# Linking Scales with Molecular Fields

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# Outline

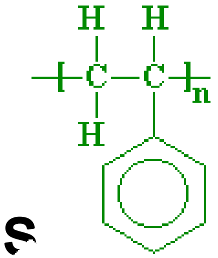
- Introduction: Molecular Fields
  - Starting Point: "Edwards" Model
  - From particles to fields (basically: SCF theory)
- Molecular Field Simulations: Examples
  - Vesicle formation in Copolymer Solutions
  - Incorporating Hydrodynamics
- An Adaptive Hybrid Scheme
  Linking Particle-based and
  Field-Based Simulations

# Part I

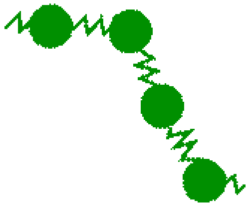
# "Molecular Fields" : A brief Introduction

# Hierarchy of coarse-grain polymer models

- **Ab initio**
- **Atomistic models**

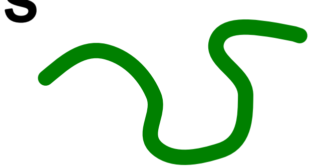


- **Mescoscopic particle-based models**
  - Particle-particle interactions
  - Density based interactions ("Edwards" Models)



Particle World

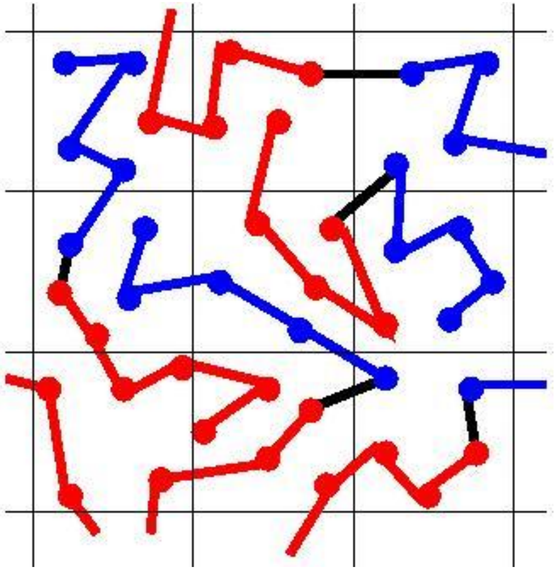
- **Mesoscopic field-based models**
  - "Molecular Fields"
  - Ginzburg-Landau models (Flory-Huggins-de Gennes, Ohta-Kawasaki, ...)



Continuum World

- **Macroscopic continuum models**

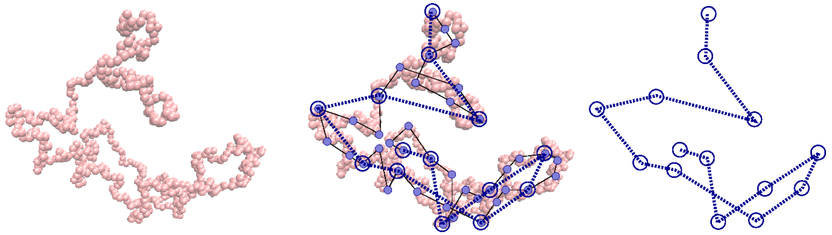
# "Edwards" models for polymers



*Example: Dense AB-copolymer melt*

**Two elements:**

- Model for bonded interactions e.g., Gaussian chains



$$\mathcal{H}_0[\mathbf{r}_i] = \frac{1}{2\sigma^2}\sum_{i=1}^{N-1}\left(\mathbf{r}_{i+1}-\mathbf{r}_i\right)^2$$

- **Density-based** model for non-bonded interactions

# Non-bonded interactions (one component)

**Weak Interactions**: 'Virial Expansion'

⇒ Additional Contribution to the Hamiltonian

$$\mathcal{H}_I[\hat{\rho}] = \frac{v}{2}\int d\mathbf{r}\;\hat{\rho}^2 + \frac{w}{6}\int d\mathbf{r}\;\hat{\rho}^3 + \cdots$$

with the 'monomer density': $\hat{\rho}(\mathbf{r}) = \sum_{\substack{\text{polymers}\\ \alpha}} \int_0^{N_\alpha} ds\;\delta\big(\mathbf{r} - \mathbf{R}_\alpha(s)\big)$

**Generalization to strong interactions**:

"Local density functional" $\mathcal{H}_I[\hat{\rho}] = \int d\mathbf{r}\;\hat{\rho}\;f(\hat{\rho})$

**Popular Ansatz**: Incompressibility $\mathcal{H}_I[\hat{\rho}] = \int d\mathbf{r}\;\delta(\hat{\rho} - \rho_0)$

# Example: Edwards model for AB blends

Most popular model in theories of (co)polymer blends

- **Continuous Gaussian chains**: $\mathcal{H}_0[\mathbf{R}(s)] = \frac{3}{2b^2}\int_0^N ds \left(\frac{d\mathbf{R}}{ds}\right)^2$
- **Two types of monomers** (j = A or B): $\theta_{\alpha j}(s) = \begin{cases} 1 & \text{j-monomer} \\ 0 & \text{Otherwise} \end{cases}$

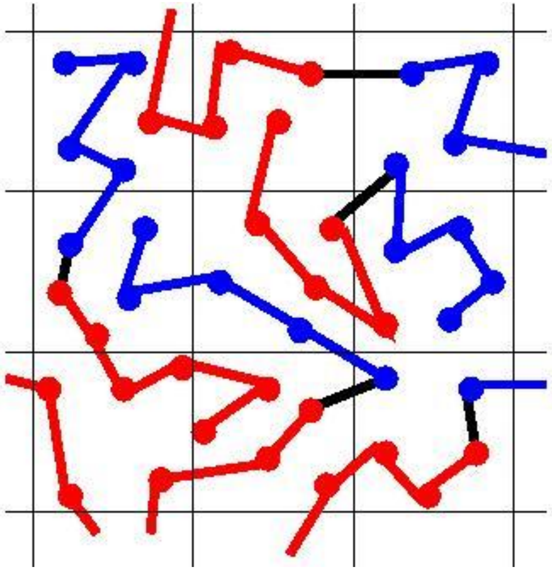
$$\hat{\rho}_j(\mathbf{r}) = \sum_{\text{polymers } \alpha} \int_0^{N_\alpha} ds \; \delta\left(\mathbf{r} - \mathbf{R}_\alpha(s)\right) \theta_{\alpha j}(s)$$

- **Incompressible:** Constraint $\hat{\rho}_A + \hat{\rho}_B \equiv \rho_0$ everywhere.
- **Flory-Huggins Interactions:**

$$\mathcal{H}_I = \rho_0 \chi \int d\mathbf{r} \; \hat{\Phi}_A \hat{\Phi}_B \qquad \text{with} \qquad \hat{\Phi}_j = \hat{\rho}_j / \rho_0$$

# Interpretation of the Edwards model

*Realization of a discrete*
*version of the Edwards model*
*for AB-copolymers*



Continuum limit?

Pragmatic of view: Continuum limit is **unphysical**!
Discrete coarse-graining length should be **part of the model**.

Alternative: Tackle continuum limit, full field theory
⇒ Ultraviolet divergencies, renormalization necessary, …
(David Morse, Glenn Fredrickson)

# Other issues and caveats

**Topological interactions** are **missing** in Edwards models

(Soft interactions, chains may cross each other.)

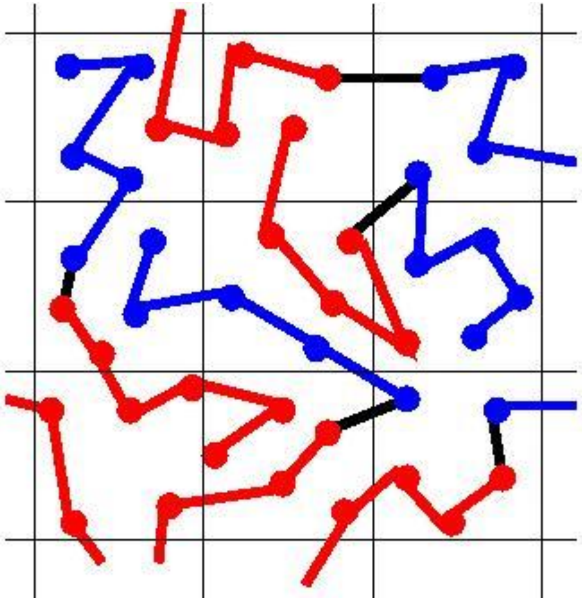
- Affects dynamical properties & statics in ultrathin films
- Does not affect statics of linear chains in 3 dimensions.

**Flory-Huggins $\chi$-parameters**:

- Can sometimes be determined experimentally, e.g. by differential scanning calorimetry, SAXS, SANS
- **But:** may depend on temperature, composition, chain length
- General, exhaustive theory still lacking
  (despite considerable efforts over decades!)
- Very concept of $\chi$-parameter has been questioned
  (e.g., Tambasco, Lipson, Higgins, 2006)

# Direct simulation of Edwards models

Most straightforward way of studying Edwards models:



Requires:

- Discretized formulation
- For convenience:
  Compressible version, e.g.,

$$\mathcal{H}_\kappa = \frac{\kappa}{2}\int d\mathbf{r}\ (\hat{\rho}_A + \hat{\rho}_B - \rho_0)^2$$

*(Laradji, Guo, Zuckermann 1994, Besold et al 1999, Müller et al 2005, de Pablo et al 2008, Q. Wang,…)*

# From Particles to Fields:

# Some Basics on the Self-Consistent Field theory (SCF theory)

# Partition function of the Edwards model

For simplicity: Canonical, one component only

$$Z = \frac{1}{n!}\prod_{\alpha=1}^{n}\left[\rho_0 \int \mathfrak{D}\mathbf{R}_\alpha \; e^{-\mathcal{H}_0[\mathbf{R}_\alpha]}\right] e^{-\mathcal{H}_I[\hat{\rho}]}$$

Path integral over all possible chain conformations **R**(s)

non-bonded interactions

Bonded interactions: Gaussian chains

# Approach I: Density functional theory

**Basis:** (Hohenberg-Kohn theorem)

Free energy of an inhomogeneous system can be described by a functional $\text{☞}[\rho(r)]$ that only depends on local densities.

→ **Task:** "Guess" $\text{☞}[\rho(r)]$

**Ansatz:** $\text{☞}[\rho(r)] = \text{☞}_{\text{♓♎}}[\rho(\mathbf{r})] + \mathcal{H}_I[\rho(\mathbf{r})]$

$\text{☞}_{\text{♓♎}}[\rho(r)]$ : Reference system of ideal, noninteracting chains

$\mathcal{H}_I[\rho(\mathbf{r})]$ : Nonbonded interactions (treated perturbatively)

# Approach I: Density functional theory

## Reference system: Noninteracting chains

- Auxiliary System: Systems with varying external field $W(\mathbf{r})$

Free energy: $G_{\mathrm{id}}[W] = -n \ln\left(Q[W]/n\right)$

→ Density: $\frac{1}{N}\rho(\mathbf{r}) = \frac{\delta G_{\mathrm{id}}[W]}{\delta W(\mathbf{r})} = -n\frac{\delta \ln Q[W]}{\delta W(\mathbf{r})}$

- Legendre transform $W(r) \rightarrow \rho(r)$

⇒ **Density functional of reference system:**

$$\boxed{F_{\mathrm{id}}[\rho] = G_{\mathrm{id}}[\rho] - \frac{1}{N}\int d\mathbf{r}\; W(\mathbf{r})\;\rho(\mathbf{r})}$$

# Approach I: Density functional theory

**Full free energy functional** (everything taken together)

$$\boxed{\mathrm{F}\left[\rho(\mathbf{r})\right] = -n\,\ln\left[{}^{\mathrm{Q}}\!/_{\mathrm{n}}\right] - \tfrac{1}{N}\int \mathrm{d}\mathbf{r}\;W\;\rho + \mathcal{H}_I[\rho]}$$

with W determined from: $\tfrac{1}{N}\rho(\mathbf{r}) = -n\,\dfrac{\delta \ln Q[W]}{\delta W(\mathbf{r})}$

**SCF theory**:

Minimize this functional with respect to $\rho(\mathbf{r})$

⇒ Gives SCF equations $\dfrac{1}{N}W(\mathbf{r}) = \dfrac{\delta \mathcal{H}_I}{\delta\rho(\mathbf{r})}$

# Approach II: Polymer field theory

## Partition function

$$\boxed{Z = \frac{1}{n!}\prod_{\alpha=1}^{n}\left[\rho_0\int\mathfrak{D}\mathbf{R}_\alpha\; e^{-\mathcal{H}_0[\mathbf{R}_\alpha]}\right] e^{-\mathcal{H}_I[\hat{\rho}]}}$$

**Faddeev-Popov transformation:** Insert

$$\delta(\rho-\hat{\rho}) = \int_{i\infty}\mathfrak{D}W\;\; \exp\left(\tfrac{1}{N}W(\rho-\hat{\rho})\right)$$

**⇒ Fluctuating field theory**

$$\boxed{Z = \int_{i\infty}\mathfrak{D}W \int_{\infty}\mathfrak{D}\rho\; \exp(-F)}$$

with

$$\boxed{F = -n\;\ln\left[Q/n\right] - \tfrac{1}{N}\int d\mathbf{r}\;\, W\rho + \mathcal{H}_I[\rho]}$$

# Derivation II: Polymer field theory

Starting from **fluctuating field theory**

$$\boxed{\mathrm{Z} = \int_{i\infty} \mathfrak{D}W \int_{\infty} \mathfrak{D}\rho \, \exp\left(-\mathrm{F}\right)}$$

with $$\mathrm{F} = -n \ln\left[\mathrm{Q}/\mathrm{n}\right] - \tfrac{1}{N}\int d\mathbf{r} \; W\rho + \mathcal{H}_I\left[\rho\right]$$

**SCF approximation**: Saddle point integral

→ Minimize ☞ with respect to $W$ and $\rho$.

⇒ Gives same SCF equations than density functional.

and, same free energy ☞ .

# Two Approaches to the SCF Theory

## Density Functional

- Good starting point for a more detailed incorporation of **microscopic** structure (packing, local monomer correlations, etc.)
  → Adjust reference system
- Established starting point for dynamical studies (dynamic density functional theories)

## Field theoretic approach

- Range of possible underlying models is restricted (incorporating hard-core interactions is difficult) .
- Good starting point for a systematic study of **long-range** ("ultrared" ) fluctuation effects.

**Otherwise, both approaches result in equivalent field theory!**

# Summary: Molecular fields

Density functional of the type

$$\boxed{\mathsf{F}\left[\rho(\mathbf{r})\right] = -n\ \ln\left[{}^{\mathsf{Q}}\!/\!_{\mathsf{n}}\right] - \tfrac{1}{N}\int d\mathbf{r}\ W\rho + \mathcal{H}_I\left[\rho\right]}$$

Degrees of freedom: Density fields $\rho(\mathbf{r})$

Free energy functional still contains information on molecular structure (connectivity etc.)

Quantitative connection to an (almost) equivalent particle-based Edwards model

# Part II
# Molecular Field Simulations: Examples

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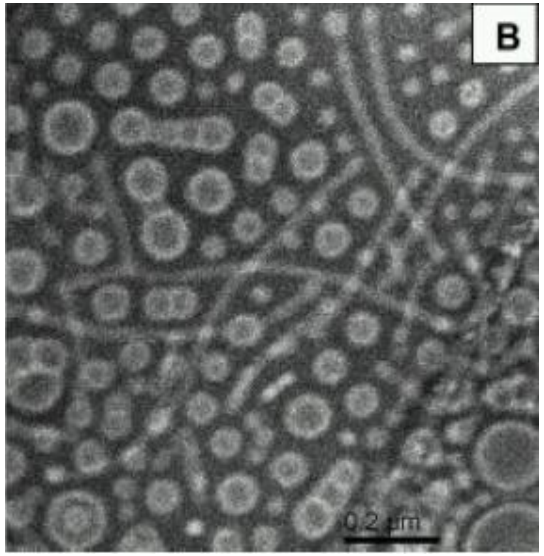
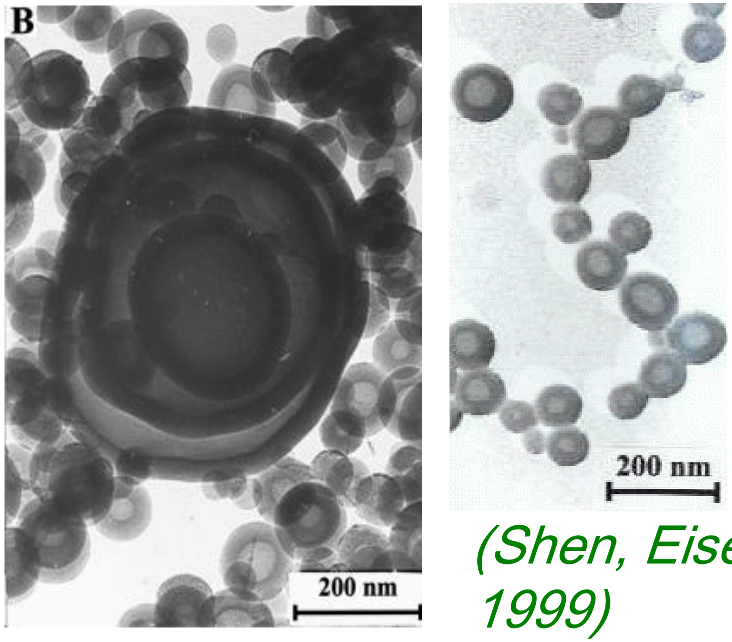
Liangshun Zhang

*(X. He, FS. Macromolecules 39, 2654 (2006) and 39, 8908 (2006),,*
*X. He, FS, Phys. Rev. Lett. 100, 137802 (2008)*
*L. Zhang, A. Sevink, FS, Macromolecules 44, 9434(2011)).*

# The problem: Copolymeric vesicles



(Y. He et al, 2006)



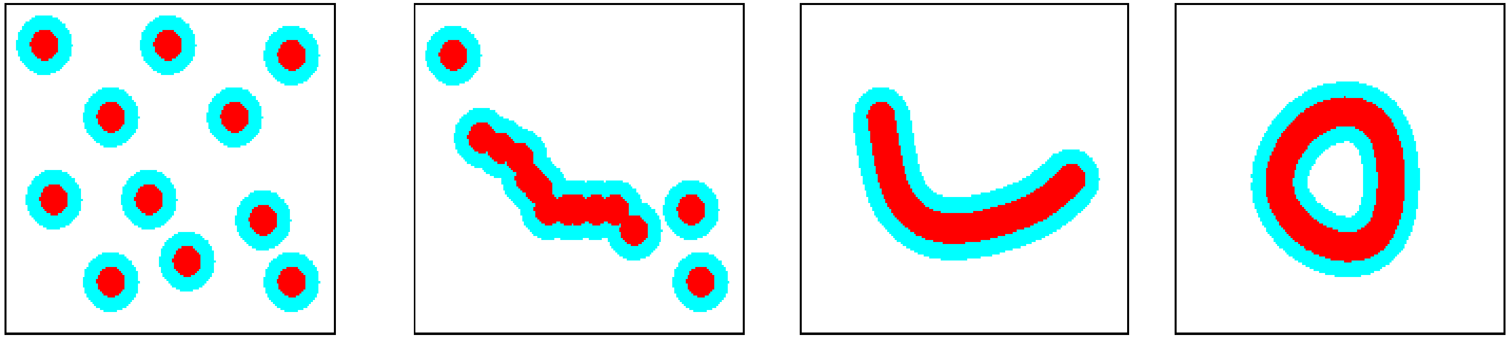
(Shen, Eisenberg, 1999)

- Structures presumably not truly at equilibrium. (nevertheless technologically interesting)
- Kinetics of vesicle self-assembly is important.

# Vesicle formation

## „Conventional“ pathway

(as observed in simulations of short chain surfactants)



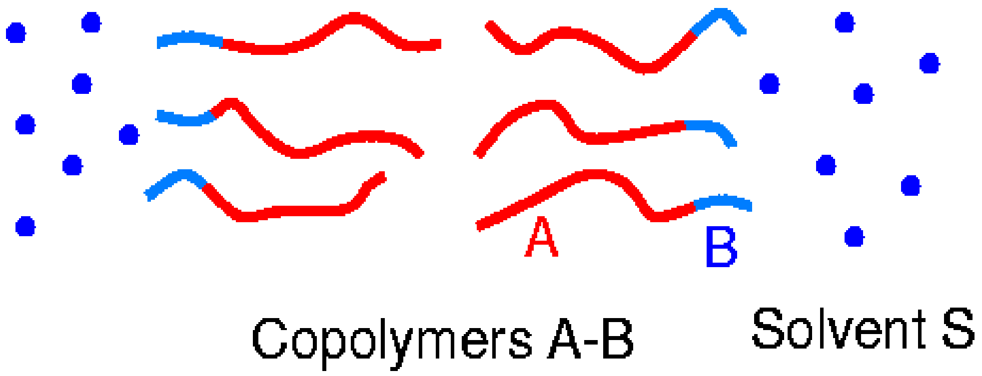
Micelle
Self-assembly

Aggregation
To Sheet

Bending

Closing
To Vesicle

# Our model system: copolymers



Molecules : Flexible (Gaussian) chains with blocks A, B

Solvent: Single, “point-like“ particles S

Interaction potential

- Compressibility term
- (In)compatibility: Flory-Huggins parameters $\chi_{AB}, \chi_{AS}, \chi_{BS}$

# Dynamic density functional theory

*(Fraaije, JCP 99, 9202 (1993); …; Maurits, Fraaije, JCP 107, 5879 (1997 ))*

## General Ansatz  (diffusive dynamics)

$$\frac{\partial \rho_j}{\partial t} = \int d\mathbf{r}' \sum_{ij} \nabla_{\mathbf{r}} \Lambda_{ij}(\mathbf{r},\mathbf{r}') \nabla_{\mathbf{r}'} \mu_j(\mathbf{r}')$$

$\Lambda_{ij}$: Onsager coefficient

$\mu_i$:  Local excess chemical potential $\mu_j = \delta F / \delta \rho_j(\mathbf{r}')$

## External Potential Dynamics *(Maurits, Fraaije, 1997)*

Rouse dynamics: $\Lambda_{ij}(r,r')$ ~ single chain correlator

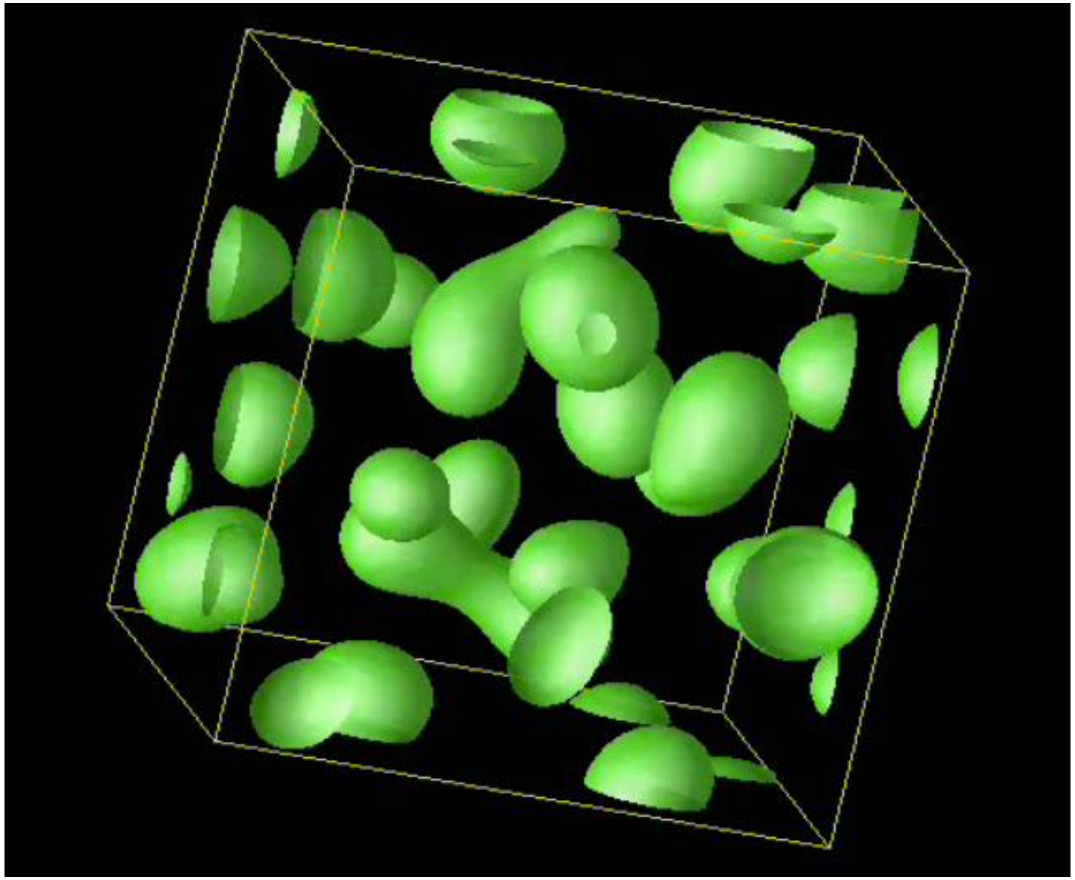
⇒ ... Dynamic equations
can be rewritten as
(approximately)

$$\frac{\partial}{\partial t} W_i = -\underset{\downarrow}{D}\,\Delta\,\mu_i$$

Diffusion constant

# Vesicle Formation Process (I)

High Copolymer volume fraction (23 %)



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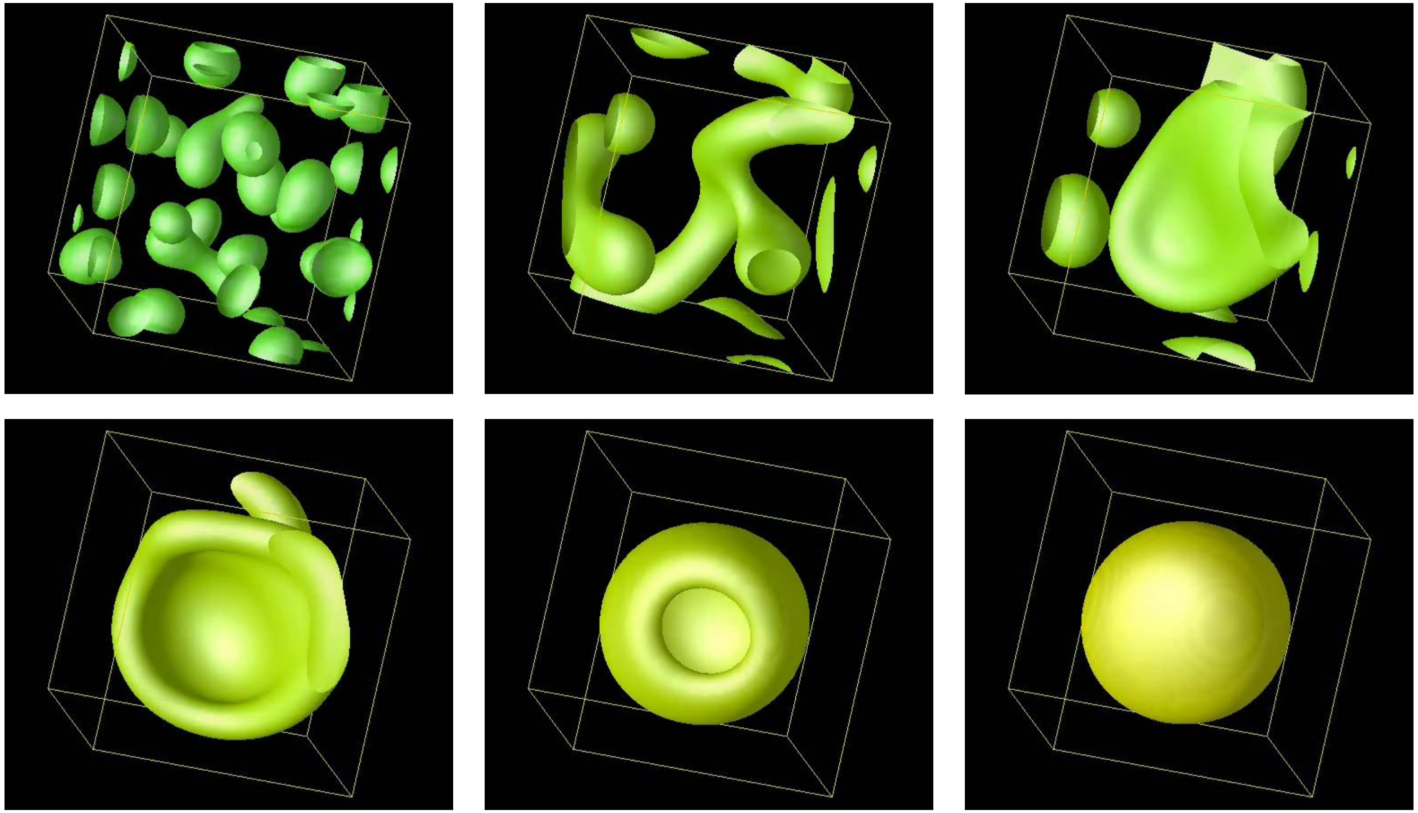
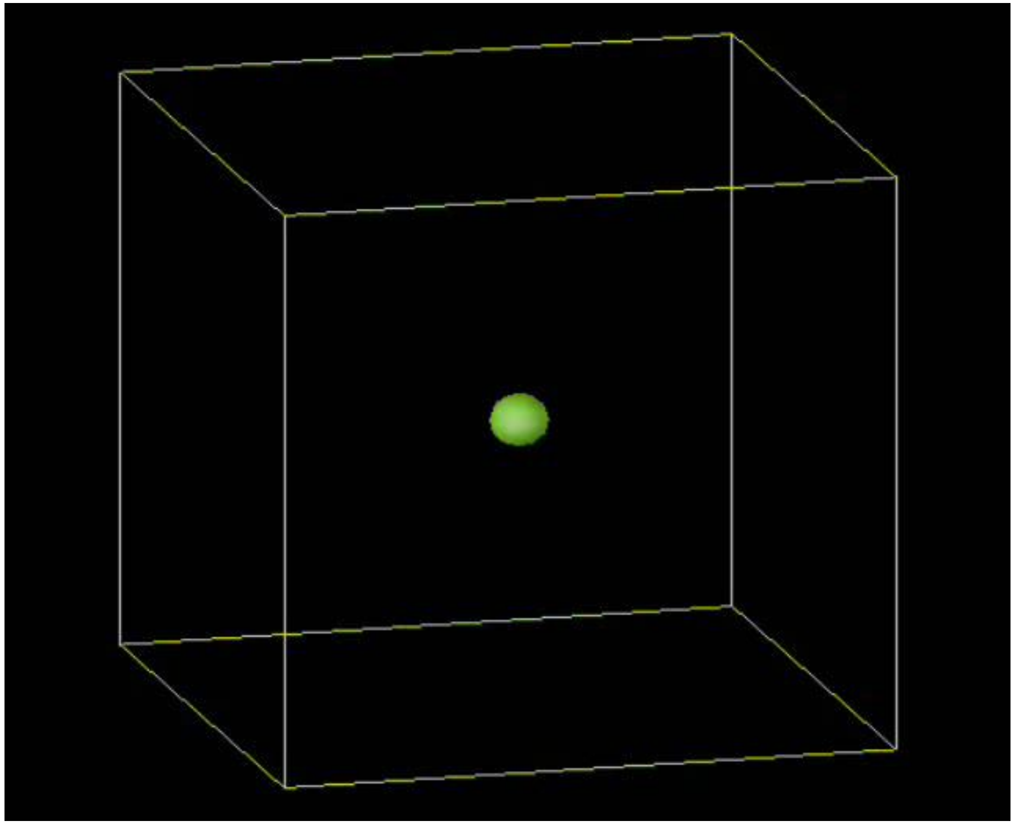
High Copolymer volume fraction (23 %)



⇒ Recover Conventional Pathway

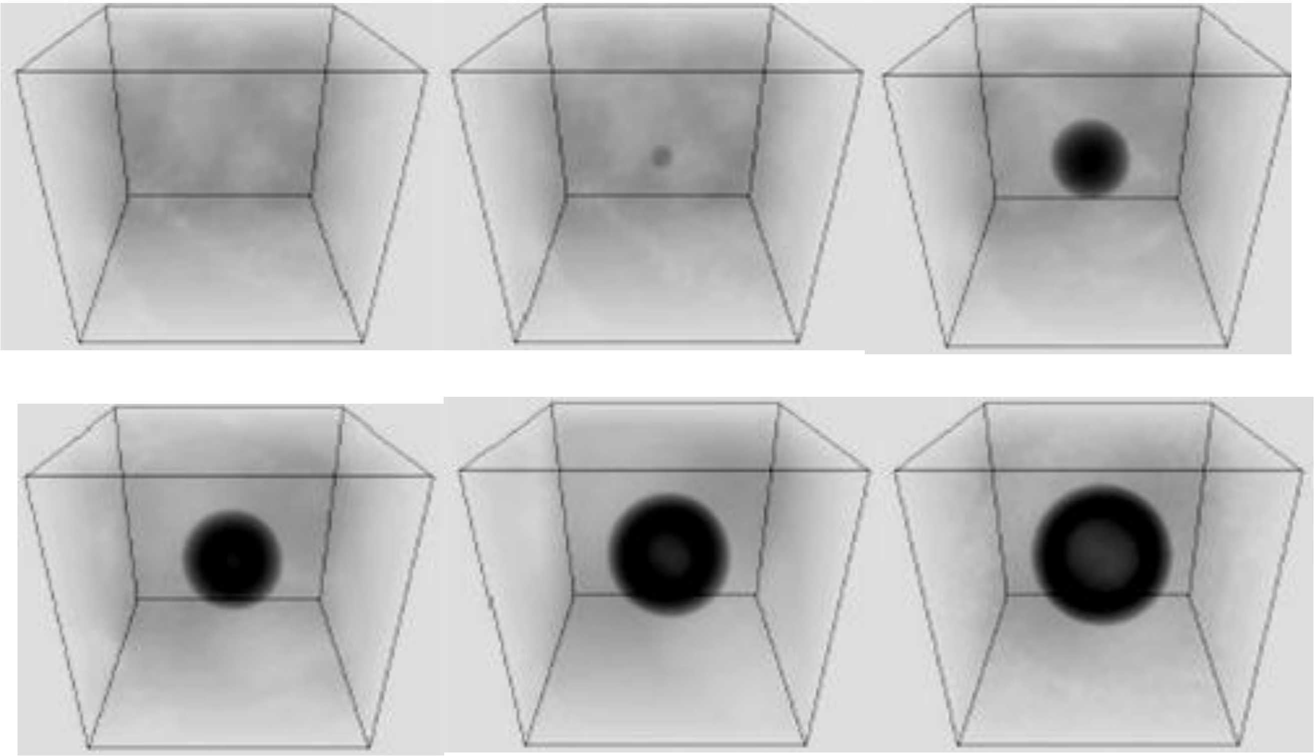
# Vesicle Formation Process (II)

Lower Copolymer volume fraction (10 %)



# Vesicle Formation Process (II)

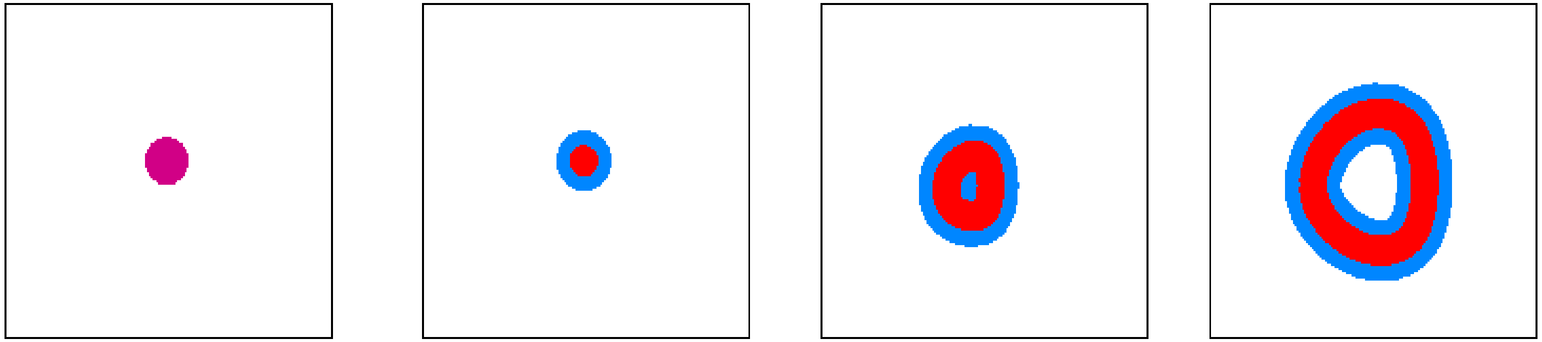
Lower Copolymer volume fraction (10 %)



⇒ New Pathway: Nucleation and Growth

# A New Pathway of Vesicle Formation

For copolymeric vesicles, at low copolymer density



Droplet
Nucleation

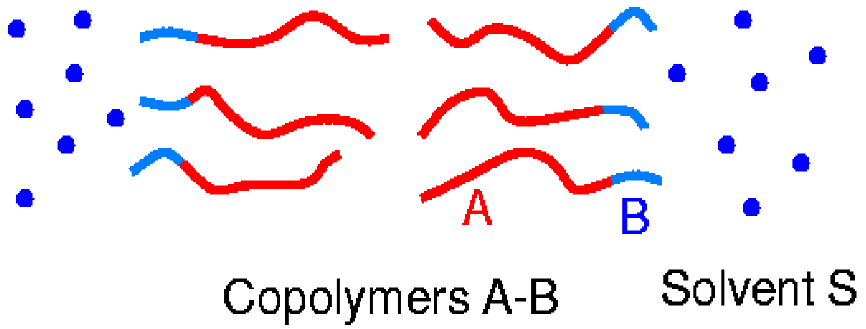
Micelle

Semivesicle

Vesicle

*( X. He, F.S., Macromolecules 06).*

# Variation of Parameters



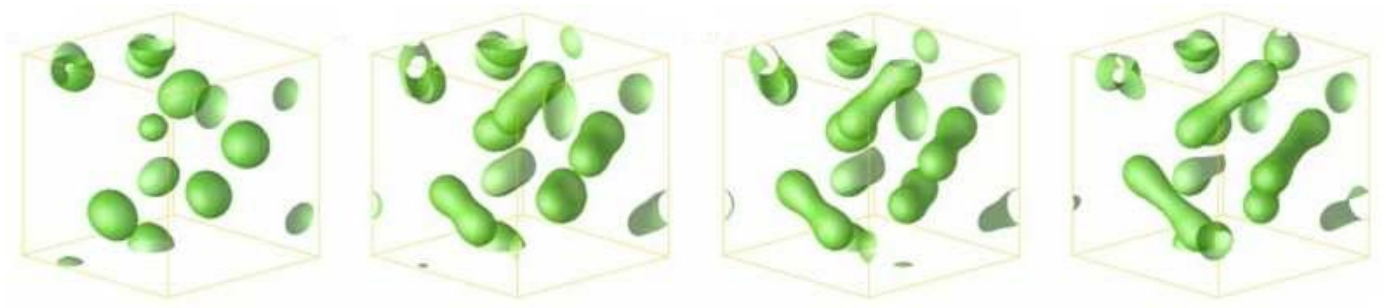
Vary systematically

- Copolymer concentration $\phi_p$
- Hydrophilicity of B-block $\chi_{BS}$

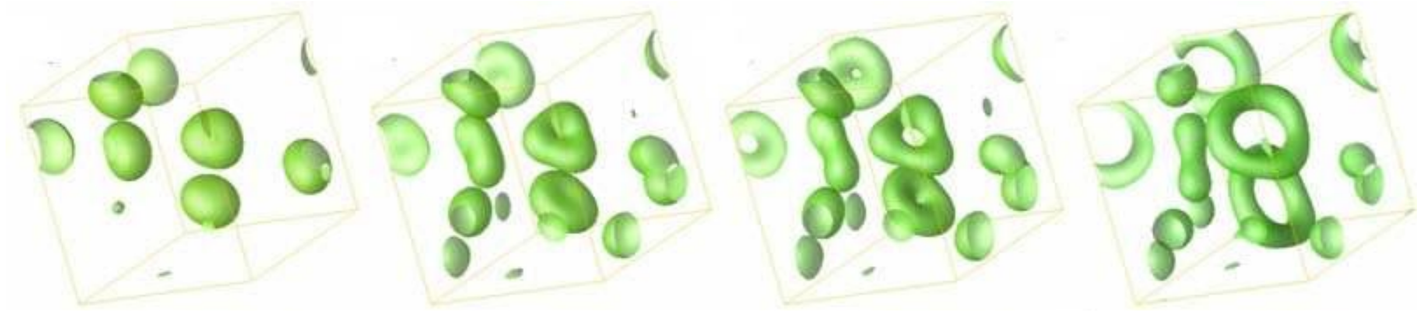
# Other possible Structures

Depending on parameters, one gets …

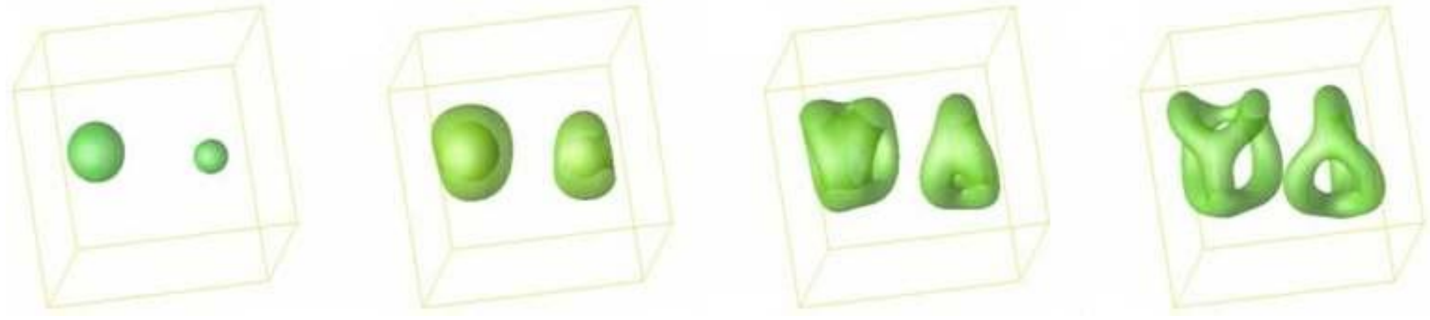
… Rods



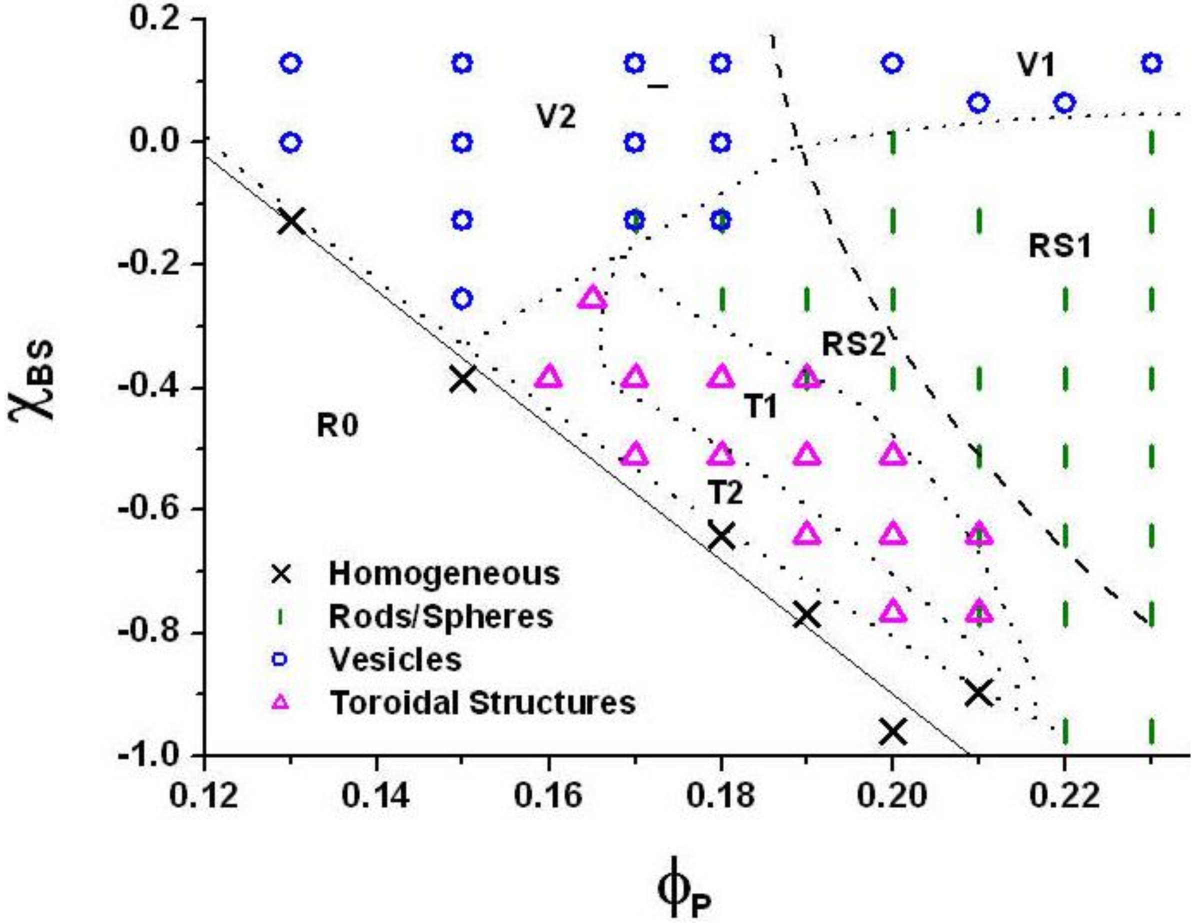
… Rings



…Toroidal structures

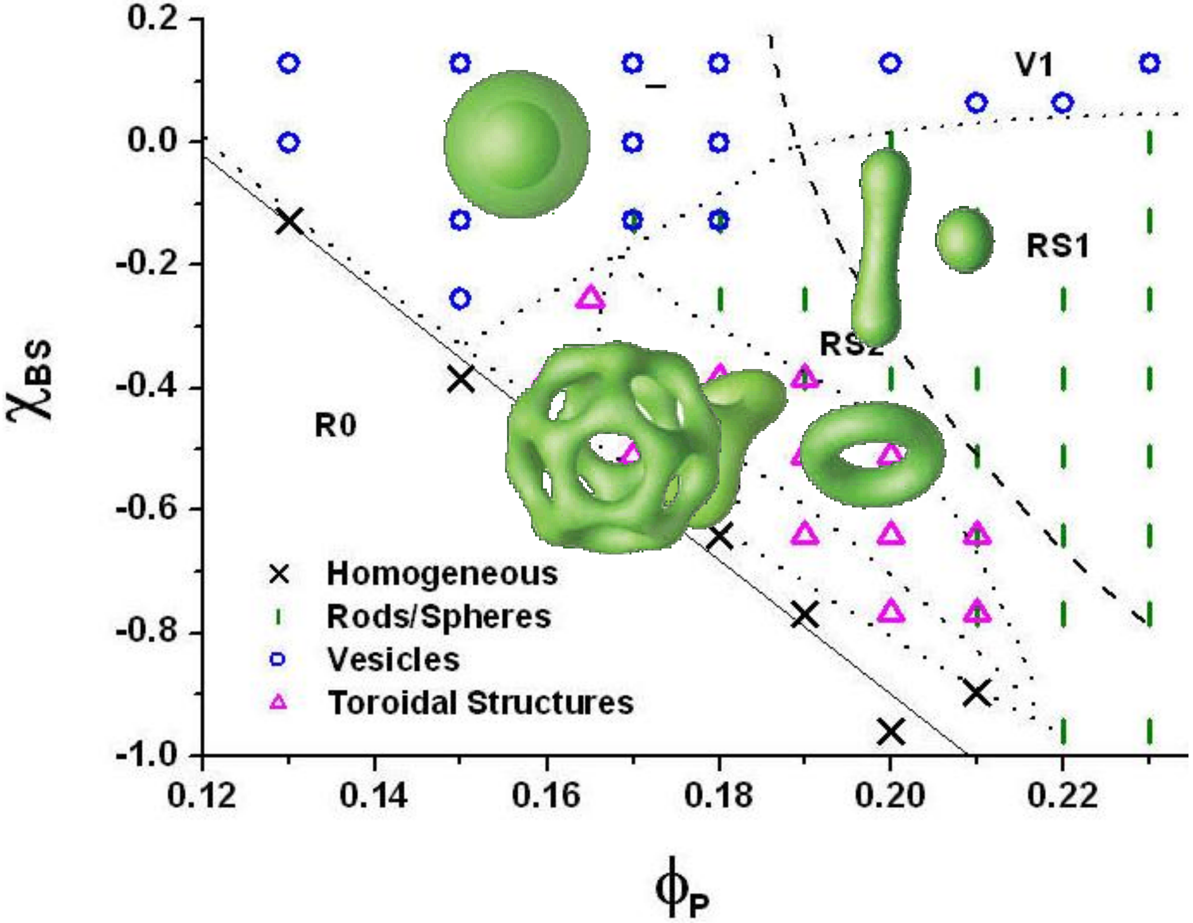


# "Phase Diagram"



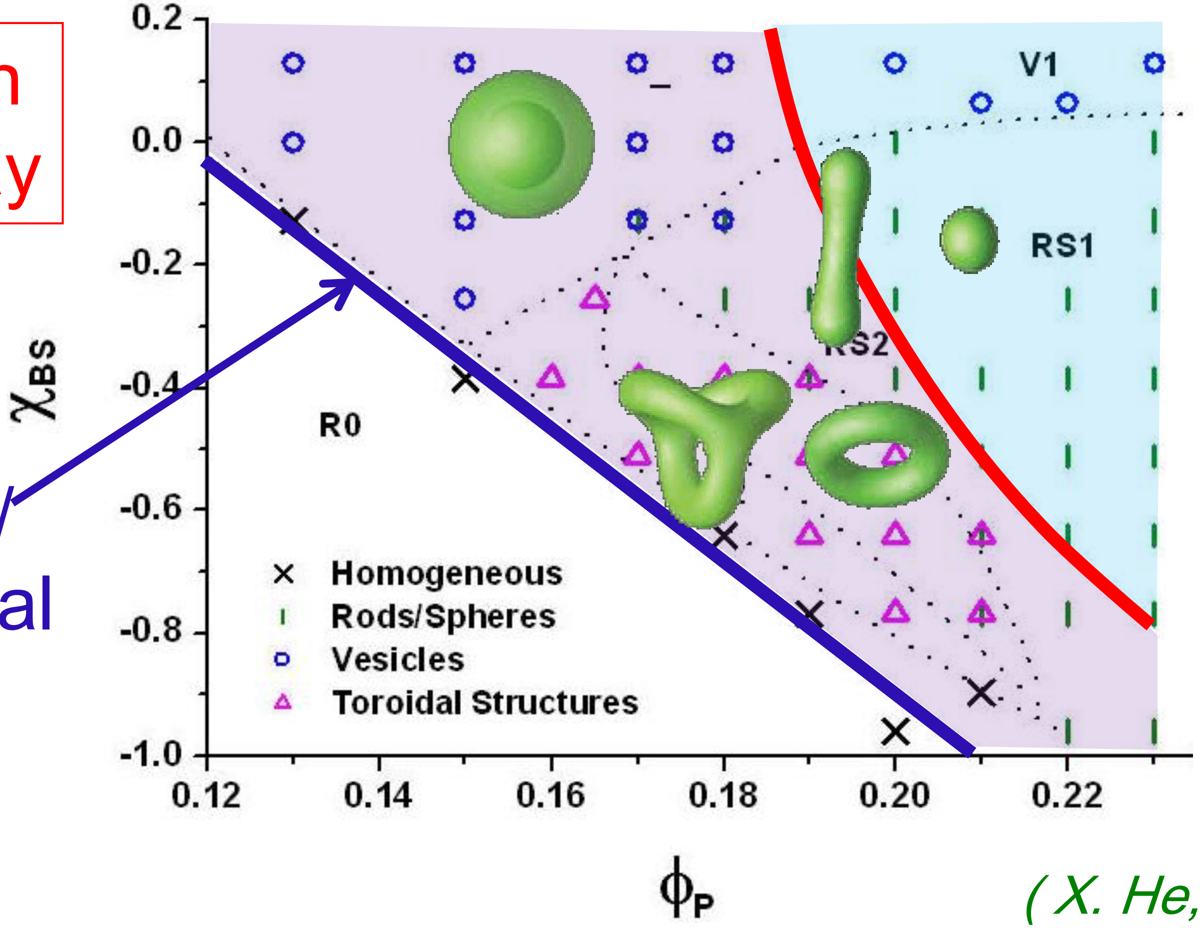
# "Phase Diagram"

## Final Structures



# "Phase Diagram"

## Dynamics of structure formation



Growth pathway

Coalescence pathway

CMC / Spinodal

*( X. He, FS, PRL 08).*

# Next step: Introduce hydrodynamics

*(L. Zhang, A. Sevink, FS, Macromolecules 44, 9434(2011)).*

Our Ansatz: Couple

**Convection-diffusion equation in flow *v*(r)**

$$\frac{\partial \rho_j}{\partial t} + \underbrace{\nabla\left(\mathbf{v}\rho_j\right)}_{\text{(convection)}} = M \int \mathrm{d}\mathbf{r}' \sum_{ij} \nabla_{\mathbf{r}} \Lambda_{ij}\left(\mathbf{r},\mathbf{r}'\right) \nabla_{\mathbf{r}'} \mu_j\left(\mathbf{r}'\right)$$

to **Navier Stokes Equations**

$$\rho_m\left(\partial_t \mathbf{v} + \mathbf{v}\left(\nabla \mathbf{v}\right)\right) = \nabla\left(\boldsymbol{\sigma} - \mathbf{P}\right) - \underbrace{\sum_i \rho_i \nabla \mu_i}_{\text{(thermodynamic force)}}$$

# Simulation method

*(L. Zhang, A. Sevink, FS, Macromolecules 44, 9434(2011)).*

## Convection-diffusion equation

$$\frac{\partial \rho_j}{\partial t} + \nabla\left(\mathbf{v}\rho_j\right) = M \int d\mathbf{r}' \sum_{ij} \nabla_{\mathbf{r}} \Lambda_{ij}(\mathbf{r},\mathbf{r}') \nabla_{\mathbf{r}'} \mu_j(\mathbf{r}')$$

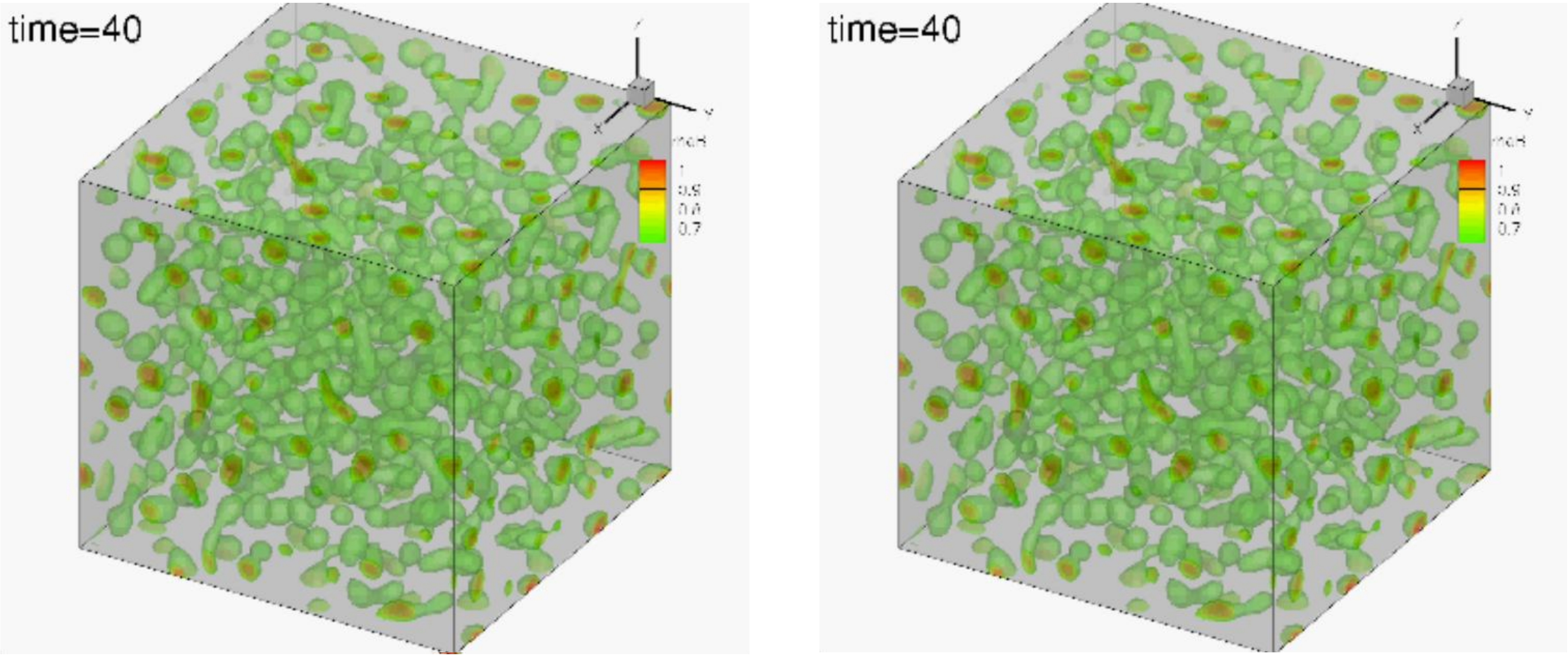
→ **Finite Difference Scheme** as before

## Navier Stokes Equations

$$\rho_m\left(\partial_t \mathbf{v} + \mathbf{v}\left(\nabla \mathbf{v}\right)\right) = \nabla\left(\boldsymbol{\sigma} - \mathbf{P}\right) - \sum_i \rho_i \nabla \mu_i$$

→ **Lattice-Boltzmann** with force coupling
(following Dünweg et al.)

# Results: Dynamics of vesicle formation

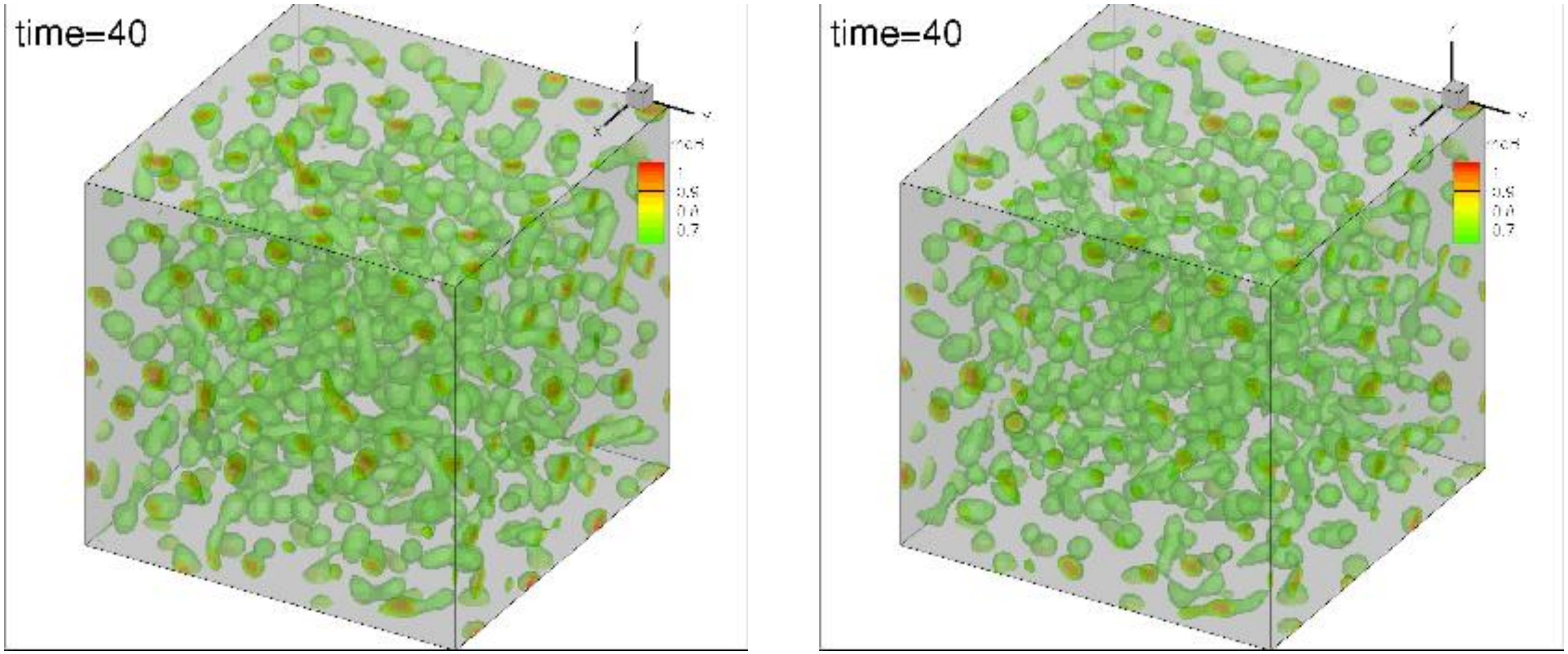


With hydrodynamics

Without hydrodynamics

*(Time unit: ~ 4$\mu$s ; Total time: ~ 200 ms)*

# Results: Dynamics of vesicle formation



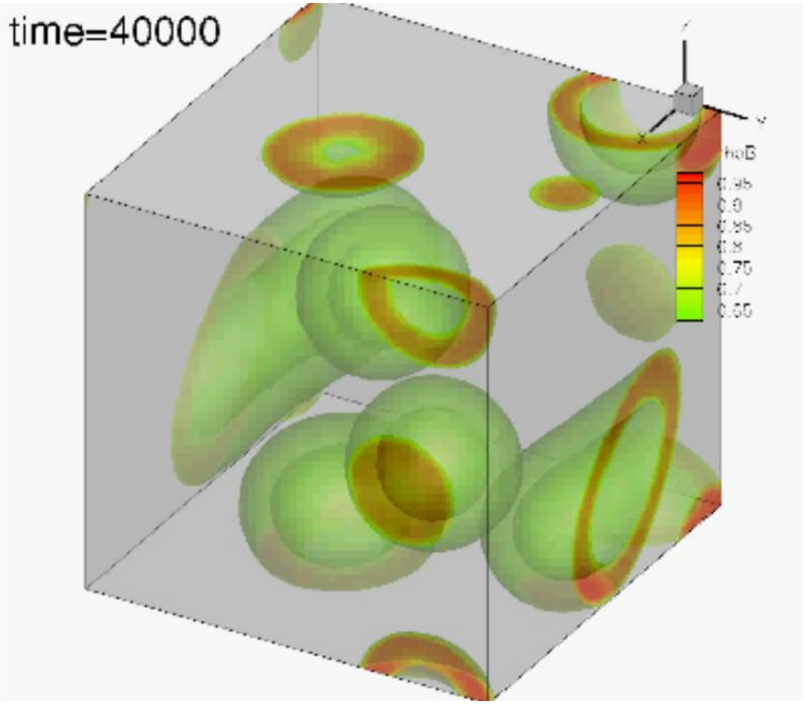
With hydrodynamics

Without hydrodynamics

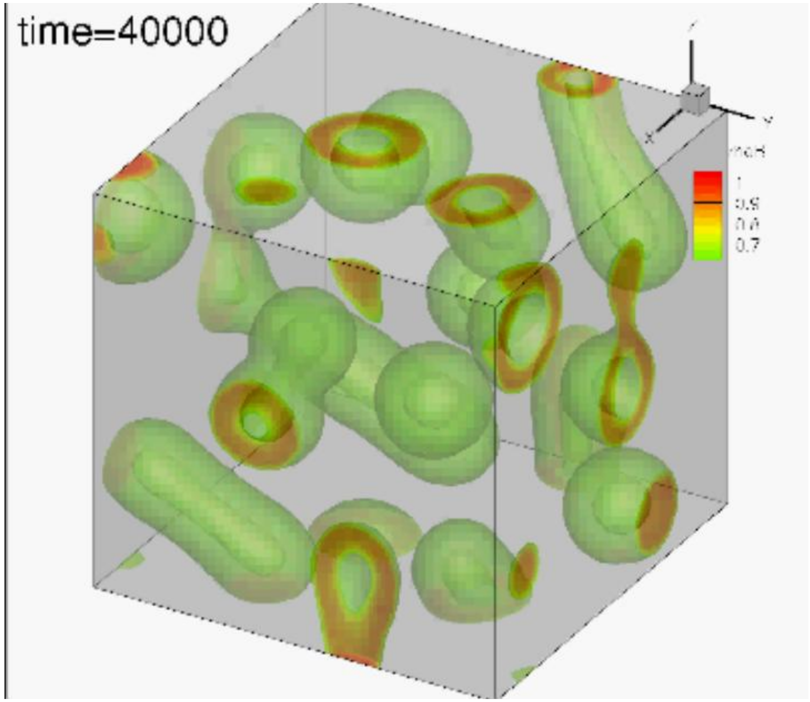
*(Time unit: ~ 4$\mu$s ; Total time: ~ 200 ms)*

# Results: Dynamics of vesicle formation

With hydrodynamics



Without hydrodynamics

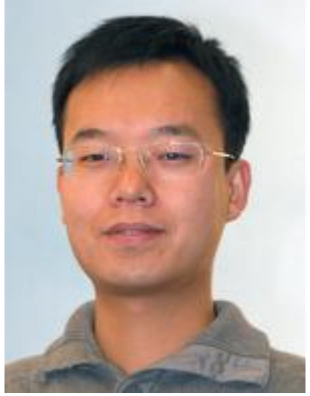


**⇒ Pathways similar with hydrodynamics**

**⇒ Hydrodynamics speed things up**

# Part III

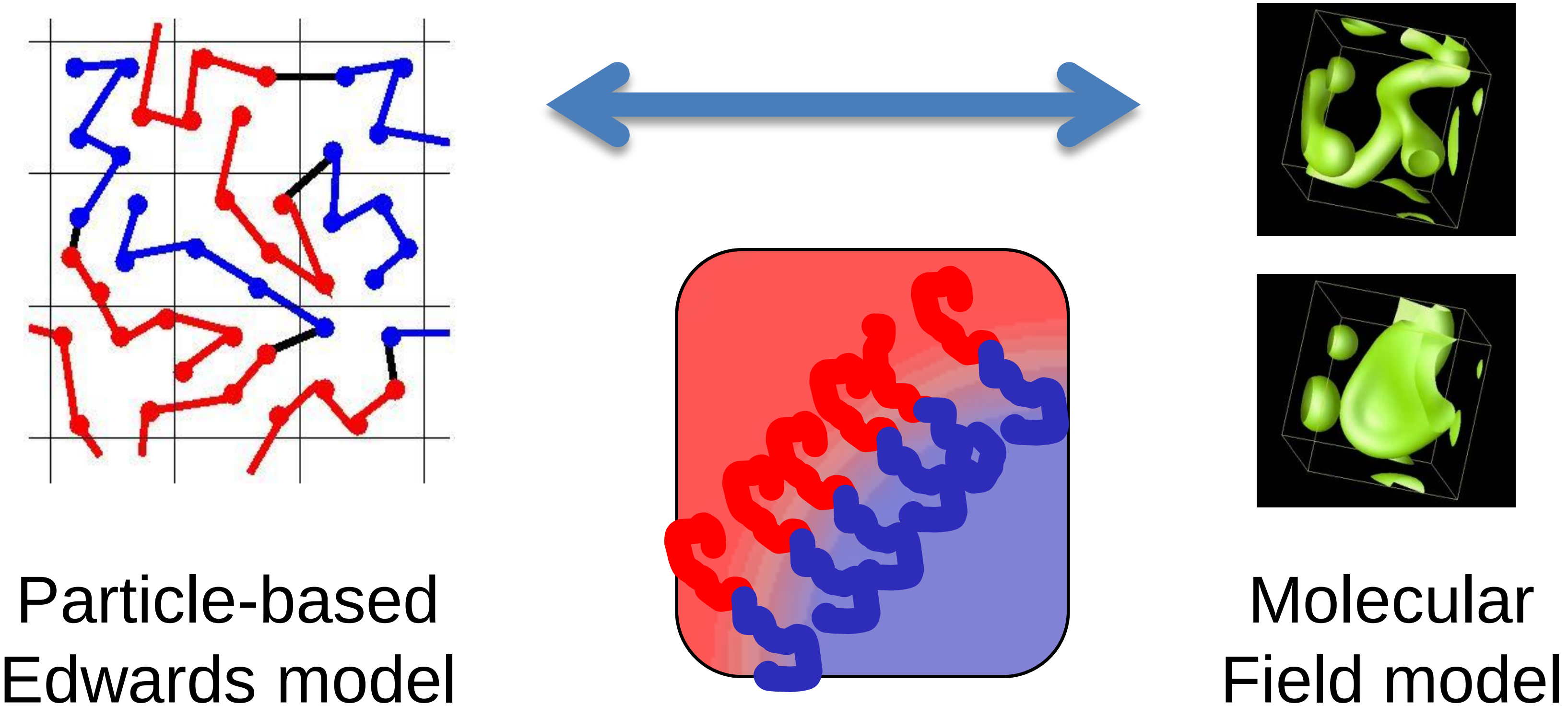
# Adaptive Multiscale Scheme Linking Particles and Fields



Shuanhu Qi

*(Work in progress).*

# The vision



Particle-based
Edwards model

Molecular
Field model

**Adaptive switching
between equivalent representations**

# Idea: Space-dependent 'identity' switches

Starting point:

$$\boxed{Z = \frac{1}{n!}\prod_{\alpha=1}^{n}\left[\rho_0 \int \mathcal{D}\mathbf{R}_\alpha \; e^{-\mathcal{H}_0[\mathbf{R}_\alpha]}\right] e^{-\mathcal{H}_I[\hat{\rho}]}}$$

- Define "local chemical potential" $\Delta\mu(\mathbf{R}^0)$ acting on first bead.
- Insert identity $\mathbf{1}_\alpha = \sum_{\tau_\alpha=0}^{1} \exp\left(-\Delta\mu\left(\mathbf{R}_\alpha^0\right)\tau_\alpha - v\left(\mathbf{R}_\alpha^0\right)\right)$

  with $v\left(\mathbf{r}\right) = \ln\left(e^{-\Delta\mu(\mathbf{r})} + 1\right)$

  → Additional degree of freedom $\tau_\alpha$

  $\tau_\alpha=0$: type f ('field')
  $\tau_\alpha=1$: type p ('particle')
- Transform polymers of type f to molecular fields

**⇒ Mixed semi-grandcanonical particle/field scheme**

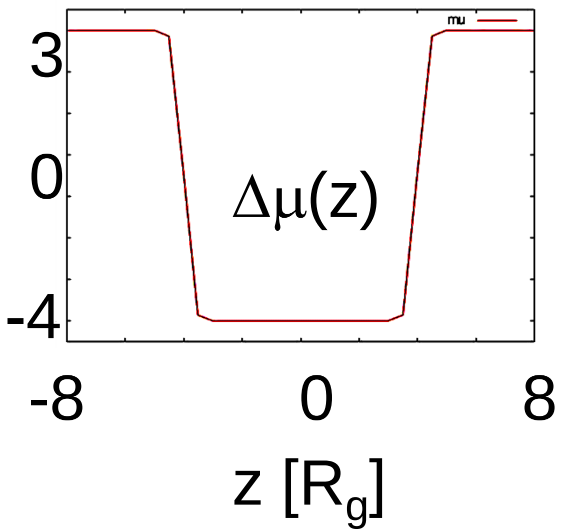
# Simulation method

- "Particle" chains: Monte Carlo monomer moves
- "Field" chains: Two implementations:
  - External potential dynamics
  - Monte Carlo moves (fluctuating densities)
- Identity switches:

  Configuration-bias Monte Carlo
  (Rosenbluth sampling)

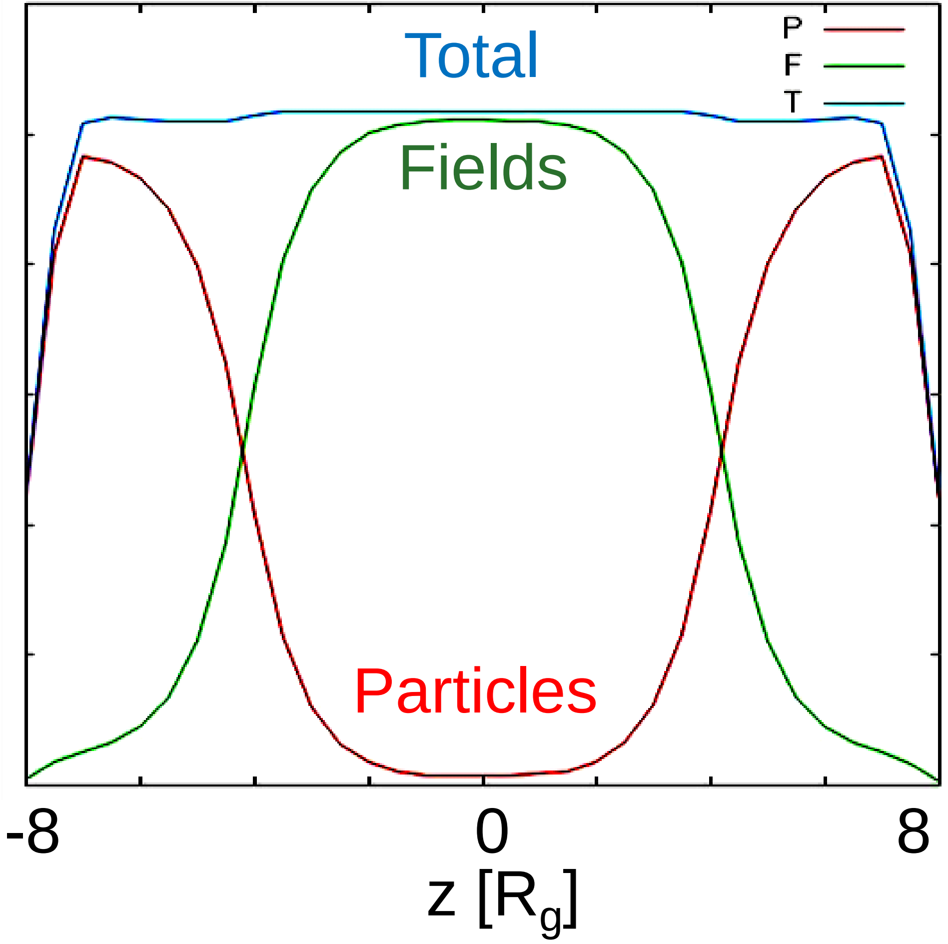
# First test: Homopolymers in thin films

Chemical potential difference



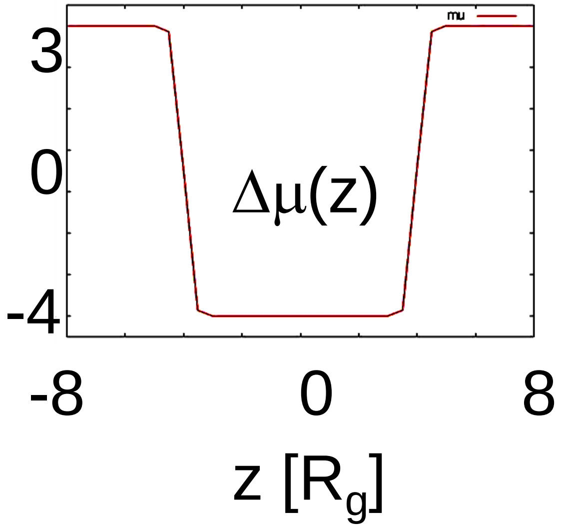
(10.000 chains, N=20
V= (8*8*16) $R_g^3$ )

Density profiles



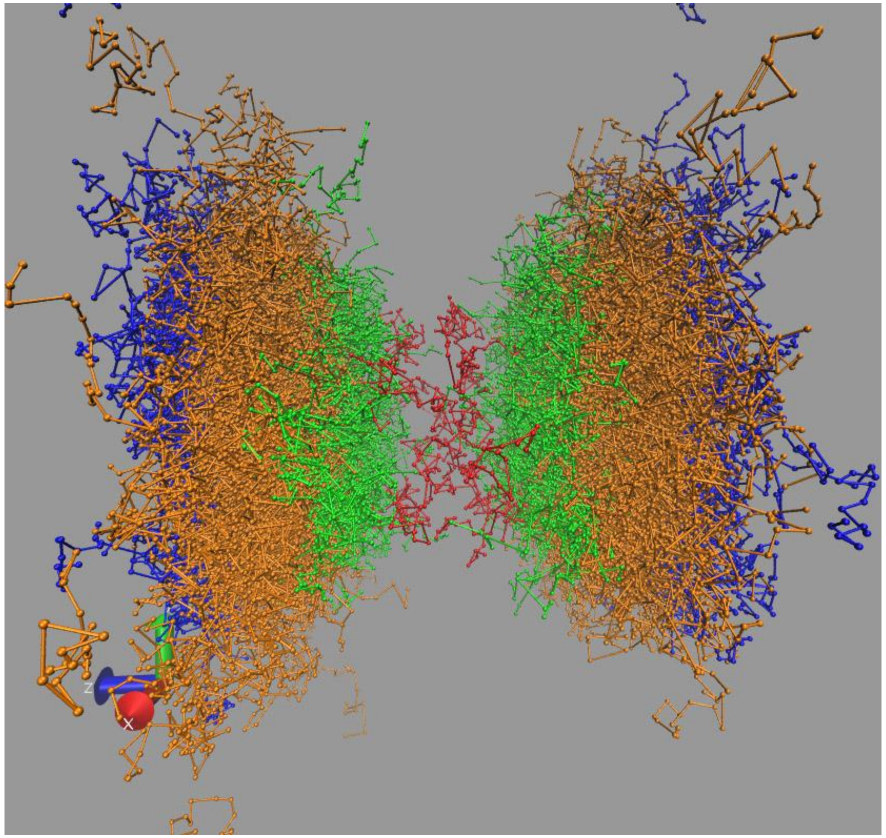
# First test: Homopolymers in thin films

Chemical potential difference



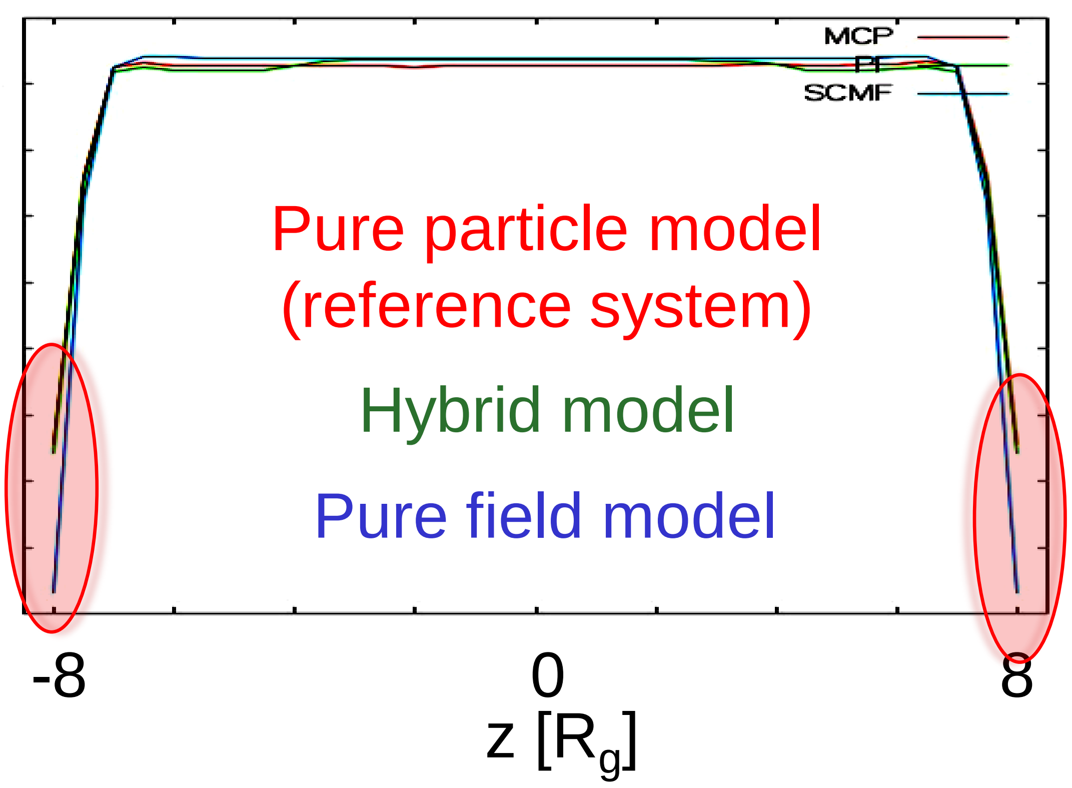
(10.000 chains, N=20
V= (8*8*16) $R_g^3$ )

Snapshot (particle chains only)



# Comparison with "pure" models

## Total density profiles



Pure particle model
(reference system)

Hybrid model

Pure field model

**⇒ Hybrid model improves on the pure field model**

# Conclusions

- Molecular field models (density functional theories) are at the interface between particle-based molecular models and continuum models, because they still keep information on molecular structure and architecture.

- Molecular field simulations can give insight into phenomena on mesoscopic scales.

- Our hybrid particle-field scheme may provide a convenient link between particle- and field-based models for soft matter in the future.

# Acknowledgments

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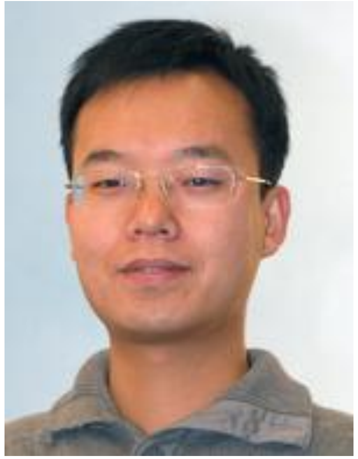

Shuanhu Qi
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# Starting Point: "Standard Model" (Recall)

## For simplicity: Single component copolymer melt

Melt of AB diblock copolymers $\alpha$ with A-monomer fraction $f$

**Hamiltonian**: $\mathcal{H} = \sum_{\text{copolymers } \alpha} \mathcal{H}_0[\mathbf{R}_\alpha] + \mathcal{H}_I[\hat{\rho}_A, \hat{\rho}_B]$

- Gaussian chains: $\mathcal{H}_0[\mathbf{R}(s)] = \frac{3}{2b^2} \int_0^N \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}s}\right)^2$
- Interaction energy: $\mathcal{H}_\mathrm{I} = \rho_0 \chi \int \mathrm{d}\mathbf{r}\; \hat{\Phi}_\mathrm{A} \hat{\Phi}_B$ with $\hat{\Phi}_j = \hat{\rho}_j / \rho_0$
- Incompressibility constraint: $\hat{\rho}_A + \hat{\rho}_B \equiv \rho_0$

Monomer densities:

$$\hat{\rho}_A(\mathbf{r}) = \sum_\alpha \int_0^{fN} \mathrm{d}s\; \delta\big(\mathbf{r} - \mathbf{R}_\alpha(s)\big)$$

$$\hat{\rho}_B(\mathbf{r}) = \sum_\alpha \int_{fN}^{N} \mathrm{d}s\; \delta\big(\mathbf{r} - \mathbf{R}_\alpha(s)\big)$$

# SCF Equations  in a Nutshell II

## Independent copolymer chains in the field $W_{A/B}(\mathbf{r})$

Define segment dependent field:

$$W(\mathbf{r},s)=\begin{cases} W_A(\mathbf{r}): & s< fN \\ W_B(\mathbf{r}): & s> fN \end{cases}$$

⇒ Single chain partition function

$$\mathcal{Q}=\rho_0\int \mathfrak{D}\mathbf{R}\ e^{-\mathcal{H}_0[\mathbf{R}]-\frac{1}{N}\int_0^N ds\ W(\mathbf{R}(s),s)}=\mathcal{Q}[W_A,W_B]$$

Monomer density distribution:

$$\left\langle \hat{\rho}_{A/B}(\mathbf{r})\right\rangle=-n\ N\,\frac{\delta\ \ln\mathcal{Q}[W_A,W_B]}{\delta\ W_{A/B}(\mathbf{r})}$$

# SCF Equations in a Nutshell I

**Basic idea (intuitive picture)**:

Chains are treated as independent paths in an average (self-consistent) field created by the other chains.

$$\hat{\rho}_A(\mathbf{r}) \rightarrow \rho_A(\mathbf{r}) = \left\langle \hat{\rho}_A(\mathbf{r}) \right\rangle$$

$$\hat{\rho}_B(\mathbf{r}) \rightarrow \rho_B(\mathbf{r}) = \left\langle \hat{\rho}_B(\mathbf{r}) \right\rangle$$

$$\mathcal{H}_I[\hat{\rho}_A, \hat{\rho}_B] \rightarrow \mathcal{H}_I[\rho_A, \rho_B]$$

Self-consistent fields: $\frac{1}{N} W_{A/B}(\mathbf{r}) = \frac{\delta \mathcal{H}_I}{\delta \rho_{A/B}(\mathbf{r})} - \frac{\xi(\mathbf{r})}{N}$

(factors 1/N
for convenience)

Flory-Huggins interactions

Incompressibility

# Practical Implementation I

## **Tasks** along the way

**?** ❖ Evaluate single-chain partition function ✈
of chains in the external fields $W_{A/B}$

**?** ❖ Evaluate average densities $\rho_{A/B}(r)$

√ ❖ Evaluate fields $W_j$: $W_{A/B}(\mathbf{r}) = N \frac{\delta \mathcal{H}_I}{\delta \rho_{A/B}(\mathbf{r})} - \xi = \chi N \Phi_{B/A} - \xi$

## **Trick**: Feynman-Kac formula

❖ Define **propagator** $G(\mathbf{r}_0,\mathbf{r}_1,s)$: Restricted partition function for chains of length $s$ with end monomers at $\mathbf{r}_i$

❖ $G(\mathbf{r}_0,\mathbf{r}_1, s)$ satisfies diffusion equation → can be evaluated.

❖ Using $G(\mathbf{r}_0,\mathbf{r}_1)$, calculate ✈ and densities $\rho_{A/B}(\mathbf{r})$.

# Practical Implementation II

## More specifically

- Define partial partition functions:
  $q(\mathbf{r},s) = \int d\mathbf{r}_0\, G(\mathbf{r}_0,\mathbf{r},s)$ and $q^{+}(\mathbf{r},s) = \int d\mathbf{r}_1\, G(\mathbf{r},\mathbf{r}_1,N-s)$
- Diffusion equations

$$\partial_s q(\mathbf{r},s) = \left[\tfrac{b^2}{6}\Delta - \tfrac{1}{N} W(\mathbf{r},s)\right] q(\mathbf{r},s)$$

$$\partial_s q^{+}(\mathbf{r},s) = \left[\tfrac{b^2}{6}\Delta - \tfrac{1}{N} W(\mathbf{r},N-s)\right] q^{+}(\mathbf{r},s)$$

with $q(\mathbf{r},0) = q^{+}(\mathbf{r},0) = 1$

⇒ Full partition function: ✈ $= \int d\mathbf{r}\, q(\mathbf{r},N) = \int d\mathbf{r}\, q^{+}(\mathbf{r},N)$

Densities: $$\langle \hat{\rho}_j(\mathbf{r}) \rangle = \frac{n}{\mathrm{Q}} \int_0^N ds\, q(\mathbf{r},s)\, q^{+}(\mathbf{r},N-s)\, \theta_j(s)$$

# Practical Implementation III

## Structure of a typical (simple) SCF program

Starting from given density profiles and guess for $\xi$

1) Calculate fields $W_{A/B}(\mathbf{r}) = \chi N \; \Phi_{B/A} - \xi$
2) Solve diffusion equations for $q(\mathbf{r},s)$, $q^{+}(\mathbf{r},s)$
3) Calculate single chain partition function ✈
4) Calculate 'new' density profiles
5) Check whether SCF equations are fulfilled within the desired accuracy.

If No: New guess for densities and $\xi$; go back to 1)

If Yes: Stop – You made it ☺

# Numerical Issues

- **Efficient solution of the diffusion equation**
  - Direct real space integration schemes (Crank-Nicholson, Dufort-Frankel,…)
  - Pseudo-spectral split operator scheme (mixed Fourier space/real space scheme)
  - Full solution in Fourier space
- **Iterative solution of SCF equations**
  - Direct iteration, mix old and new densities with factor $\lambda$
  - Somewhat more refined: Anderson mixing
  - Newton Raphson method  (requires Jacobians)
  - Broyden method

# Derivation II: Field-Theoretic Approach

Analysis of saddle point approximation:

$$\boxed{Z = \int_{i\infty} \mathfrak{D}W_A\, \mathfrak{D}W_B\, \mathfrak{D}\xi \int_{\infty} \mathfrak{D}\rho_A\, \mathfrak{D}\rho_B\, \exp(-F)}$$

Rewrite

$$F = C\left\{\chi N \int d\mathbf{r}\, \Phi_A \Phi_B - \sum_j \int d\mathbf{r}\, W_j\, \Phi_j - \int d\mathbf{r}\, \xi\, (\Phi_A + \Phi_B - 1) - V \ln\left[Q/n\right]\right\}$$

with $C = \frac{\rho_0}{N}$: Ginzburg parameter

⇒ Saddle point approximation is good, if **$C$** is large.

# Dynamic Density Functional Theory

## Diffusive dynamics in external flow *v(r)*

$$\frac{\partial \rho_j}{\partial t} + \nabla\left(\mathbf{v}\rho_j\right) = \int d\mathbf{r}' \sum_{ij} \nabla_{\mathbf{r}} \Lambda_{ij}\left(\mathbf{r},\mathbf{r}'\right) \nabla_{\mathbf{r}'} \frac{\delta \mathrm{F}}{\delta \rho_{\mathrm{j}}\left(\mathbf{r}'\right)} + \eta_i\left(\mathbf{r},t\right)$$

$\Lambda_{ij}(\mathbf{r},\mathbf{r}')$: Generalized mobility (kinetic Onsager coefficient)

$\eta_i(\mathbf{r},t)$: Gaussian white noise ( $\langle\eta_i(\mathbf{r},t)\rangle = 0$ )

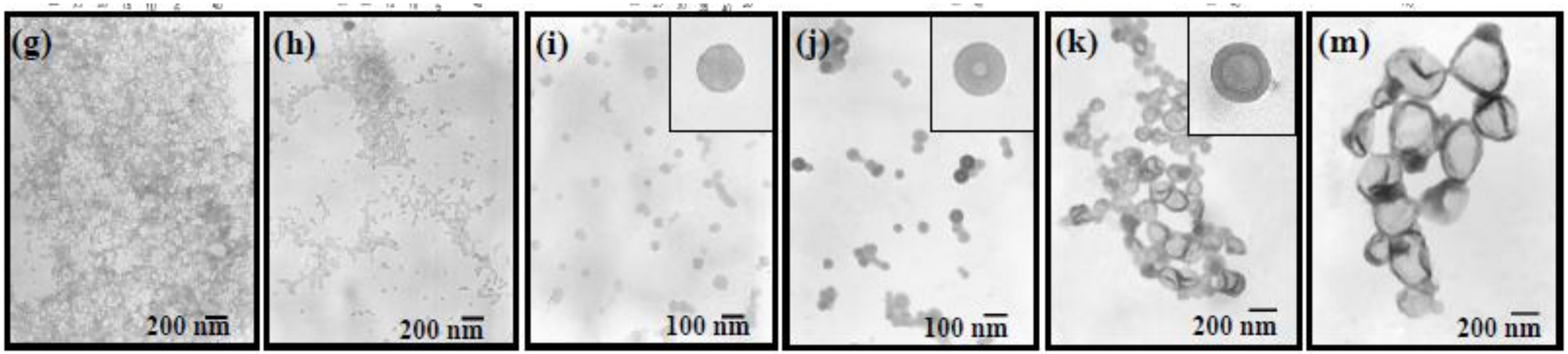
- Mean-field dynamics: $\eta_i(\mathbf{r},t) \equiv 0$
- Fluctuating dynamics: 'Fluctuation Dissipation Theorem'

$$\left\langle \eta_i\left(\mathbf{r},t\right)\ \eta_i\left(\mathbf{r}',t'\right)\right\rangle = -2\ \delta\left(t-t'\right)\ \nabla_{\mathbf{r}} \Lambda_{ij}\left(\mathbf{r},\mathbf{r}'\right) \nabla_{\mathbf{r}'}$$

→ Ensures distribution $P[\rho] \sim \exp(-☞[\rho])$ at equilibrium.

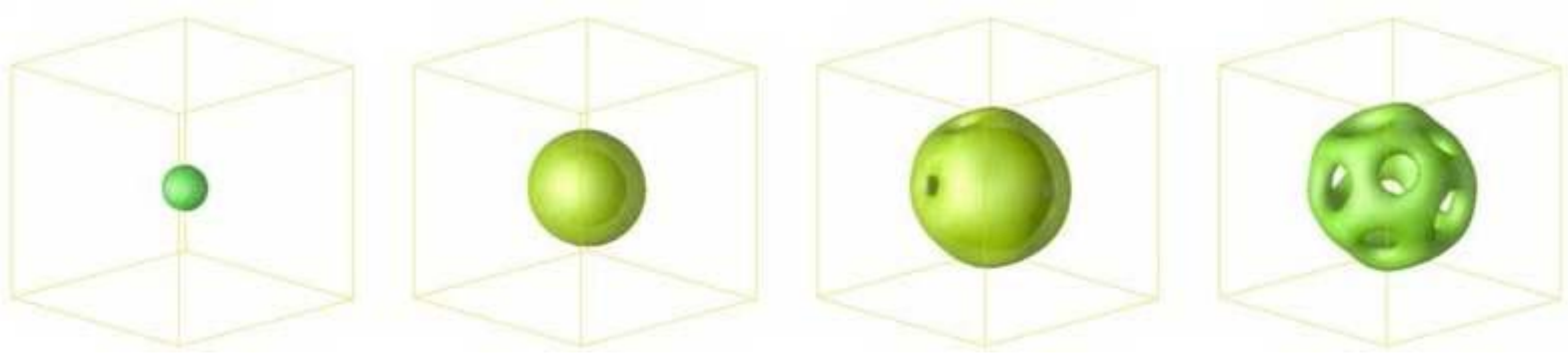
# Experimental Example

(Han,Yu,Du,Wei, JACS 2010
ABA amphiphilic triblocks)



# When do complex micelles form?

Consider formation process of cage micelles



⇝ Involves <u>unperturbed growth</u> over long time period

Requirements:

- ➢ Growth pathway
- ➢ Little interaction with other nuclei
  - → Parameter region close to CMC/Spinodal

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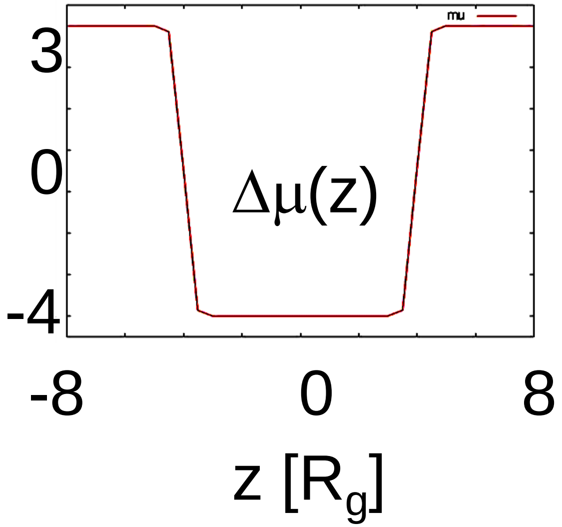

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