int d\mathbf{r}_{n+1}\dots\int d\mathbf{r}_N\oint d\hat{\omega}_{n+1}\dots\oint d\hat{\omega}_N \mathrm{P}(\mathbf{r}^N,\hat{\omega}^N,t)$$

We obtain the DDFT key equation:

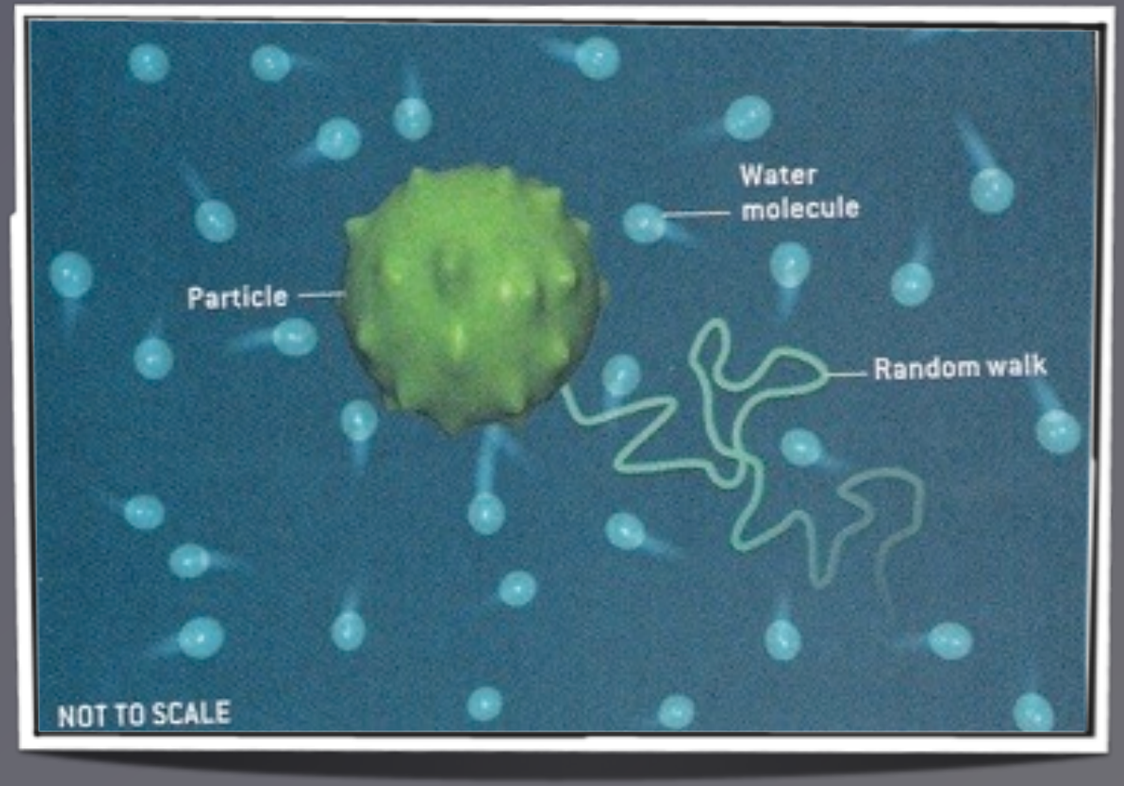
$$\Gamma^{-1}\frac{\partial\rho(\mathbf{r},\hat{\omega},t)}{\partial t} = \nabla\left[\rho(\mathbf{r},\hat{\omega},t)\nabla\frac{\delta F[\rho(\mathbf{r},\hat{\omega},t)]}{\delta\rho(\mathbf{r},\hat{\omega},t)}\right] + \hat{\mathcal{R}}\left[\rho(\mathbf{r},\hat{\omega},t)\hat{\mathcal{R}}\frac{\delta F[\rho(\mathbf{r},\hat{\omega},t)]}{\delta\rho(\mathbf{r},\hat{\omega},t)}\right]$$

Methods

(I) Computer simulations

$$m\ddot{\mathbf{r}}_i = -\gamma\dot{\mathbf{r}}_i - \nabla_i U(\mathbf{r}_1, \mathbf{r}_2, \ldots, t) + \xi_i(t)$$

inertia friction forces noise



- Full dynamics with interactions
- Orientation, hydrodynamics etc.
- Difficult to solve

Methods

(I) Computer simulations

$$m\ddot{\mathbf{r}}_i = -\gamma\dot{\mathbf{r}}_i - \nabla_i U(\mathbf{r}_1, \mathbf{r}_2, \ldots, t) + \xi_i(t)$$

inertia friction forces noise

(II) Density functional theories

Static DFT

- Equilibrium properties, microscopic description
- Phase diagrams, interfaces, nucleation barriers

Dynamic DFT

- States out of equilibrium, time-dep. order parameter
- Relaxation into equilibrium of $\rho(\mathbf{r}, t)$, $m(\mathbf{r}, t)$

Outline

(I) Introduction

(II) Equilibrium theory (EDFT)

- Model
- Phase diagram
- Static results

(III) Out of equilibrium (DDFT)

- Comparison to EDFT
- Nucleation

(IV) Conclusion

DDFT for binary mixtures

DDFT key equation:

$$\Gamma_\alpha^{-1}\frac{\partial\rho_\alpha(\mathbf{r},t)}{\partial t}=\nabla\cdot\left[\rho_\alpha(\mathbf{r},t)\nabla\frac{\delta\mathcal{F}[\rho_A(\mathbf{r},t),\rho_B(\mathbf{r},t)]}{\delta\rho_\alpha(\mathbf{r},t)}\right]$$

U. Marconi, P. Tarazona, JCP **110** 8032, 1999

Note, that

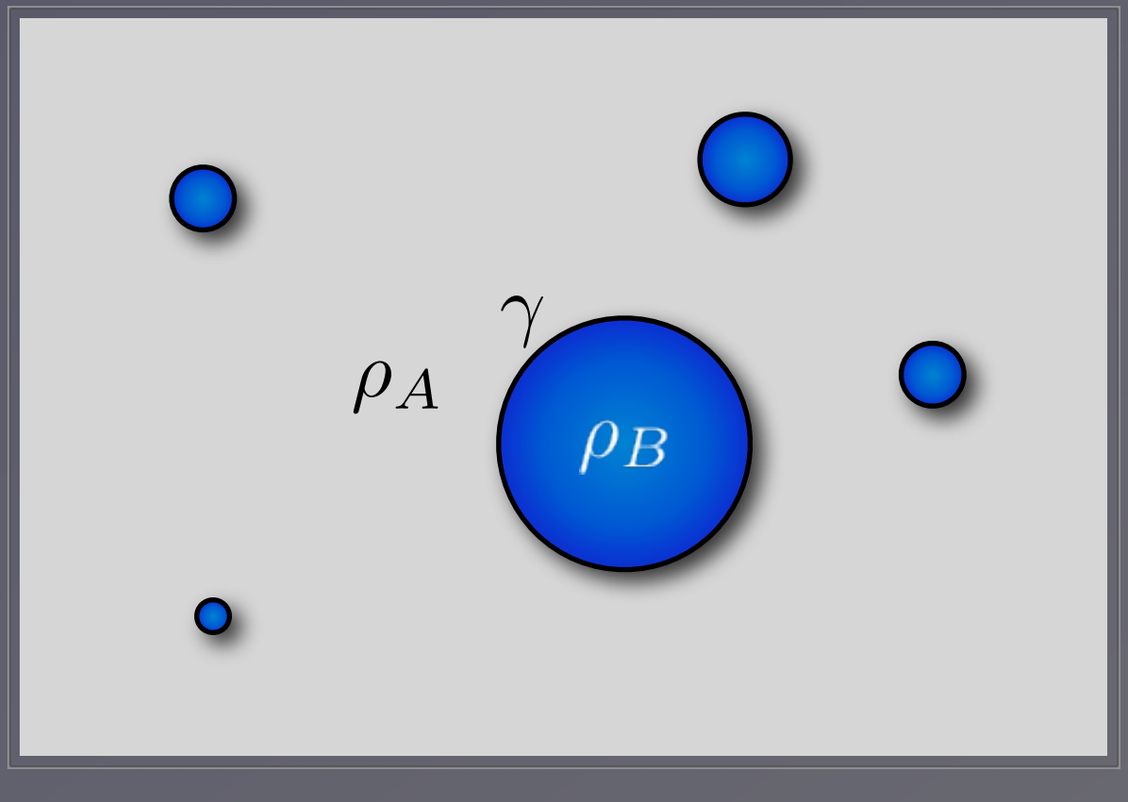
- we assume magnetic moments have very short relaxation time

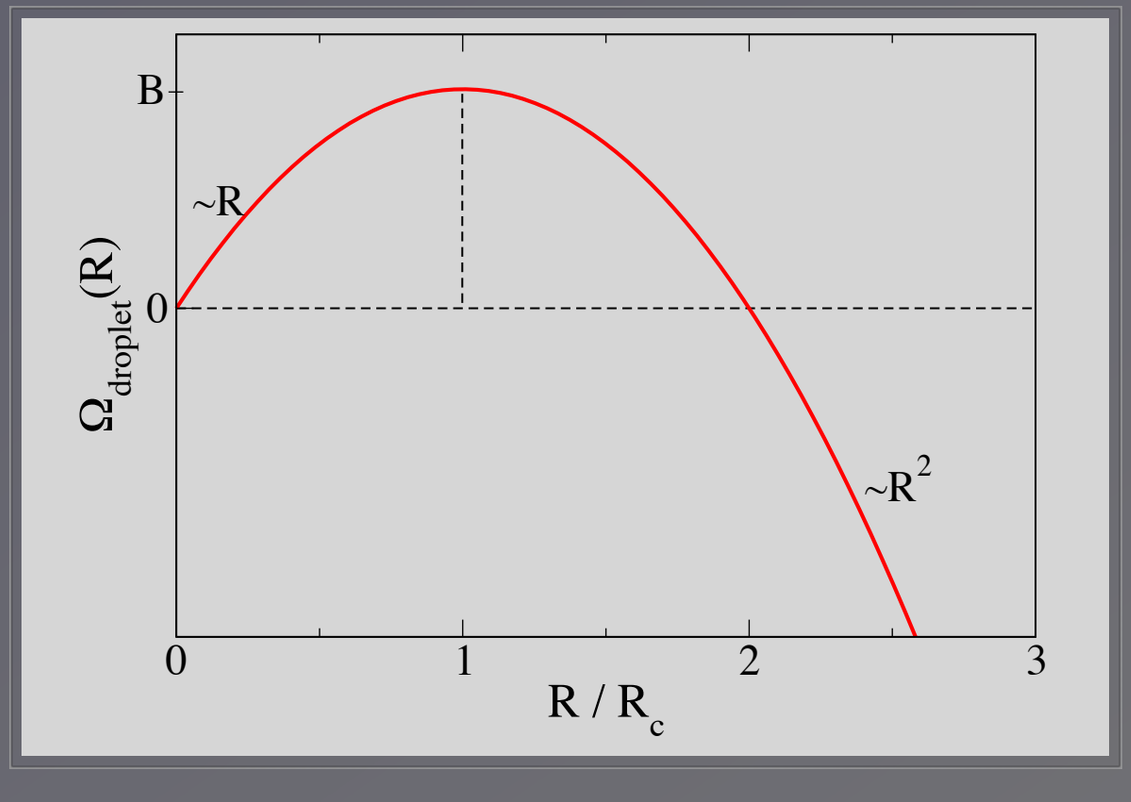
  so that m can be minimized at each time instant: $\left.\frac{\partial\Omega[\rho_\alpha,h]}{\partial h_\alpha(\mathbf{r},\omega)}\right|_{h_\alpha^{(0)}(\mathbf{r},\omega)}=0$

- we use the same Helmholtz free energy as above (EDFT):

$$\mathcal{F}[\{\rho_\alpha\}]=\quad\mathcal{F}_{\mathrm{id}}[\{\rho_\alpha\}]+\mathcal{F}_{\mathrm{ex}}[\{\rho_\alpha\}]$$

Nucleation: critical droplet theory (2d)





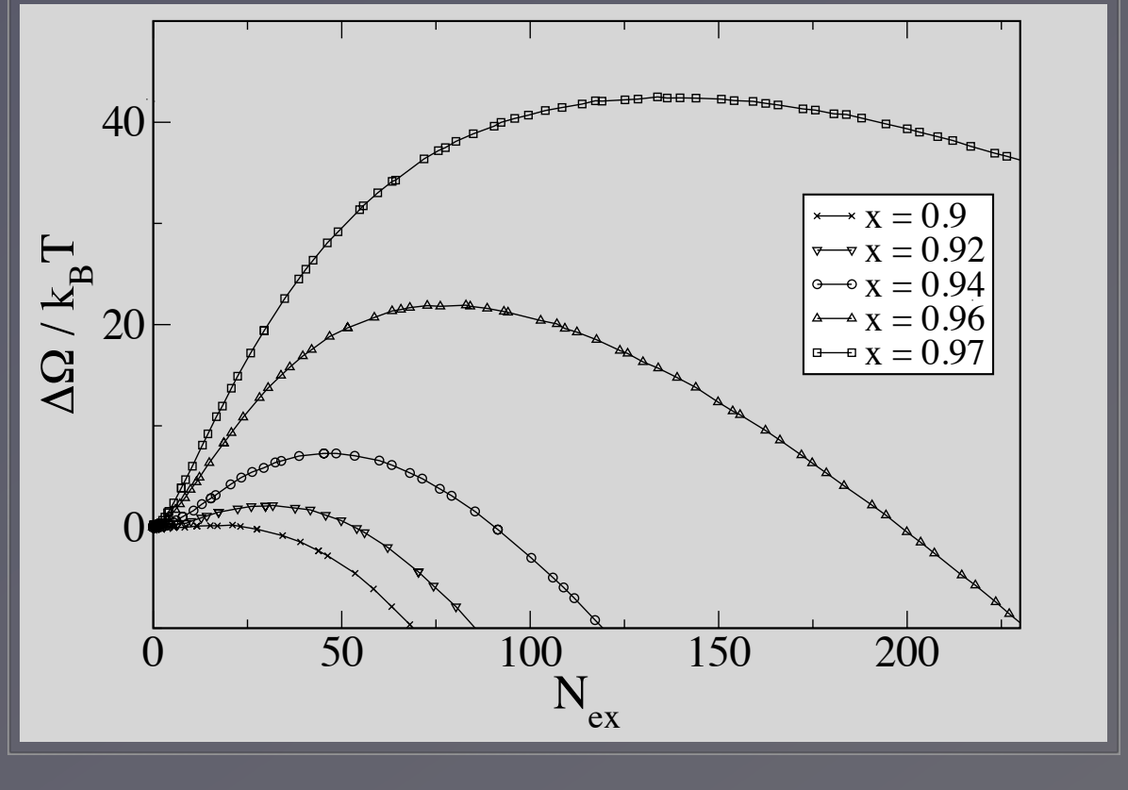
- Exchange of energy, volume or particles such that:

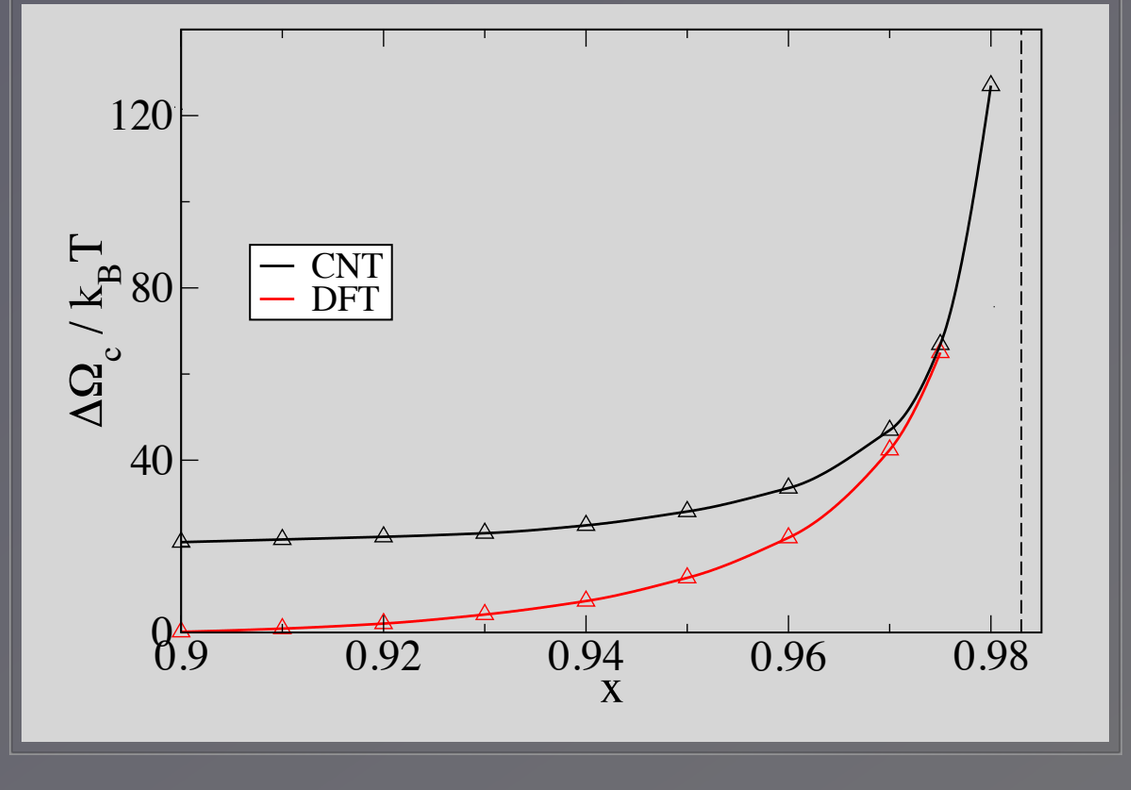
$$T_A = T_B, \quad P_A = P_B, \quad \mu_A = \mu_B$$

- surface tension impedes the formation of droplets:

$$\Omega_{\text{droplet}}(R) = 2\pi R\gamma - \pi R^2 |\Delta P|$$

Nucleation barrier





- Results consistent for concentrations near binodal
- CNT is weak for smaller concentrations (near the spinodal)

  Reason: CNT is clearly a macroscopic theory