Speeding-up collective processes in particle simulations by concurrent coupling to a continuum description

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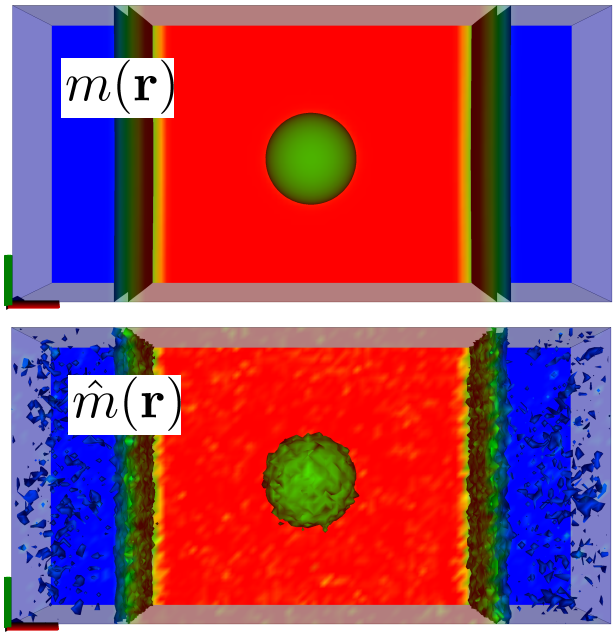


outline:

- minimal, soft, coarse-grained model
- particle models *vs* continuum models

  a) **heterogeneous multiscale modeling** (HMM)

  ➡ droplet evaporation (Lifshitz-Slyozov)

  with ***Kostas Ch. Daoulas***

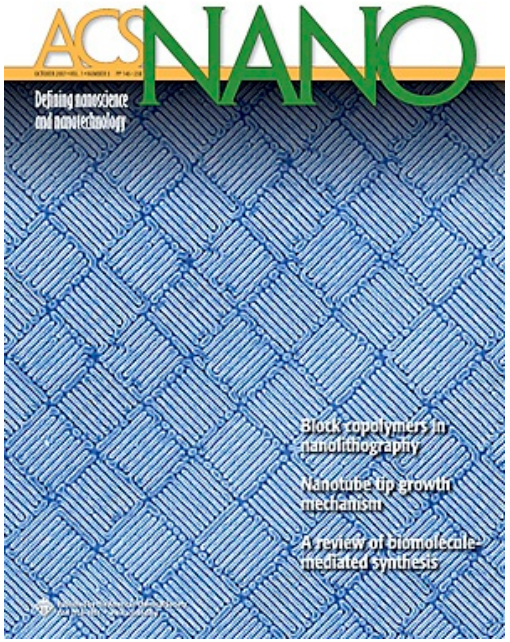
  b) **on-the-fly string method**

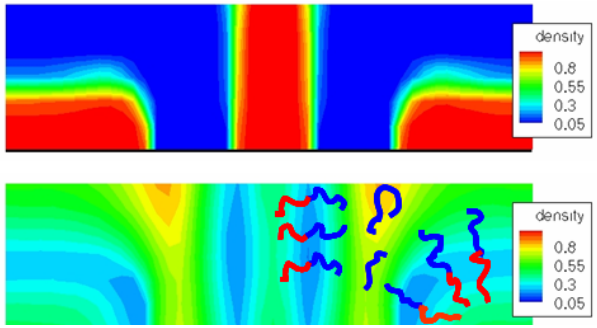
  ➡ stalk formation between apposed bilayers

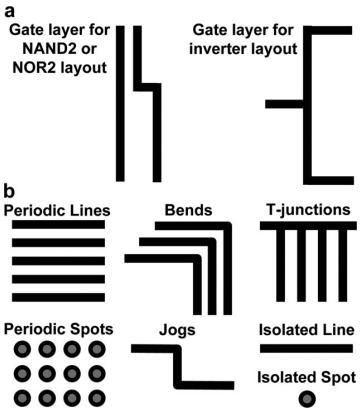
  with ***Yuliya Smirnova, Giovanni Marelli, Marc Fuhrmans, An-Chang Shi***

Santa Barbara, April 5, 2012

collective phenomena in amphiphilic systems
e.g., pattern replication by copolymer materials

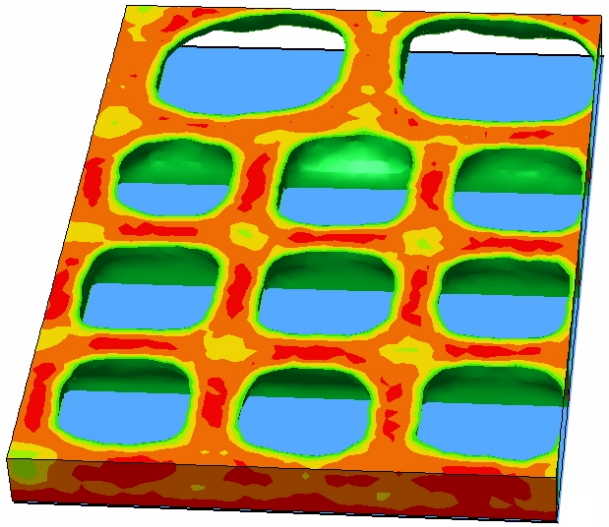




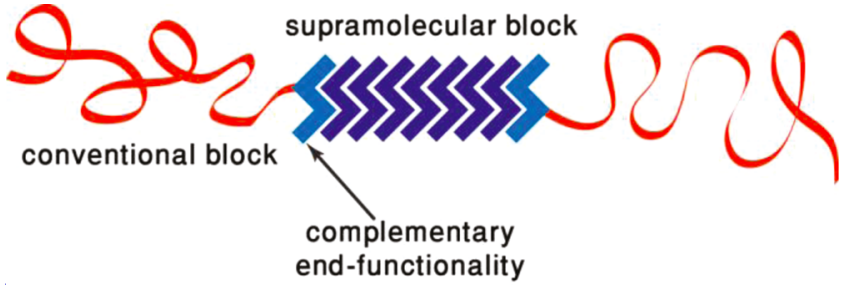


suitable choice of "defectants" allows directed assembly into irregular patterns

Stoykovich, Kang, Daoulas, Liu, Liu, de Pablo, Müller, Nealey, ACS Nano **1**, 168 (2007)



supramolecular copolymers locally create "defectants" and avoid diffusive sorting



Daoulas, Cavallo, Shenhar, Müller, PRL **105**, 108301 (2010)

Weiss, Daoulas, Müller, Shenhar, Macro **44**, 9773 (2011)

top-down approach: **minimal soft** coarse-grained models

bead-spring model with soft, pairwise interactions

$$\frac{\mathcal{H}_{\rm b}[\mathbf{r}_i(s)]}{k_BT} = \sum_{s=1}^{N-1} \frac{3(N-1)}{2{R_{\rm eo}}^2} \left[\mathbf{r}_i(s) - \mathbf{r}_i(s+1)\right]^2$$

molecular architecture: Gaussian chain

$$\frac{\mathcal{H}_{\rm ord}[\hat{\phi}_A, \hat{\phi}_B]}{k_BT\sqrt{\bar{\mathcal{N}}}} = -\frac{\chi_{\rm o} N}{4} \int \frac{{\rm d}^3\mathbf{r}}{{R_{\rm eo}}^3} \left[\hat{\phi}_A(\mathbf{r}) - \hat{\phi}_B(\mathbf{r})\right]^2$$

with $\sqrt{\bar{\mathcal{N}}} \equiv \Phi_{\rm p} R_{\rm eo}^3$

$$\frac{\mathcal{H}_{\rm melt}[\hat{\phi}_A, \hat{\phi}_B]}{k_BT\sqrt{\bar{\mathcal{N}}}} = +\frac{\kappa_{\rm o} N}{2} \int \frac{{\rm d}^3\mathbf{r}}{{R_{\rm eo}}^3} \left[\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}) - 1\right]^2$$

effective interactions become weaker for large degree of coarse-graining

➡ no (strict) excluded volume, soft, effective segments can overlap, rather enforce low compressibility on length scale of interest, $R_{\rm eo}$

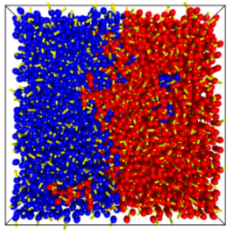
$$\text{``}\ \hat{\phi}_A(\mathbf{r}) = \frac{1}{\rho_{\rm o}} \sum_{i_A=1}^{nNf} \delta(\mathbf{r} - \mathbf{r}_{i_A})\ \text{''}$$

$\hat{\phi}^2$-terms generate pairwise interactions

particle-based description for MC, BD, DPD, or SCMF simulations

Müller, Smith, J. Polym. Sci. B **43**, 934 (2005); Daoulas, Müller, JCP **125**, 184904 (2006); Detcheverry, Kang, Daoulas, Müller, Nealey, de Pablo, Macromolecules **41**, 4989 (2008); Pike, Detcheverry, Müller, de Pablo, JCP **131**, 084903 (2009); Detcheverry, Pike, Nealey, Müller, de Pablo, PRL **102**, 197801 (2009)

particle simulation and continuum description



system: symmetric, binary AB homopolymer blend

degrees of freedom:

particle coordinates, $N(n_A + n_B)$
$\{\mathbf{r}_i(s)\}$

composition field (and density), ∞
$m(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$
$\rho(\mathbf{r}) = \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) \approx \rho_0$

model definition:

intra- and intermolecular potentials
(here: soft, coarse-grained model, SCMF)

free-energy functional, $\mathcal{F}_{\mathrm{GL}}[m(\mathbf{r})]$
(Ginzburg-Landau-de Gennes or Ohta-Kawasaki)

single-chain dynamics
(here: Rouse dynamics)

time-dependent GL theory
(model B according to Hohenberg & Halperin)

segmental friction, ζ

Onsager coefficient, $\Lambda(\mathbf{r} - \mathbf{r}')$

projection:

$$\hat{\phi}_A(\mathbf{r}) \text{“} = \text{”} \frac{1}{\rho_0} \sum_{i=1}^{n_A} \sum_{s=1}^{N} \delta\left(\mathbf{r} - \mathbf{r}_i(s)\right)$$

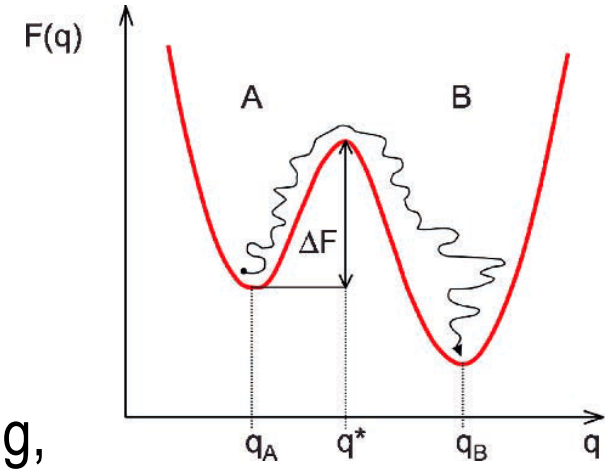
$$\frac{\mathcal{F}[m]}{k_B T} \equiv -\ln \int \mathcal{D}[\{\mathbf{r}_{i,s}\}]\, e^{-\frac{\mathcal{H}(\{\mathbf{r}_{i,s}\})}{k_B T}}\, \delta[m - (\hat{\phi}_A - \hat{\phi}_B)]$$

$$\Lambda(\mathbf{r} - \mathbf{r}') = \left\langle \frac{\partial \hat{\phi}(\mathbf{r})}{\partial \mathbf{r}_i(s)} M_{\zeta,i,j}(s,t) \frac{\partial \hat{\phi}(\mathbf{r}')}{\partial \mathbf{r}_j(t)} \right\rangle$$

Kawasaki, Sekimoto, Physica **143A** , 349 (1987)

speed-up particle simulations by concurrent coupling

question: why are particle simulations slow?



1) ***barrier problem (b)***:

system has to overcome a **free-energy barrier**,

Kramer's theory $\tau \sim \exp(-\Delta F/k_B T)$

solutions: WL sampling, conf.T-WL, conf. flooding, metadynamics, transition-path sampling, forward flux sampling, …

Dellago, Bolhuis, Adv. Polym. Sci **221**, 167 (2008)

2) ***time-scale problem (a)***: "**intrinsically slow processes**"

downhill in continuum free energy but **small Onsager coefficient** (response to TD force) and/or two **vastly different time scales** (stiff equations)

stiff interaction dictates time step, weak interaction drives slow time evolution

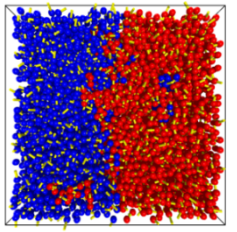
solutions: •reversible multiple time step MD (RESPA)

Tuckerman, Berne, Martyna, JCP **97**, 1990 (1992)

•SCMF simulation Müller, Smith J.Polym.Sci.B **43**, 934 (2005)

•**HMM** E, Engquist, Li, Ren, Vanden-Eijnden, Comm. Comp. Phys. **2**, 367 (2007)

time scale and free-energy separation in polymer blends



system: symmetric, binary AB homopolymer blend

bonded interactions (stiff) $f_{\mathrm{b}} \sim \frac{k_B T}{b} \sim \frac{k_B T \sqrt{N}}{R_{\mathrm{eo}}}$

non-bonded interactions (weak) $f_{\mathrm{nb}} \sim \frac{k_B T \chi}{w} \sim \frac{k_B T \chi N}{R_{\mathrm{eo}}} N^{-1}$

➡ **Ginzburg-Landau models do not include stiff bonded interactions and approximate limiting slow time evolution**

recap: kinetics of phase separation in a symmetric binary polymer blend:

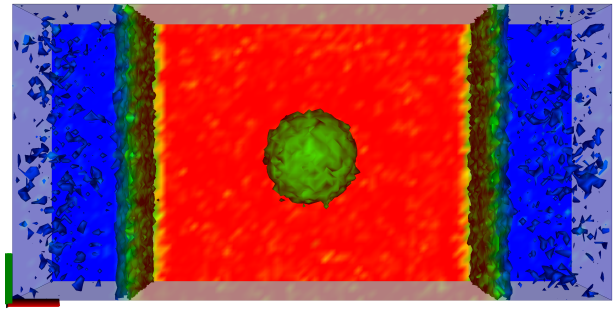
- spinodal decomposition
- ***Lifshitz-Slyozov coarsening*** (diffusive regime)

  Gibbs-Thomson equation $\mu^\star = \frac{R_{\mathrm{eo}}}{R} \frac{\gamma^\star}{m_{\mathrm{coex}}}$

$$\frac{\partial m}{\partial t} = \nabla \Lambda \nabla \mu$$

$$\frac{1}{t} \sim \frac{1}{L} \Lambda \frac{1}{L} \frac{\gamma}{L} \quad \Rightarrow \quad L^3 \sim \gamma \Lambda t$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\Delta_{\mathrm{o}}}{N\sqrt{\mathcal{N}}} = -\frac{2\pi}{\tau}(1 - m_{\mathrm{coex}}^2) \frac{\gamma {R_{\mathrm{eo}}}^2}{k_B T \sqrt{\mathcal{N}}}$$



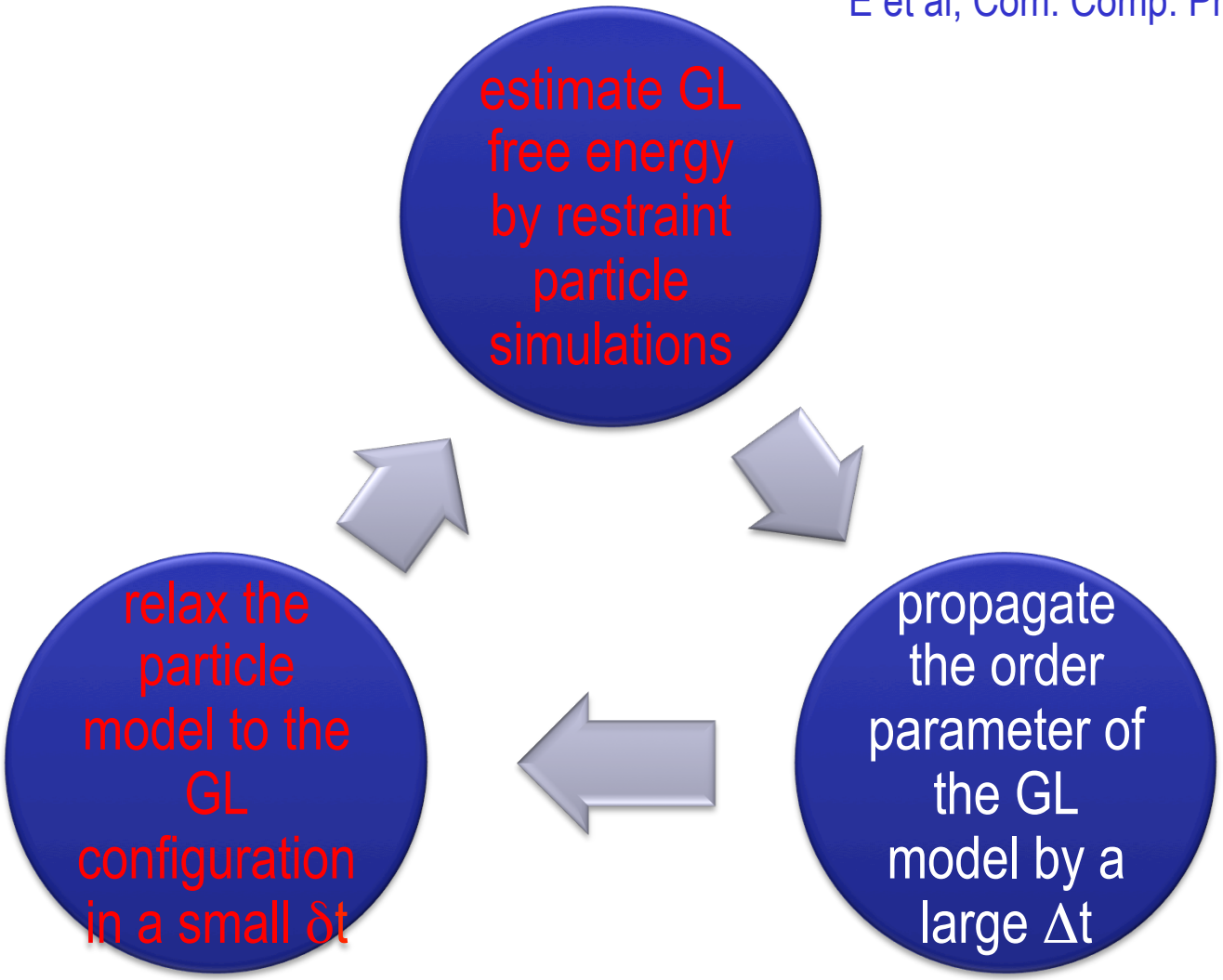
$$\Lambda = \frac{R_{\mathrm{eo}}^5}{\tau k_B T \sqrt{\mathcal{N}}}(1 - m^2)$$

$$1 - m_{\mathrm{coex}} \approx 2 \exp(-\chi_{\mathrm{o}} N)$$

- alternative: droplet coagulation by Brownian motion irrelevant due to large viscosity of polymer melt

heterogeneous multiscale modeling (HMM)

E, Ren, Vanden-Eijnden, J. Comp. Phys. **228**, 5437 (2009)
E et al, Com. Comp. Phys **2**, 367 (2007)



to show: steps that involve particle simulation require a time of the order $\frac{\tau}{\lambda N}$

free-energy functional from restraint simulations

idea: restrain the composition, $\hat{m} \equiv \hat{\phi}_A - \hat{\phi}_B$, of particle model to fluctuate around the order-parameter field, $m(\mathbf{r})$, of the continuum description (**field-theoretic umbrella sampling** for order-parameter field, $m(\mathbf{r})$)

$$\frac{\mathcal{H}_\mathrm{b}[\mathbf{r}_i(s)]}{k_B T} = \sum_{s=1}^{N-1} \frac{3(N-1)}{2{R_\mathrm{eo}}^2} \left[\mathbf{r}_i(s) - \mathbf{r}_i(s+1)\right]^2$$ bead-spring model

$$\frac{\mathcal{H}_\mathrm{nb}[\hat{\phi}_A,\hat{\phi}_B]}{k_B T\sqrt{\bar{\mathcal{N}}}} = \int \frac{\mathrm{d}^3\mathbf{r}}{R_\mathrm{eo}^3} \left(\frac{\kappa_\mathrm{o} N}{2} \left[\hat{\phi}_A + \hat{\phi}_B - 1\right]^2 - \frac{\chi_\mathrm{o} N}{4} \left[\hat{\phi}_A - \hat{\phi}_B\right]^2 \right)$$ soft, non-bonded

$$\frac{\mathcal{H}_{\lambda N}}{k_B T\sqrt{\bar{\mathcal{N}}}} = \frac{\lambda N}{2} \int \frac{\mathrm{d}^3\mathbf{r}}{R_\mathrm{eo}^3} \left\{ \left[\hat{\phi}_A - \frac{1+m}{2}\right]^2 + \left[\hat{\phi}_B - \frac{1-m}{2}\right]^2 \right\}$$ restrain composition

$\lambda N \gg \chi_\mathrm{o} N$ strong coupling between particle model and continuum description

$$\exp\left(-\frac{\mathcal{H}_{\lambda N}}{k_B T}\right) \overset{\lambda N\to\infty}{\to} \delta\left(m(\mathbf{r}) - \hat{\phi}_A + \hat{\phi}_B\right) \delta\left(\hat{\phi}_A + \hat{\phi}_B - 1\right)$$

$$\mu(\mathbf{r}) = \frac{\delta\mathcal{F}}{\delta m(\mathbf{r})} \overset{\lambda N\to\infty}{\approx} \frac{\delta\mathcal{F}_{\lambda N}}{\delta m(\mathbf{r})} = \left\langle \frac{\delta\mathcal{H}_{\lambda N}}{\delta m(\mathbf{r})} \right\rangle$$

$$\mu^* \equiv \frac{\mu R_\mathrm{eo}^3}{k_B T\sqrt{\bar{\mathcal{N}}}} \overset{\lambda N\to\infty}{\approx} \frac{\lambda N}{2} \left(m(\mathbf{r}) - \left\langle \hat{\phi}_A(\mathbf{r}) - \hat{\phi}_B(\mathbf{r}) \right\rangle\right) = \frac{\lambda N}{2} \left(m(\mathbf{r}) - \langle \hat{m}(\mathbf{r}) \rangle\right)$$

inspired by Maragliano, Vanden-Eijnden, Chem. Phys. Lett. **426**, 168 (2006)

free-energy functional from restraint simulations

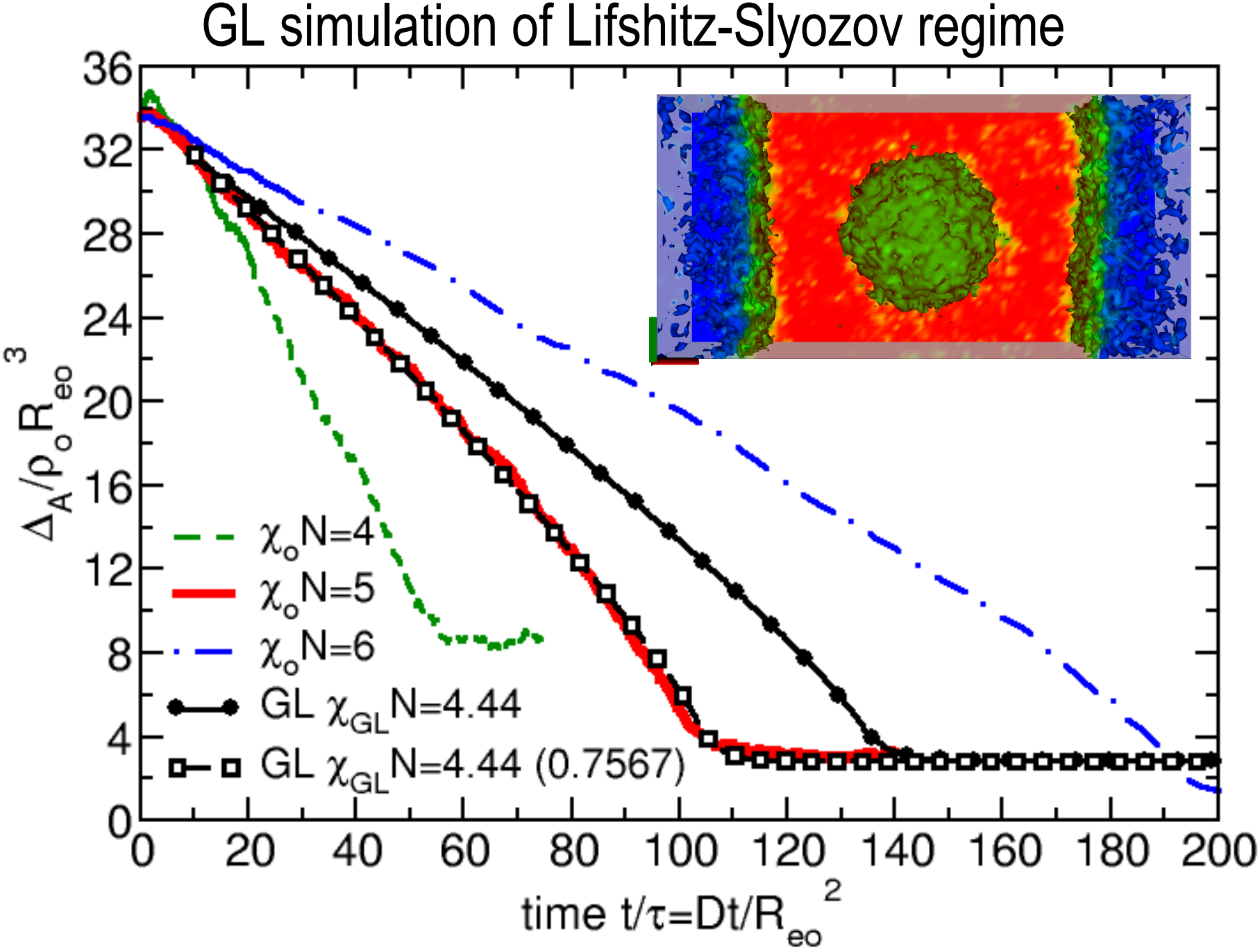
idea: restrain the composition, $\hat{m} \equiv \hat{\phi}_A - \hat{\phi}_B$, of particle model to fluctuate around the order-parameter field, $m(\mathbf{r})$, of the continuum description (**field-theoretic umbrella sampling** for order-parameter field, $m(\mathbf{r})$)

make an **Ansatz for the continuum description** with a few parameters $\{a_r\}, a_g$
determine parameters by comparing $\mu(\mathbf{r}|m)$ with result of Ansatz

GL ***model*** required, not "equation-free" Kevrekidis, Gear, Hummer AICHE J. **50**, 1346 (2004)

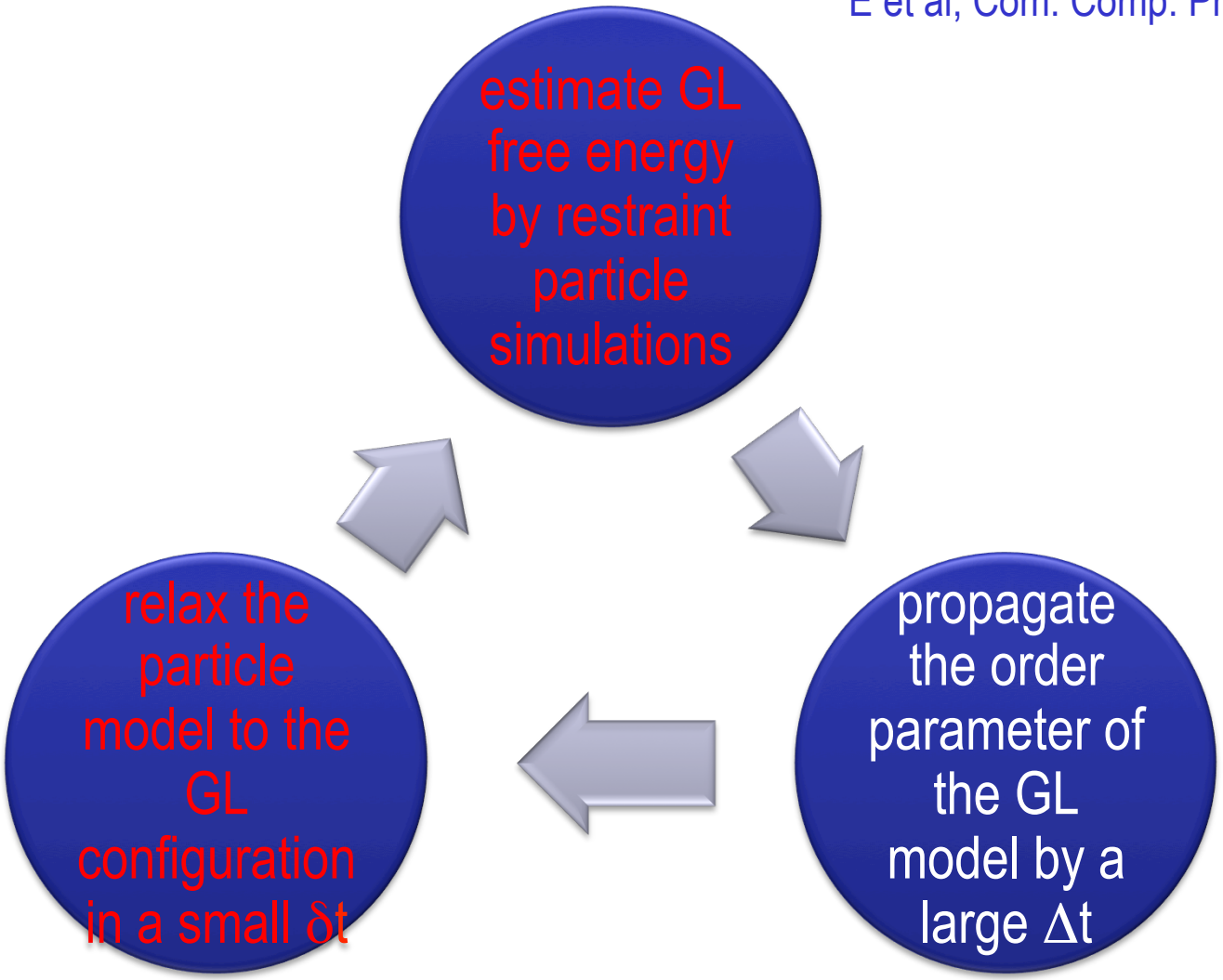
- **average over space** (instead of time) to determine the few parameters of the Ginzburg-Landau model (spatial homogeneity of GL model)
- result: Ginzburg-Landau model for a particle model at a specific state
  large time step Δt is limited by the condition that parameters do not vary on scale Δt
  e.g., intrinsic structure of interface must not vary WSL *vs* SSL
  but location of interface may move

Müller, EPJ Special Topics **177**, 149 (2009)


GL simulation of Lifshitz-Slyozov regime
$\Delta_A/\rho_o R_{eo}^3$
time $t/\tau=Dt/R_{eo}^2$
$\chi_o N=4$
$\chi_o N=5$
$\chi_o N=6$
GL $\chi_{GL} N=4.44$
GL $\chi_{GL} N=4.44$ (0.7567)
0
4
8
12
16
20
24
28
32
36
0
20
40
60
80
100
120
140
160
180
200

heterogeneous multiscale modeling (HMM)

E, Ren, Vanden-Eijnden, J. Comp. Phys. **228**, 5437 (2009)
E et al, Com. Comp. Phys **2**, 367 (2007)



to show: steps that involve particle simulation require a time of the order $\frac{\tau}{\lambda N}$

Onsager coefficient from relaxation of simulations

idea: study relaxation of restraint system towards equilibrium, $\langle \hat{m} \rangle$
relaxation time of the constraint system is speeded-up by a factor λN

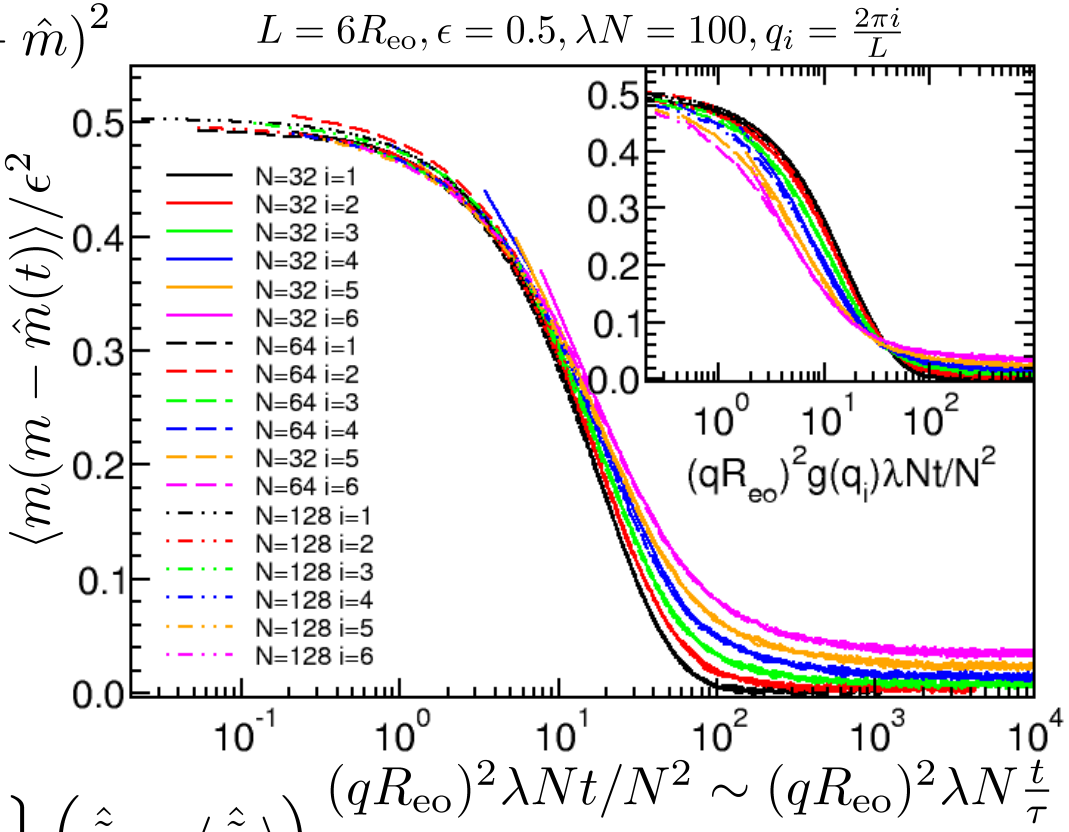
$$\frac{\mathcal{F}_{\lambda N}[\hat{m}]}{k_B T \sqrt{\bar{\mathcal{N}}}} = \frac{\mathcal{F}[\hat{m}]}{k_B T \sqrt{\bar{\mathcal{N}}}} + \frac{\lambda N}{4} \int \frac{\mathrm{d}^3 \mathbf{r}}{R_\mathrm{e}^3} \; (m - \hat{m})^2$$

$$\mu^*_{\lambda N}(\mathbf{r}) = \mu^*[\hat{m}] + \frac{\lambda N}{2}(\hat{m} - m)$$

$$\tilde{\mu}^*_{\lambda N}(\mathbf{q}) = \frac{1}{2}\left\{ \frac{\hat{\tilde{m}}}{2h(\mathbf{q})} + \lambda N (\hat{\tilde{m}} - \tilde{m}) \right\}$$

$$\tilde{\Lambda}(\mathbf{q}) \approx \frac{R_\mathrm{e}^5}{V k_B T \sqrt{\bar{\mathcal{N}}}} \frac{g(q)}{\tau_\mathrm{GL}}$$

$$\frac{\partial \hat{\tilde{m}}(\mathbf{q},t)}{\partial t} = -\frac{(qR_\mathrm{eo})^2 g(\mathbf{q})}{2\tau_\mathrm{GL}} \left\{ \lambda N + \frac{1}{2h(\mathbf{q})} \right\} \left(\hat{\tilde{m}} - \langle \hat{\tilde{m}} \rangle \right)$$



➡ constraint system exponentially relaxes towards $\langle \hat{\tilde{m}} \rangle = \frac{\tilde{m}}{1 + \frac{1}{2\lambda N h(\mathbf{q})}}$
with a fast relaxation time scale $\tau_{\lambda N} = \frac{2\tau_\mathrm{GL}}{\lambda N} \frac{1}{(qR_\mathrm{e})^2 g(\mathbf{q})}$ (fraction of Rouse time)

speed-up and scale separation

question: What limits the increase of λN ?

- accurate measurement of the chemical potential $\lambda N \sim \frac{V\sqrt{\bar{N}}}{R_{\mathrm{eo}}^3}$
- forces due to the restraint must be smaller than the original forces that dictate the intrinsic kinetics of the particle model
  - bonded force per segment
  - non-bonded, thermodynamic force
  - restraint force

$$f_{\mathrm{b}} \sim \frac{k_B T}{b} \sim \frac{k_B T\sqrt{N}}{R_{\mathrm{eo}}}$$
$$f_{\mathrm{nb}} \sim \frac{k_B T\chi}{w} \sim \frac{k_B T\chi N}{R_{\mathrm{eo}}} N^{-1}$$
$$f_{\lambda N} \sim \frac{k_B T\lambda}{\Delta L} \sim \frac{k_B T\lambda N}{R_{\mathrm{eo}}} N^{-1/2}$$

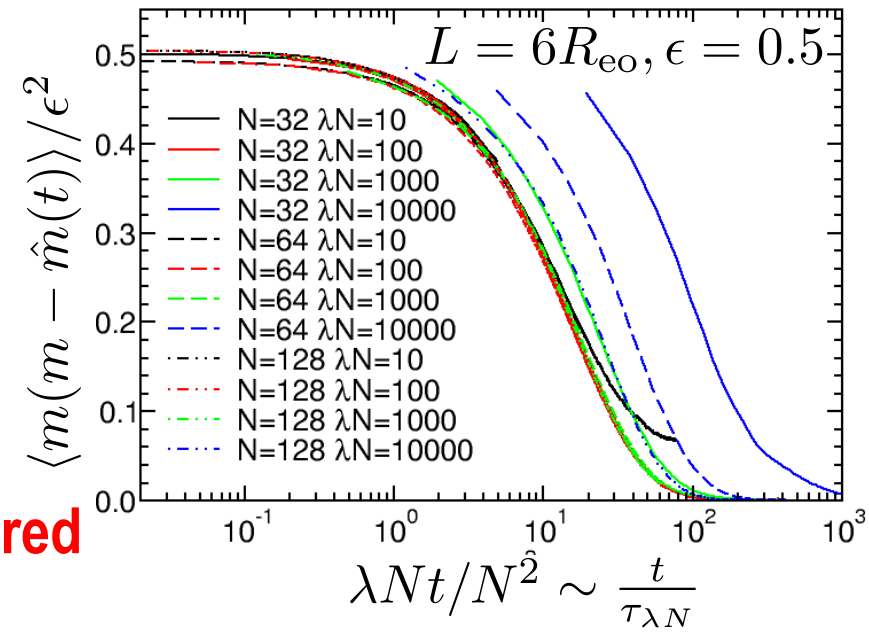
$f_{\mathrm{nb}} \ll f_{\lambda N} \ll f_{\mathrm{b}}$ ➡ $\chi_{\mathrm{o}} N \ll \lambda N\sqrt{N} \ll N^{3/2}$

➡

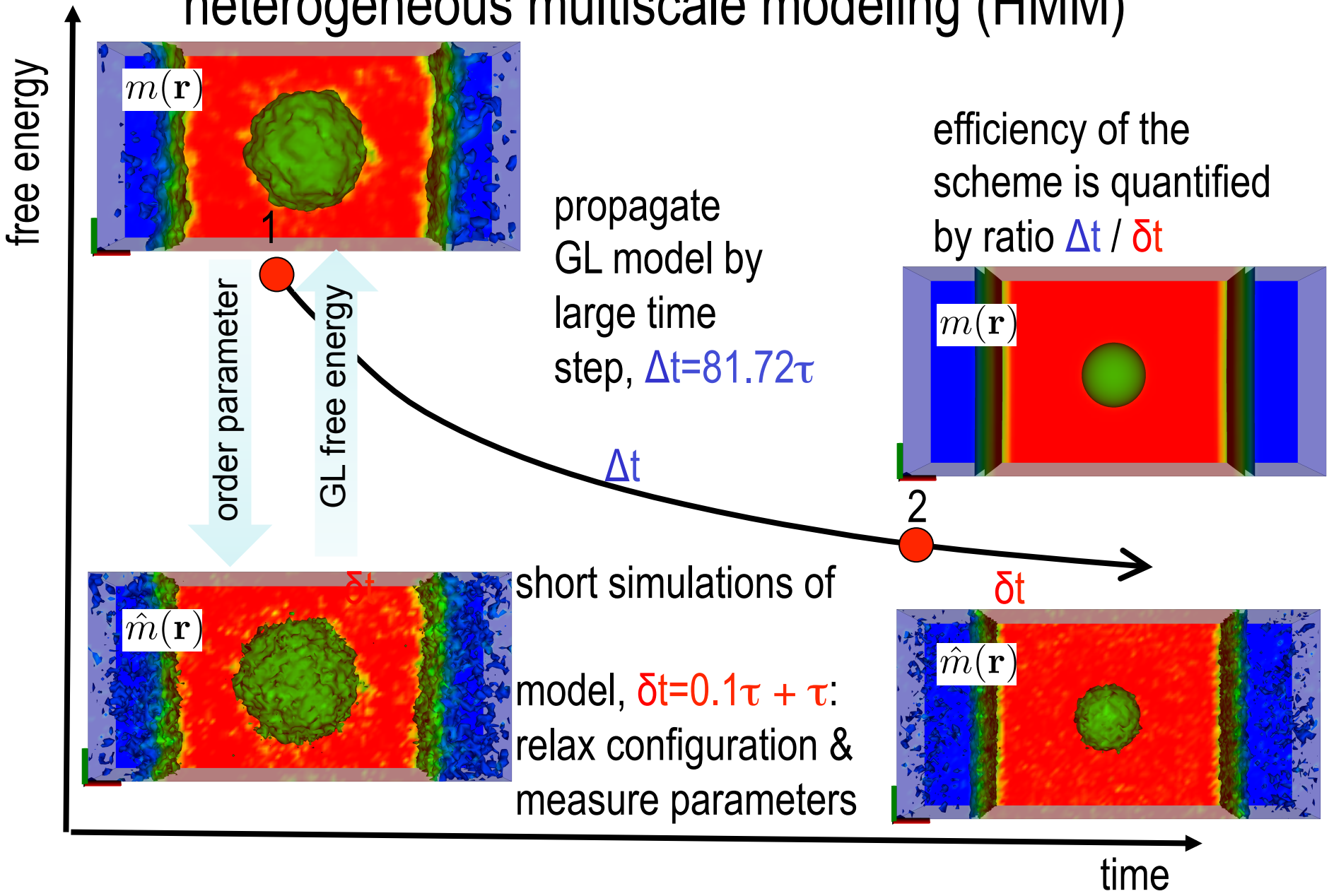
relaxation rate is increase by a factor λN for small composition/density variations $\hat{m}$

caveat : λN ≥ 1 not linear response, dynamic RPA fails

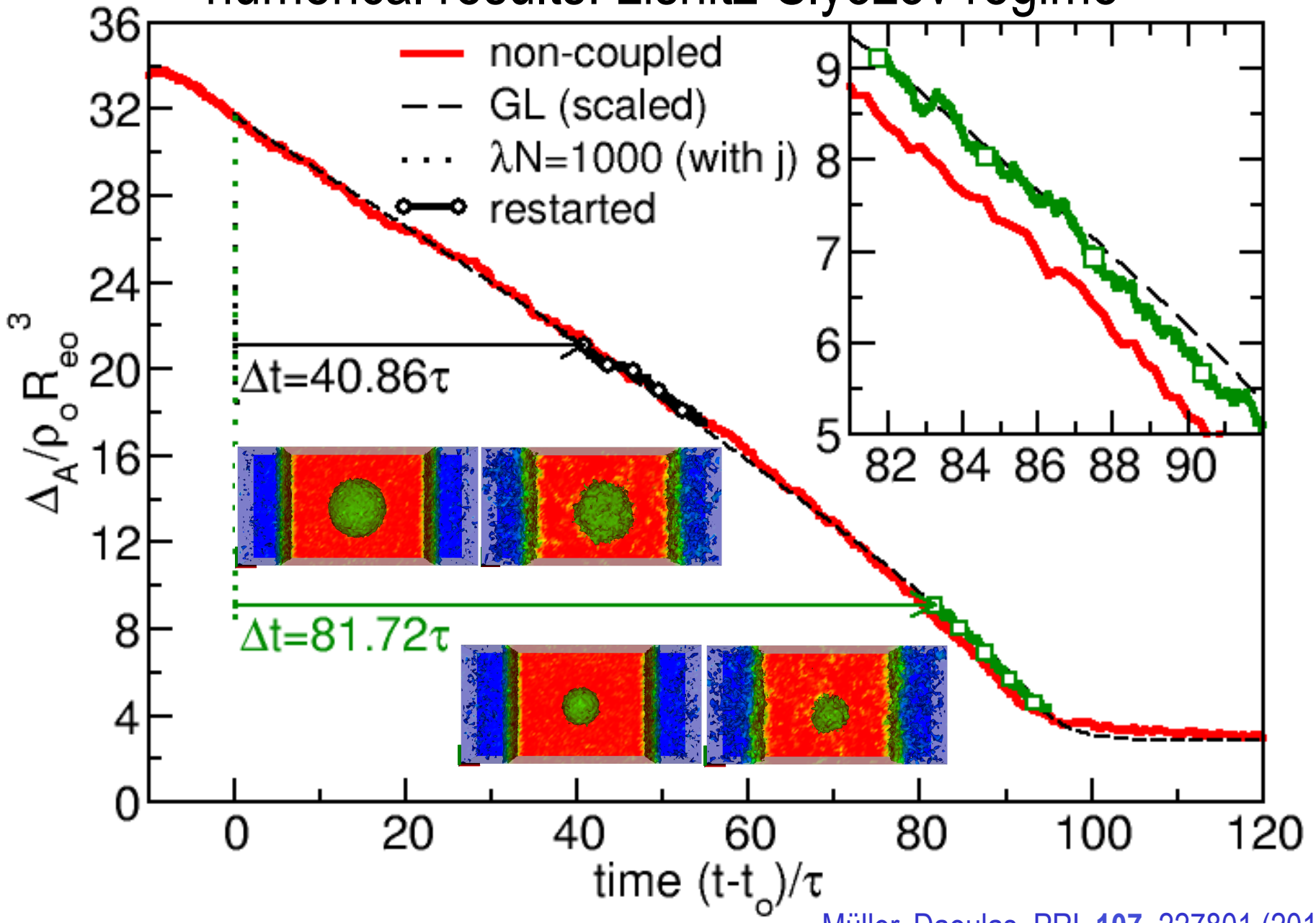
➡ **additional relaxation τ may be required**



heterogeneous multiscale modeling (HMM)



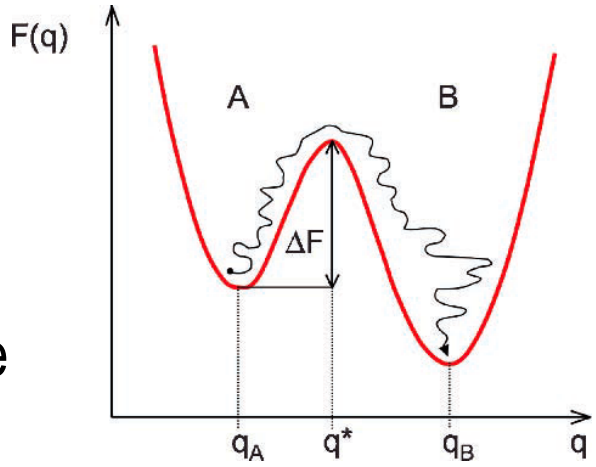
numerical results: Lishitz-Slyozov regime



Müller, Daoulas, PRL **107**, 227801 (2011)

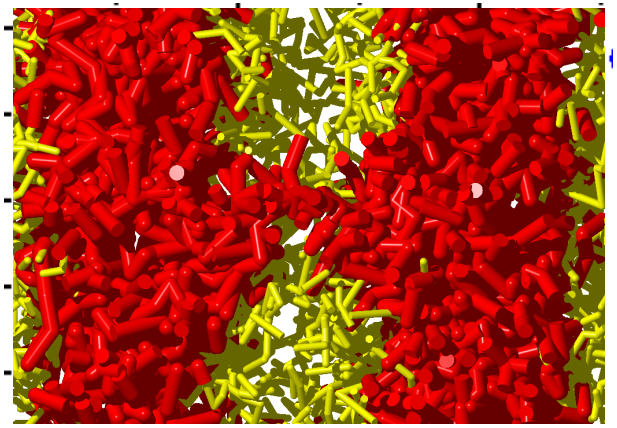
b) collective transformation between morphologies

problem: find a **physical reversible path**
that identifies the barrier to stalk formation



Dellago, Bolhuis, Adv. Polym. Sci **221**, 167 (2008)

- which "coordinates" describe transformation?
  particle coordinates in liquid are impractical because (i) missing entropy and (ii) permutation symmetry
  ➡ use order parameter field $m(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$
  DFT suggests that collective densities are suitable

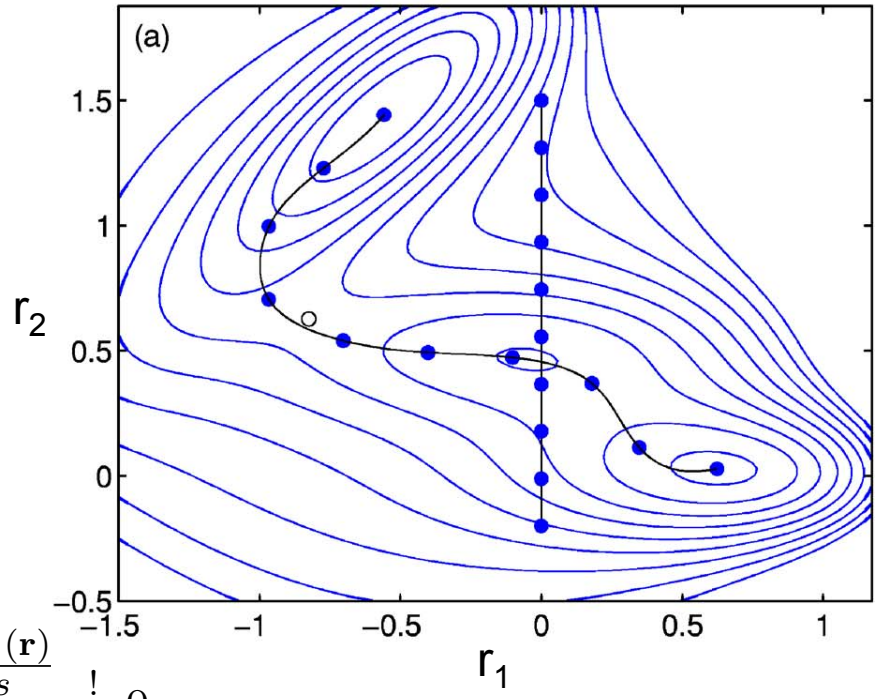


- compute free-energy functional
  $\frac{\mathcal{F}[m]}{k_\mathrm{B}T} = -\ln \int \mathcal{D}[\{\mathbf{r}\}]\, e^{-\frac{\mathcal{H}[\{\mathbf{r}\}]}{k_\mathrm{B}T}}\, \delta\left[m(\mathbf{r}) - \hat{m}(\mathbf{r})\right]$
  ➡ field-theoretic umbrella sampling,
  on-the-fly string method (particle-based)
- find minimal free-energy path (MFP) in high-dimensional "coordinate" space (for functional $\mathcal{F}[m]$ on collocation lattice)
  ➡ improved string method

E, Ren, Vanden-Eijnden, JCP **126**, 164103 (2007)
Maragliano, Vanden-Eijnden. Chem. Phys. Lett., **446**, 182 (2007)

on-the-fly string method and improved string method

describe the transformation path by a string of morphologies $m_s(\mathbf{r})$ that is parameterized by a contour variable $0 \le s \le 1$



the minimum free-energy path (MFP) is defined by condition that the derivative perpendicular to the path vanishes

$$\nabla_\perp \mathcal{F}[m] = \frac{\delta \mathcal{F}}{\delta m_s(\mathbf{r})} - \frac{\mathrm{d}m_s(\mathbf{r})}{\mathrm{d}s} \frac{\int \mathrm{d}^3\mathbf{r}\, \frac{\delta \mathcal{F}}{\delta m_s(\mathbf{r})} \frac{\mathrm{d}m_s(\mathbf{r})}{\mathrm{d}s}}{\int \mathrm{d}^3\mathbf{r}\, \left(\frac{\mathrm{d}m_s(\mathbf{r})}{\mathrm{d}s}\right)^2} \stackrel{!}{=} 0$$

on-the-fly string method and improved string method:

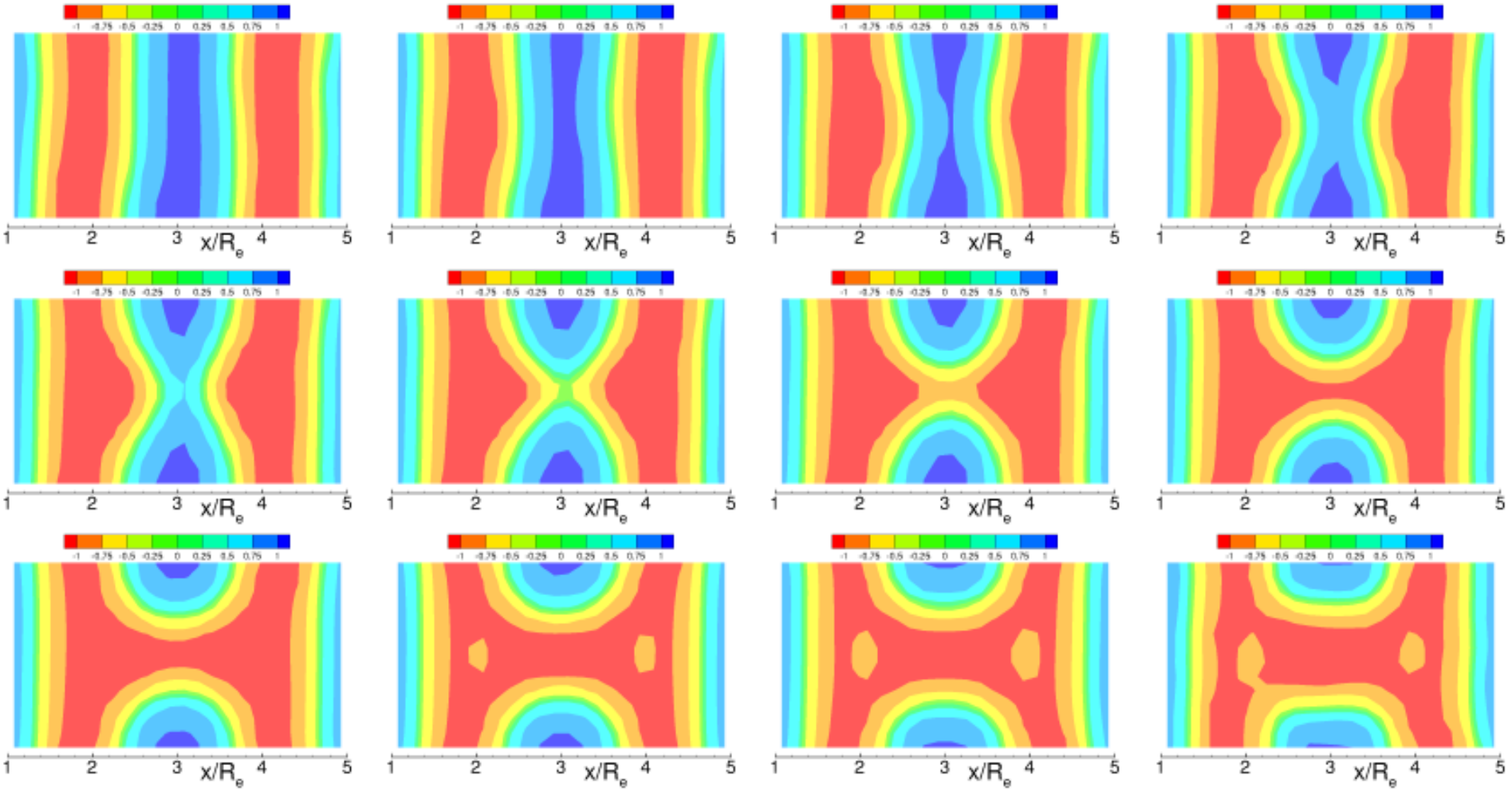
1. evolve each morphology $m_s(\mathbf{r})$ as to minimize the free energy

$$\frac{\delta F_\mathrm{c}[m_\mathrm{c}]}{\delta m_\mathrm{c}(\mathbf{r})} = \lambda k_\mathrm{B} T \left[m_\mathrm{c}(\mathbf{r}) - \langle \hat{m}(\mathbf{r}) \rangle_\mathrm{c}\right] \stackrel{\lambda \to \infty}{\to} \mu(\mathbf{r}|m_\mathrm{c}) \qquad \Delta m_s(\mathbf{r}) = -\mu(\mathbf{r}|m_s)\Delta$$

2. re-parameterize the string to equal distance Δs (pointwise 3rd order spline)

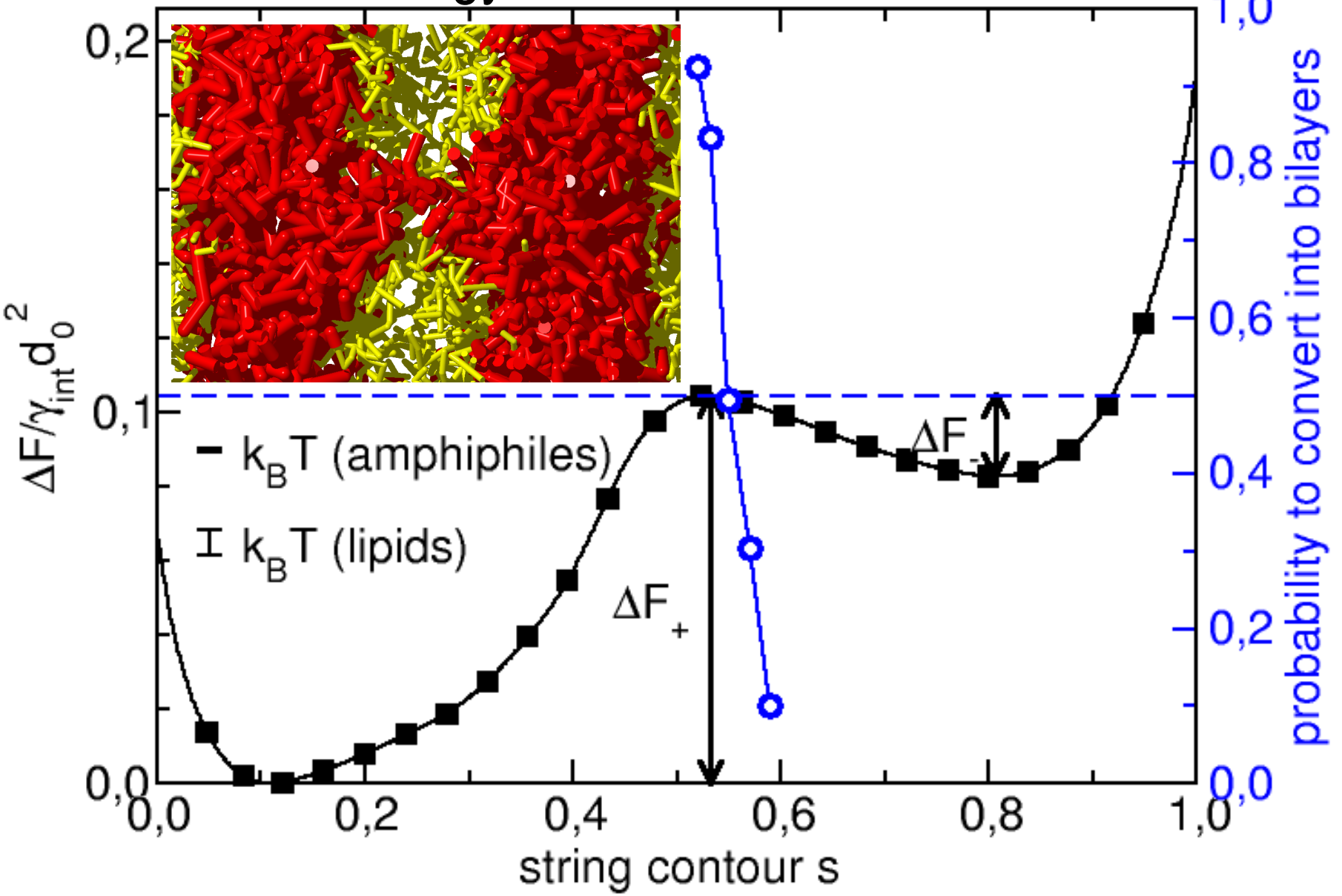
E, Ren, Vanden-Eijnden, JCP **126**, 164103 (2007)
Maragliano, Vanden-Eijnden. Chem. Phys. Lett., **446**, 182 (2007)

string of morphologies for stalk formation



Müller, Smirnova, Marelli, Fuhrmans, Shi, submitted (2012)

free-energy barrier for stalk formation



Müller, Smirnova, Marelli, , Shi, submitted (2012)