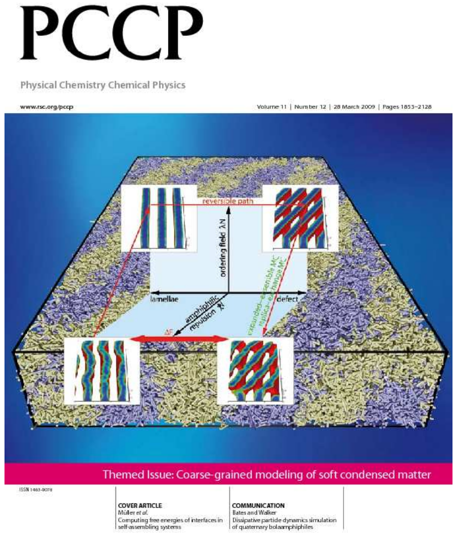
Mesoscopic and Monte Carlo Simulations

Marcus Müller

- recap of basic concepts (Mikhail Tamm, Alexey Shaytan): thermodynamics, statistical mechanics, phase transitions
- Monte-Carlo simulations:
  detailed balance, force-bias Monte-Carlo,
  phase coexistence
- free-energy of soft-condensed matter:
  thermodynamic integration in a spatially varying field
- speeding-up intrinsically slow processes
  field-theoretic umbrella sampling and HMM
- finding barriers via the on-the-fly string method



PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp Volume 11 | Number 12 | 28 March 2009 | Pages 1853–2128

Themed Issue: Coarse-grained modeling of soft condensed matter

ISSN 1463-9076

COVER ARTICLE
Müller *et al.*
Computing free energies of interfaces in self-assembling systems

COMMUNICATION
Bates and Walker
Dissipative particle dynamics simulation of quaternary bolaamphiphiles

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Published by
American Physical Society™

APS physics

Volume 108, Number 22

GEORG-AUGUST-UNIVERSITÄT
GÖTTINGEN

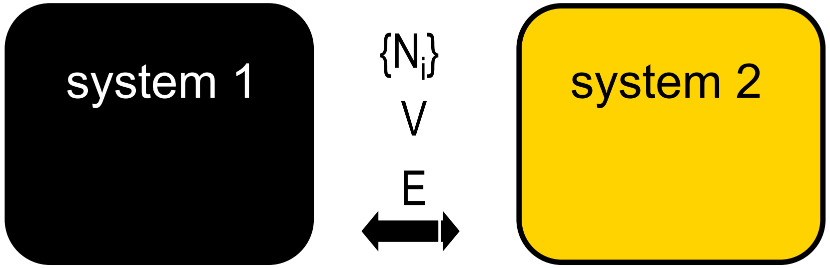
Moscow, July 18, 2012

basics: thermodynamics

physical system is comprised of very many degrees of freedom, $N_A \sim 10^{23}$
description of the microscopic state impractical but simple relations emerge
for thermodynamic variables in the limit $N \to \infty$ (***thermodynamic limit***)

description of a physical system in terms of a **small number of state variables**
extensive variables: number of particles $\{N_i\}$, volume V, and internal energy E (***0. postulate***)

fundamental question: consider systems that can exchange properties



exchange of N ➡ equality of chem. pot. μ
exchange of V ➡ equality of pressure p
exchange of E ➡ equality of temperature T

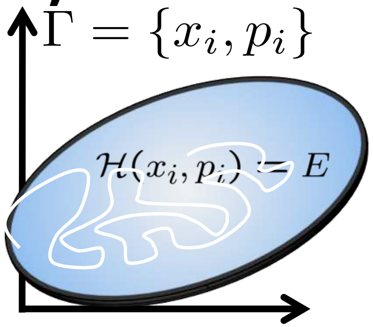
$\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}N_i$ energy conservation (***1. postulate***)

reversible transformation equality of entropy, S (i.e., reversible process, ΔS=0)
entropy is additive, $S(N,V,E) \to \max$ in equilibrium (***2. postulate***)
S monotonously increasing in E, $\partial S/\partial E|_{N,V} = \frac{1}{T} > 0$ $E(N,V,S) \to \min$

$\partial E/\partial S|_{N,V} = 0 \;\Rightarrow\; S = 0$ (Planck) (***3. postulate***)

other ensembles via ***Legendre transform***: $F(N,V,T) = E - TS$ $T = \frac{\partial E}{\partial S}\Big|_{N,V}$

basics: statistical mechanics (classical)



calculate thermodynamic properties for microscopic model

consider Hamiltonian $\mathcal{H}(x_i, p_i) = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} V(q_i - q_j)$

motion in phase space Γ on energy hypersurface, $\mathcal{H}(x_i, p_i) = E$

calculate the time average of a quantity $A(x_i, p_i)$ along trajectory

$$\begin{aligned}
\bar{A}(\Gamma_0) &= \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathrm{d}t\; A(\Gamma(t, \Gamma_0)) \\
&= \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathrm{d}t\; \int_\Gamma \mathrm{d}\Gamma'\; A(\Gamma')\delta[\Gamma' - \Gamma(t, \Gamma_0)] \\
&= \int_\Gamma \mathrm{d}\Gamma'\; A(\Gamma') \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathrm{d}t\; \delta[\Gamma' - \Gamma(t, \Gamma_0)] \\
&= \frac{1}{N!h^{3N}} \int_\Gamma \mathrm{d}\Gamma'\; A(\Gamma') \quad \rho_{\mathrm{mc}}(\Gamma') \qquad \textbf{\textit{(ergodicity)}}
\end{aligned}$$

phase space density of microcanonical ensemble $\rho_{\mathrm{mc}} = \frac{1}{\mathcal{Z}_{\mathrm{mc}}(N,V,E)}$

is constant on hypersurface $\mathcal{H}(x_i, p_i) = E$ and vanishes elsewhere

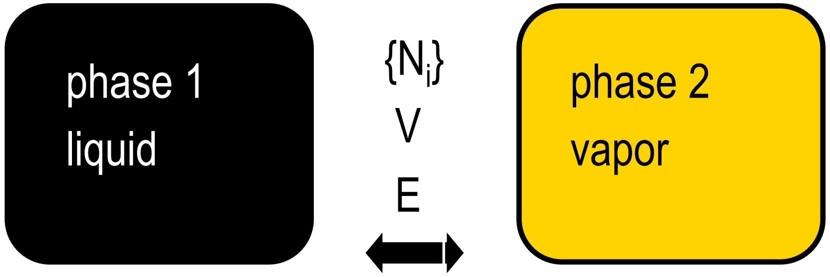
connection to thermodynamics via ***Boltzmann’s entropy functional***

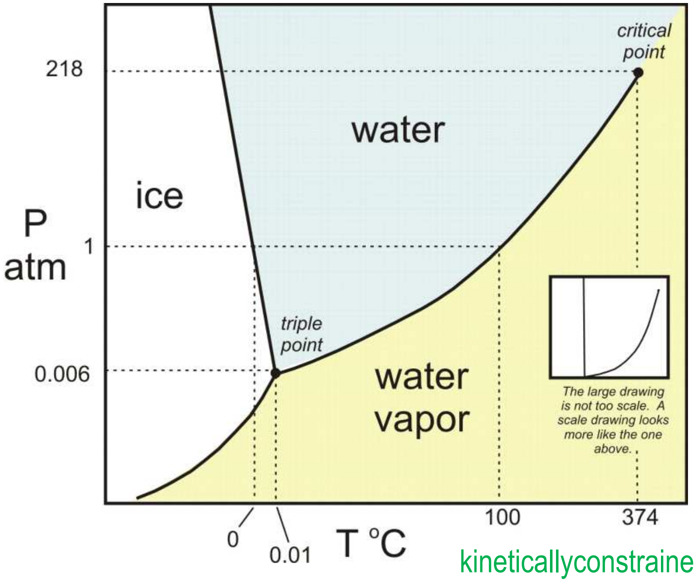
$S[\rho] = -k_B \frac{1}{N!h^{3N}} \int \mathrm{d}\Gamma\; \rho(\Gamma) \ln \rho(\Gamma)$ ➡ $S(N,V,E) = -k_B \langle \ln \rho_{\mathrm{mc}}(\Gamma) \rangle = k_B \ln \mathcal{Z}_{\mathrm{mc}}$

other ensembles: $F(N,V,T) = -k_B T \ln \mathcal{Z}$ with $\mathcal{Z} = \frac{1}{N!h^{3N}} \int \mathrm{d}\Gamma\; \exp\left(-\frac{E(\Gamma)}{k_B T}\right)$

phase coexistence and transitions

example: liquid-vapor ***coexistence***





kineticallyconstrained.
blogspot.com/2009/05
critical-point.html

coexistence rule: two phases coexist if they have the same pressure, temperature and chemical potential

grandcanonical ensemble $\Omega(\mu,V,T) = -pV$

describe the phases by two thermodynamic potentials, $\Omega_{\mathrm{liq}}(\mu,V,T)$ and $\Omega_{\mathrm{vap}}(\mu,V,T)$

➡ coexistence: $\Omega_{\mathrm{liq}}(\mu,V,T) = \Omega_{\mathrm{vap}}(\mu,V,T)$

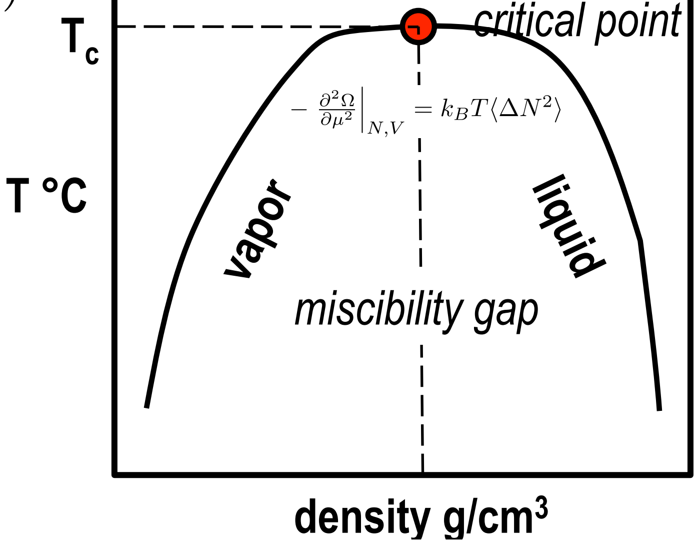
phase transition (Ehrenfest)

first order: 1^{st} derivative of thermodyn. potential (state variable) is not continuous

➡ miscibility gap $N = -\left.\frac{\partial\Omega}{\partial\mu}\right|_{V,T}$

second order: 2^{nd} derivative of TP (response function) is not continuous $-\left.\frac{\partial^2\Omega}{\partial\mu^2}\right|_{N,V} = \frac{\partial N}{\partial\mu} = \frac{N^2}{V}\kappa_T$

➡ compressibility diverges at critical point



basics: Monte-Carlo simulation

canonical ensemble (N,V,T) and thermal averages

$$\mathcal{Z} = \int \frac{\prod_{i=1}^{N} \mathrm{d}\mathbf{p}\mathrm{d}\mathbf{r}}{N!h^{3N}} \exp\left(-\frac{\mathcal{H}(\{p,r\})}{k_B T}\right)$$

$$= \int \frac{\prod_{i=1}^{N} \mathrm{d}\mathbf{r}}{N!\Lambda_T^{3N}} \exp\left(-\frac{V(\{r\})}{k_B T}\right)$$

$$\frac{1}{\Lambda_T} = \frac{1}{h}\int \mathrm{d}p\, e^{-\frac{p^2}{2mk_B T}}$$

thermal de Broglie wavelength

$$\rho(\{r\})N!\Lambda_T^{3N} = \frac{1}{\mathcal{Z}} \exp\left(-\frac{V(\{r\})}{k_B T}\right)$$

sharply peaked distribution in high-dimensional space

idea: generate sequence of points in phase space or configuration space that are distributed according to the statistical weight of the appropriate ensemble (***importance sampling***)

$$\langle A\rangle = \int \prod_{i=1}^{N} \rho(\{r\})A(\{r\})$$

$$= \lim_{T\to\infty} \frac{1}{T}\sum_{t=1}^{T} A(\{r\}_t)$$

generate the sequence of configurations $\{r\}_t$ as a ***Markov chain***, i.e. the probability of generating the next configuration only depends on the previous state but not on the history

➡ choose the transition probability from one state to the next $\{r\} \to \{r'\}$ as to generate ρ

basics: Monte-Carlo simulation

master equation: continuity equation for probabilities

$$\frac{\partial \rho(\{r\})}{\partial t} = + \underbrace{\sum_{\{r'\}} \rho(\{r'\}) p(\{r'\} \to \{r\})}_{\text{transitions into } \{r\}} - \underbrace{\rho(\{r\}) \sum_{\{r'\}} p(\{r\} \to \{r'\})}_{\text{transitions out of } \{r\}}$$

stationary $\frac{\partial \rho_{\text{eq}}(\{r\})}{\partial t} = 0$

$$\sum_{\{r'\}} \rho_{\text{eq}}(\{r'\}) p(\{r'\} \to \{r\}) = \rho_{\text{eq}}(\{r\}) \sum_{\{r'\}} p(\{r\} \to \{r'\})$$

detailed balance: reversibility between all pairs of microstates (sufficient condition)

$$\rho_{\text{eq}}(\{r'\}) p(\{r'\} \to \{r\}) = \rho_{\text{eq}}(\{r\}) p(\{r\} \to \{r'\}) \qquad \forall \{r\} \leftrightarrow \{r'\}$$

decompose the transition probability into a proposal and acceptance probability

$$p(\{r\} \to \{r'\}) = p_{\text{prop}}(\{r\} \to \{r'\}) p_{\text{acc}}(\{r\} \to \{r'\})$$

$$\frac{p_{\text{acc}}(\{r\} \to \{r'\})}{p_{\text{acc}}(\{r'\} \to \{r\})} = \frac{p_{\text{prop}}(\{r'\} \to \{r\})}{p_{\text{prop}}(\{r\} \to \{r'\})} \frac{p_{\text{eq}}(\{r'\})}{p_{\text{eq}}(\{r\})}$$

➡ $p_{\text{acc}}(\{r\} \to \{r'\}) = \text{metrop}\left[\frac{p_{\text{prop}}(\{r'\} \to \{r\})}{p_{\text{prop}}(\{r\} \to \{r'\})} \frac{p_{\text{eq}}(\{r'\})}{p_{\text{eq}}(\{r\})}\right]$

with $\text{metrop}[x] = \min(1, x)$ and $\frac{\text{metrop}[x]}{\text{metrop}[1/x]} = x$

basics: Monte-Carlo simulation

advantages of Monte-Carlo sampling:

- fast exploration of phase space (configuration space) by moves that efficiently renew configurations (non-local Monte-Carlo moves like (re)growing part of a macromolecule or all-chemical mutations)
- can be formulated in various ensembles (e.g., moves that insert or remove particles, change volume)
- a priori no information about the dynamics but "sometimes" can mimic the dynamics of molecules

example: force-bias Monte-Carlo move or Smart-Monte-Carlo move (Rossky, Doll, Friedman, 1978)

idea: use Brownian dynamics with a large time step to propose a move

$$\mathbf{r}_i(t+\mathrm{d}t) - \mathbf{r}_i(t) = \frac{\mathrm{d}t}{\zeta}\mathbf{F}_i(t) + \sqrt{2k_BT\frac{\mathrm{d}t}{\zeta}}\eta + \mathcal{O}(\mathrm{d}t^2)$$

$$= \mathrm{d}A\mathbf{F}_i(t) + \mathrm{d}R\eta + \mathcal{O}(\mathrm{d}t^2) \qquad \text{with} \quad \mathrm{d}A = \frac{\mathrm{d}t}{\zeta} \quad \mathrm{d}R = \sqrt{2k_BT\mathrm{d}A}$$

propose $\mathbf{r}_i \to \mathbf{r}'_i = \mathbf{r}_i + \Delta A\mathbf{F}_i + \Delta\mathbf{R}_i \qquad \text{with} \quad P(\Delta R_i)\frac{1}{\sqrt{4\pi k_BT\Delta A}}\exp\left[-\frac{\Delta R_i^2}{4k_BT\Delta A}\right]$

$$p_{\mathrm{prop}}(\{r\} \to \{r'\}) = \frac{1}{(4\pi k_BT\Delta A)^{3/2}}\exp\left[-\frac{(\mathbf{r}'_i - \mathbf{r}_i - F_i\Delta A)^2}{4k_BT\Delta A}\right]$$

➡

$$p_{\mathrm{acc}}(\{r\} \to \{r'\}) = \mathrm{metrop}\left[\exp\left(-\frac{V'-V}{k_BT} - \frac{\mathbf{F}'_i + \mathbf{F}_i}{2k_BT}(\mathbf{r}'_i - \mathbf{r}_i) - \frac{\Delta A}{4k_BT}\left\{\mathbf{F}'^2_i - \mathbf{F}^2_i\right\}\right)\right]$$

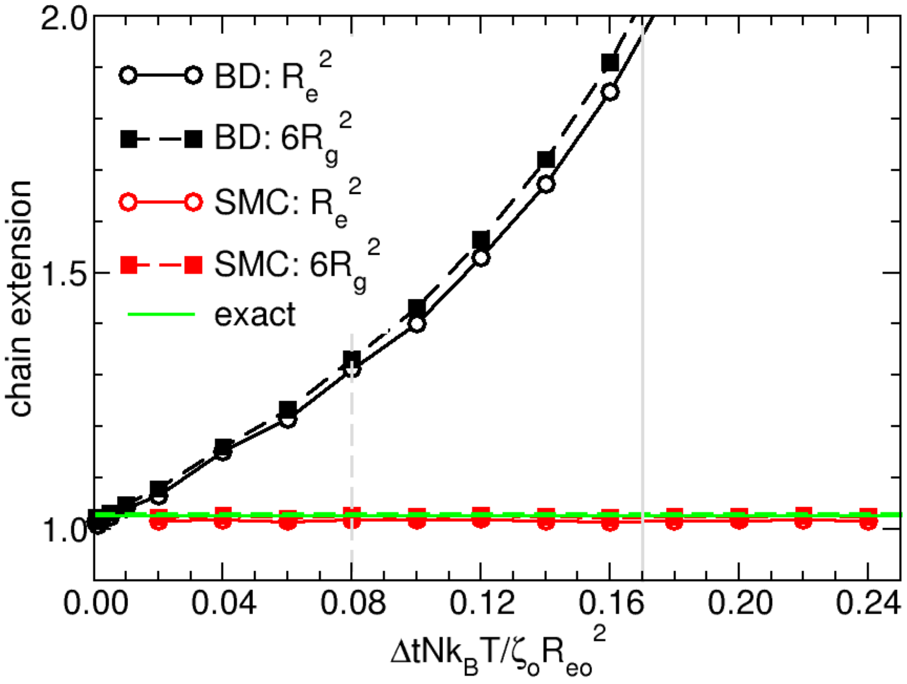
Rouse-like dynamics via Smart-MC simulations

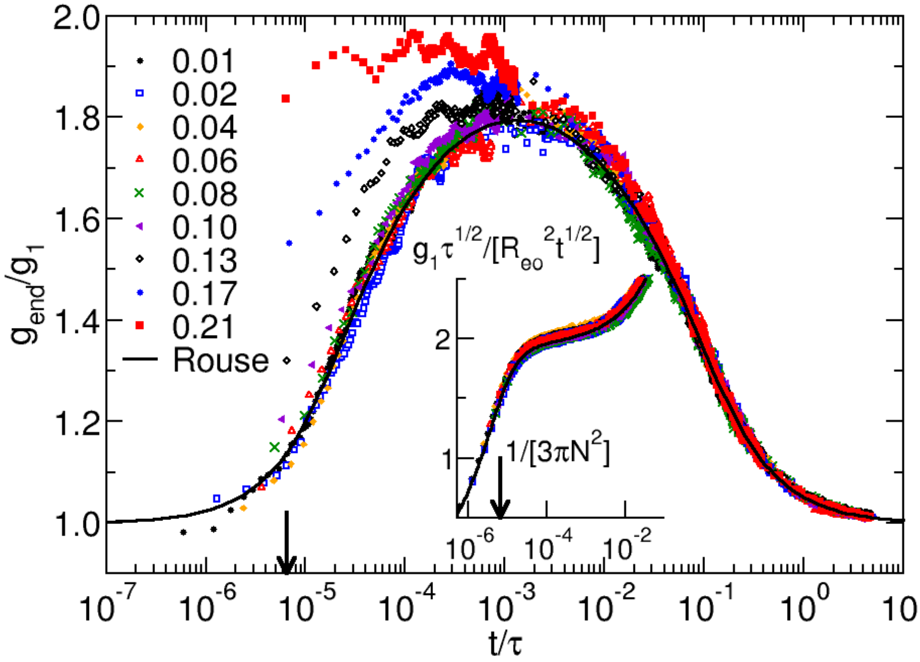
SMC: Brownian dynamics as smart-MC (Rossky, Doll, Friedman, 1978)

idea: uses forces to construct trial displacements Δr

application: soft, coarse-grained polymer model

- SMC or force-bias MC allows for a larger time step (factor 100) than BD with Euler integration
- rather realistic dynamics (diffusive) after a few Smart-Monte-Carlo steps



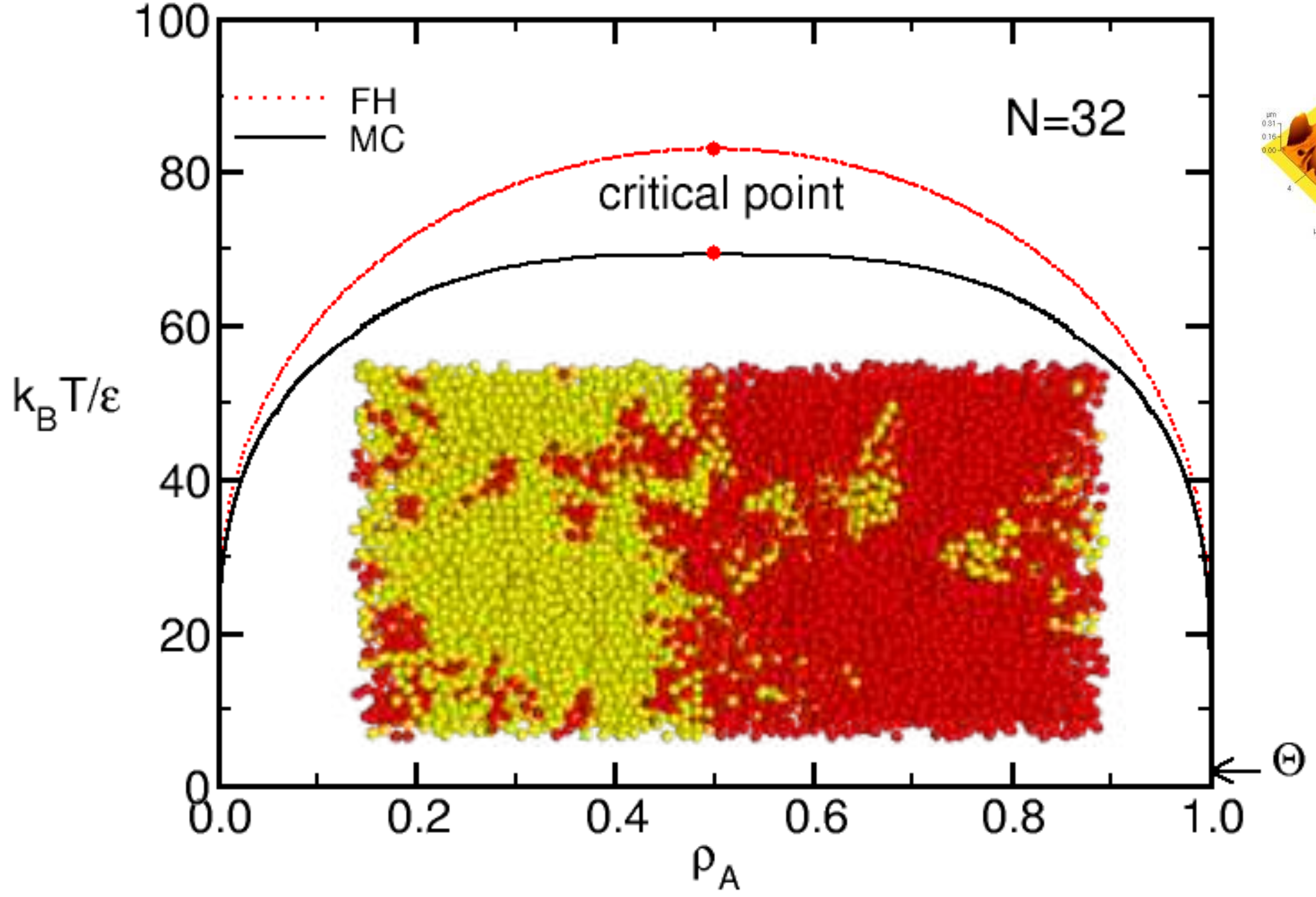


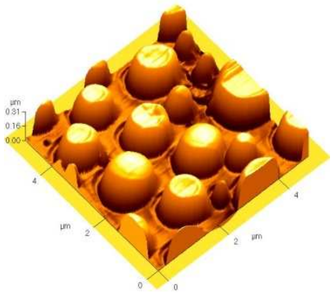
Müller, Daoulas, JCP **129**, 164906 (2008)

prototypical example:
liquid-liquid phase separation in blends

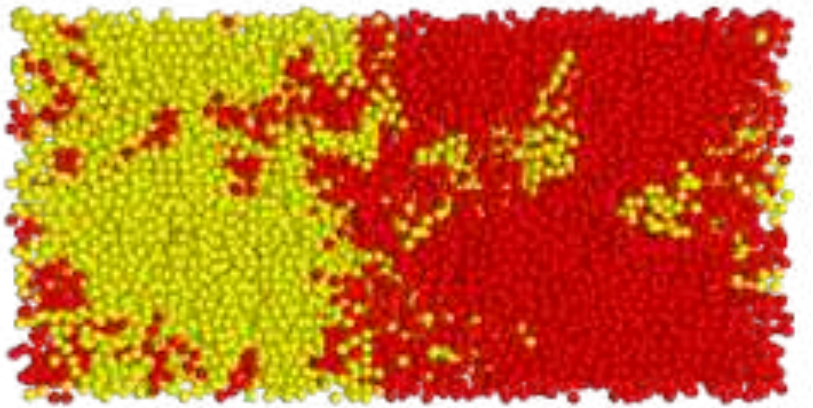
demixing into A-rich and B-rich regions, interfaces in a polymer blend

order parameter: composition difference between coexisting phases





methods to locate phase coexistence (1)



1. **direct simulation** of phase coexistence:
   two phases simultaneously present in a simulation box separated by interfaces

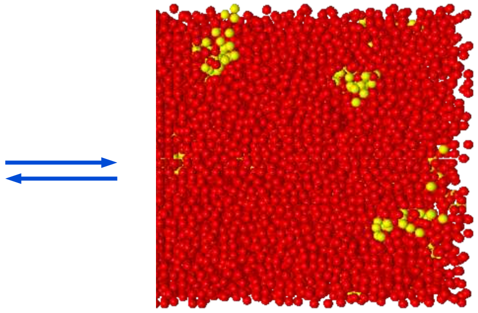
advantage:
simple, does not require special simulation techniques, does not require priori knowledge of coexistence value of pressure or chemical potential
interface tension accessible via anisotropy of pressure across interface

$$\gamma = \int_{-\infty}^{\infty} \mathrm{d}z \ [p_N(z) - p_T(z)]$$

disadvantage:
requires very large systems to distinguish interface and bulk properties
often kinetics of phase separation is very slow and equilibration difficult

methods to locate phase coexistence (2)

2. **Gibbs-Ensemble Monte-Carlo simulations**:
two simulation boxes which exchange particles and volume to ensure that boxes are at constant chemical potential and pressure



advantage:
no interfaces present, does not require a priori knowledge of coexistence value of pressure or chemical potential

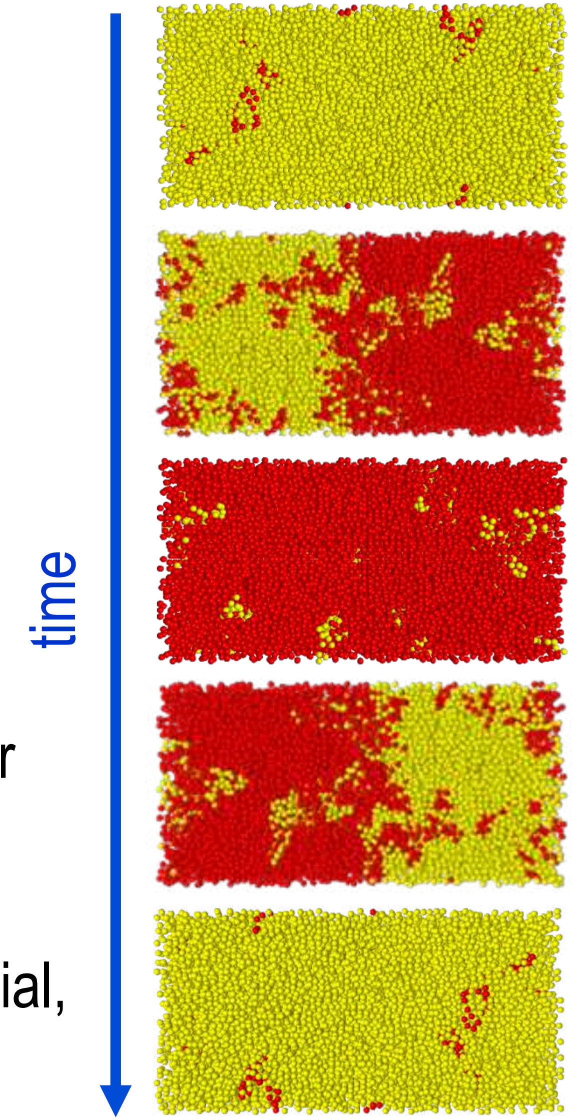
disadvantage:
requires additional MC moves for volume and particle exchange that might be difficult to implement (e.g., lattice models)

methods to locate phase coexistence (3)

(semi-) grandcanonical ensemble:
control temperature T, volume V, and total number of polymers, exchange potential, $\Delta\mu$ (semi-gc) or chemical potential, μ (grandcanonical)
order parameter fluctuates

advantage:
probability distribution of order parameter (density or composition) contains information about bulk phases and interfaces, efficient relaxation of order parameter

disadvantage:
needs prior “guess” for coexistence chemical potential, special techniques to (i) change order parameter and (ii) efficiently sample the order parameter distribution



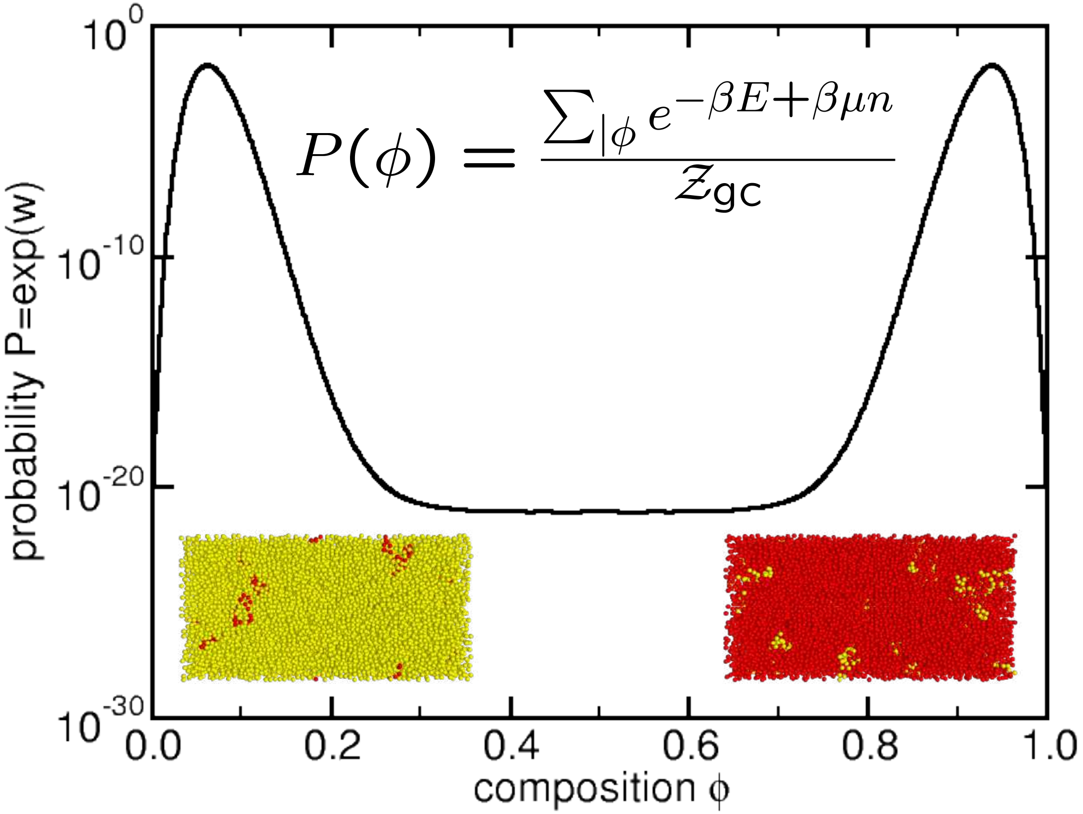
phase coexistence and equal weight rule

thermodynamics:
two phases coexist at μ if they have the same grand potential

$$\Omega(\mu,T) = -k_B T \ln \mathcal{Z}_{\mathrm{gc}} = -pV$$

statistical mechanics:

$$\mathcal{Z}_{\mathrm{gc}} = \sum_{\{\mathrm{conf}\}} e^{-\beta E+\beta\mu n}$$



$$\mathcal{Z}_A = \sum_{\{A\}} e^{-\beta E+\beta\mu n} = \mathcal{Z}_{\mathrm{gc}} \int_A \mathrm{d}\phi \, P(\phi)$$
$$\mathcal{Z}_B = \sum_{\{B\}} e^{-\beta E+\beta\mu n} = \mathcal{Z}_{\mathrm{gc}} \int_B \mathrm{d}\phi \, P(\phi)$$

$$\Omega_A \overset{!}{=} \Omega_B \quad \Rightarrow \quad \int_A \mathrm{d}\phi \, P(\phi) = \int_B \mathrm{d}\phi \, P(\phi)$$

➡ exponentially small finite-size effects

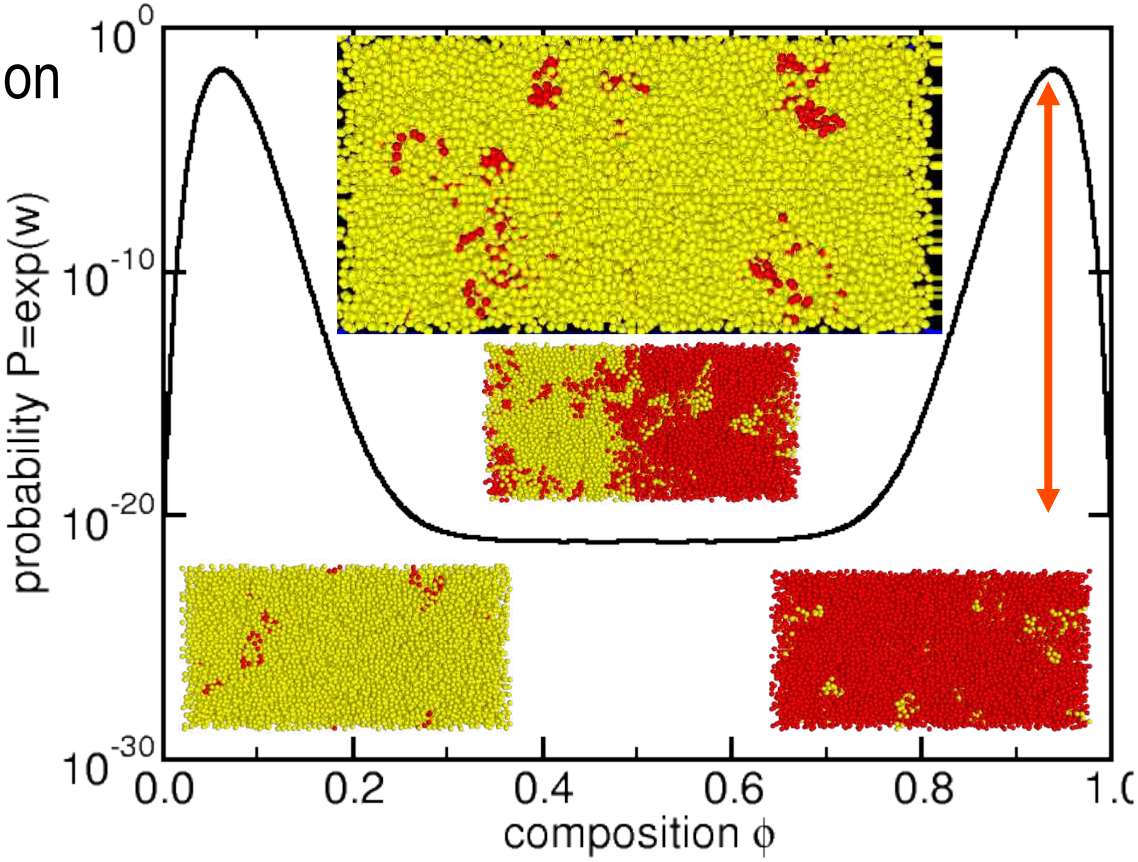
semi-grandcanonical simulations

canonical moves:
local displacements+reptation

grand-canonical identity switch:

A ⇄ B

- phase coexistence via equal weight rule
- interface properties via "depth of valley"



flat valley in order parameter indicates that interfaces do not interact
use elongated simulation cell, displaces the interfaces further

how to tunnel between the two phases?

non-Boltzmann sampling
(reweighting)

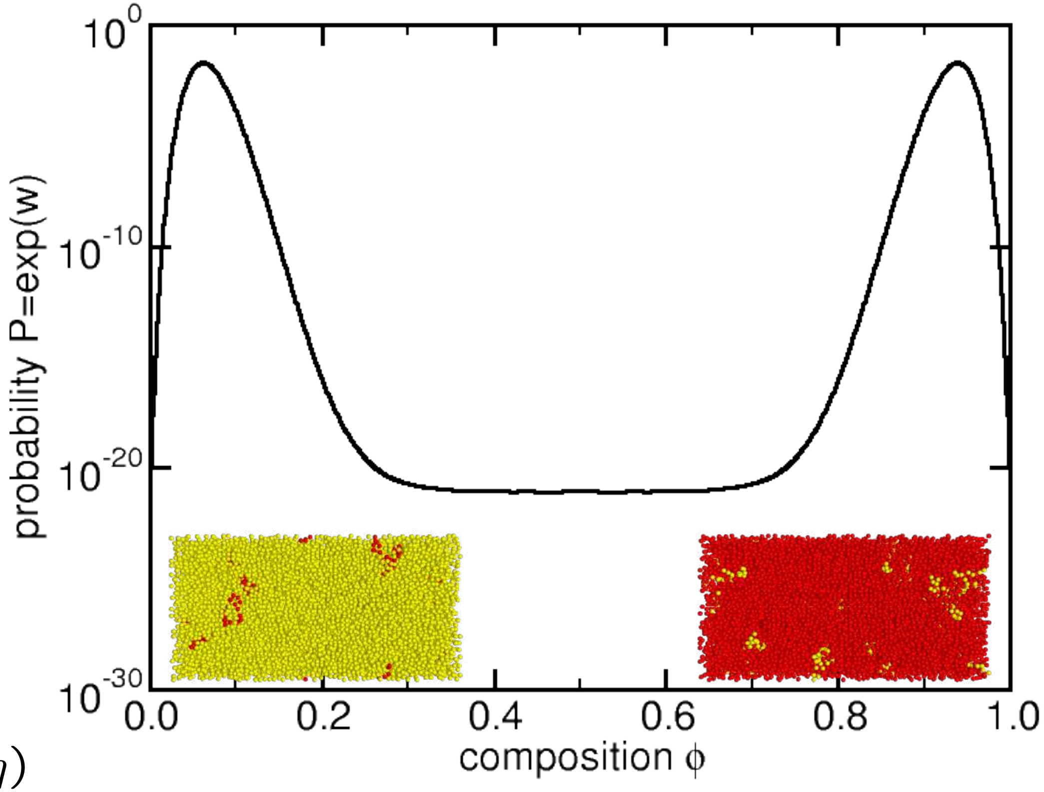
$$\mathcal{H}(\{r\}) = \mathcal{H}_0(\{r\}) + k_B T \eta(\phi)$$

additional term only depends on composition ϕ but not on detailed configuration {r}

idea $\eta(\phi) = \ln P_{\mathrm{gc}}$

$$\begin{aligned} P_{\mathrm{rw}}(\phi) &\sim e^{-\beta(\mathcal{H}_0 - \mu n + k_B T \eta)} \\ &\approx e^{-\beta(\mathcal{H}_0 - \mu n)}/P \\ &\sim 1 \end{aligned}$$

➡ uniform sampling



relative probability of configurations with same n (order par.) remains unaffected

estimating the reweighting function

Wang-Landau algorithm

Wang, Landau PRL **86**, 2050 (2001)

adjust η every step

$\eta \to \eta + \ln f$

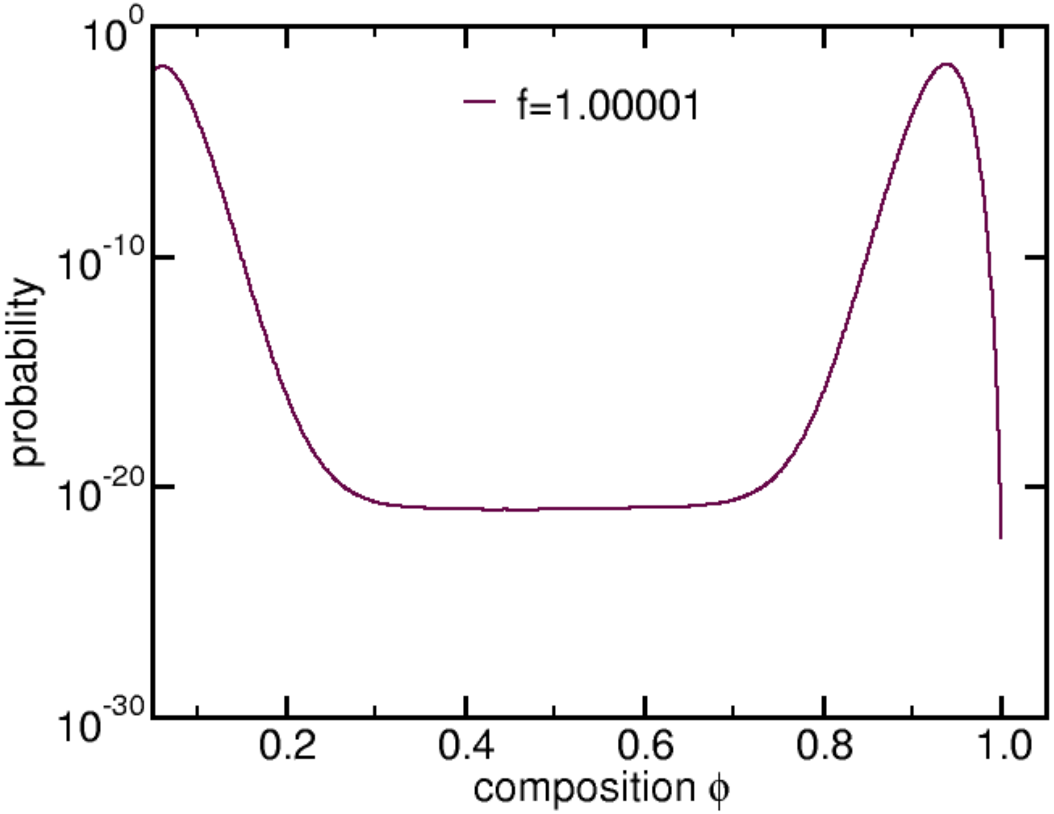
$P_{\mathrm{rw}}(\phi) \sim P(\phi) e^{-\eta(\phi)}$

accumulate histogram

flat histogram?

$f \to \sqrt{f} \qquad (\to 1)$

reset histogram



but: no detailed balance for f>1

errors difficult to estimate

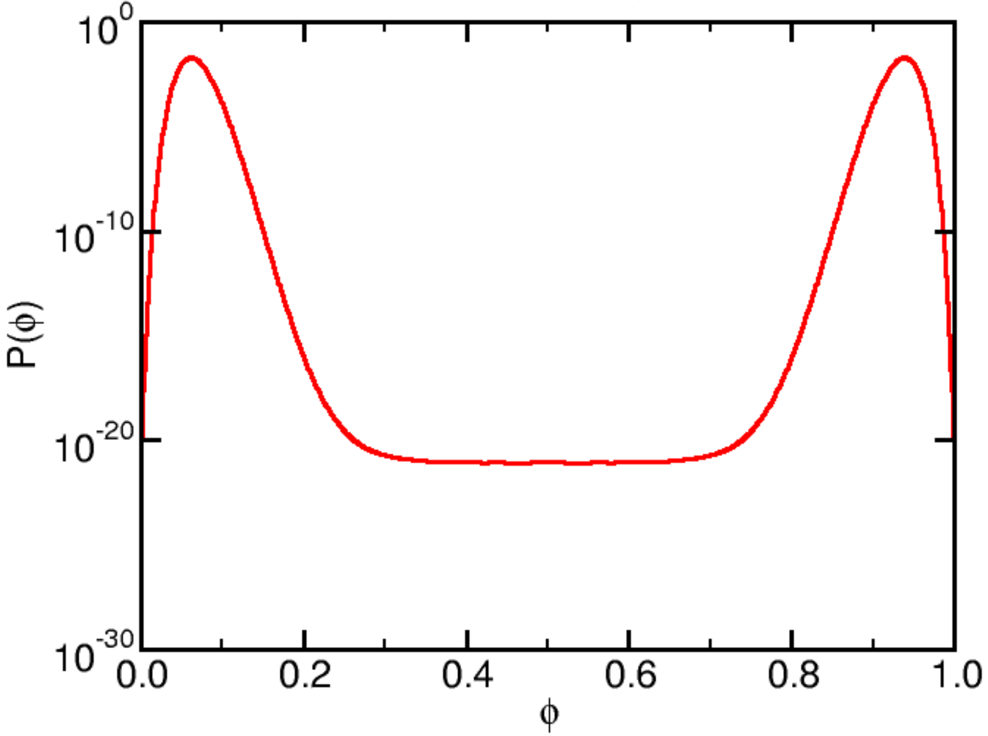
idea: push out the simulation of states that were already visited

umbrella sampling

divide the interval of particle numbers into overlapping subintervals

obtain $P_i(\phi)$ in
each subinterval

match distributions
at boundaries



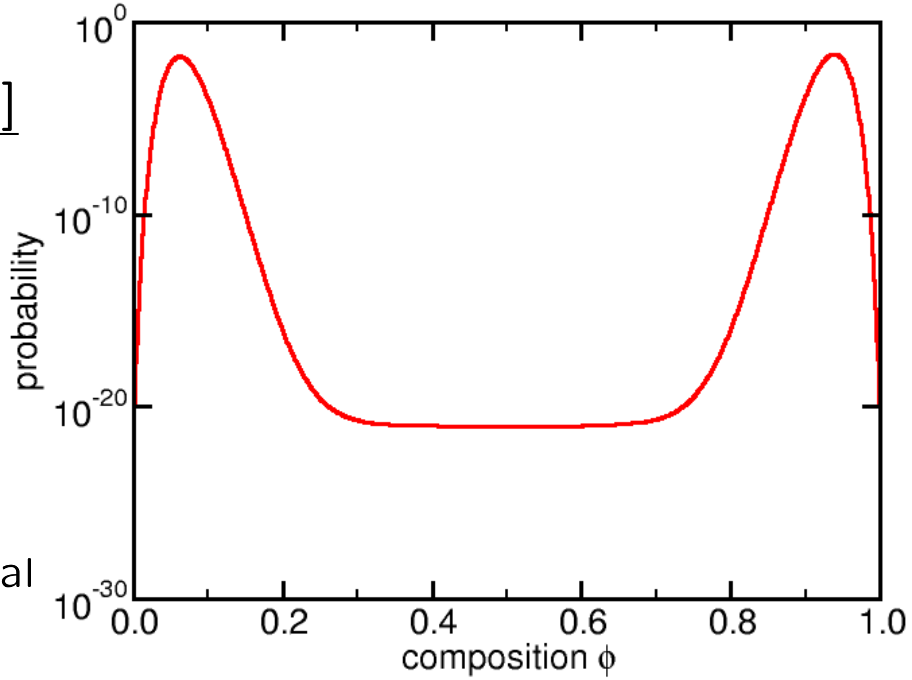
window size:

- smaller windows are easier to sample because weight does not vary
- larger windows might allow for additional relaxation modes and prevent sampling difficulties

successive umbrella sampling

simulate intervals [j, j+1] of A-polymers

$$P[i] \sim \Pi_{j<i}\frac{P[j+1]}{P[j]} \approx \Pi_{j<i}\frac{H[j+1]}{H[j]}$$



error:

$$(\Delta P[n])^2 \sim n\left(\Delta\frac{H[j+1]}{H[j]}\right)^2 \sim n \underbrace{\frac{n}{\#MCS}}_{\text{time spent in interval}}$$

- in the absence of sampling difficulties, similar to a simulation of complete interval with perfect reweighting

$$(\Delta P[n])^2 \sim \frac{1}{\text{tunnellings } 1\leftrightarrow n} \sim \frac{n^2}{\#MCS}$$

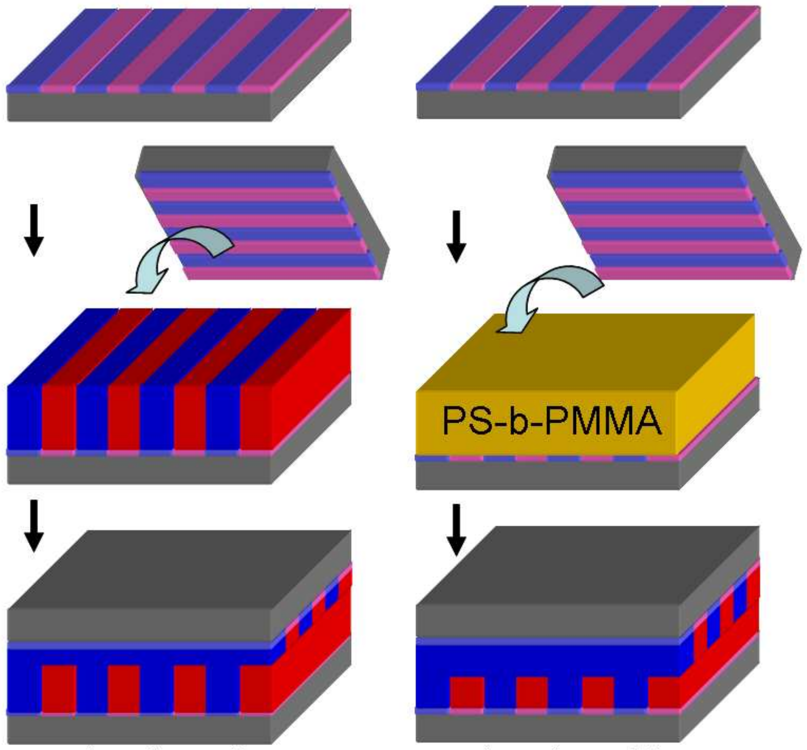
- error allows for identification of sampling errors

➡ total error does not depend on the window size

Virnau, Müller JCP **120**, 10925 (2004)

interface localization delocalization-transition

morphology between apposing stripe patterns



boundaries stabilize a twist grain boundary, which resembles Scherk's first surface

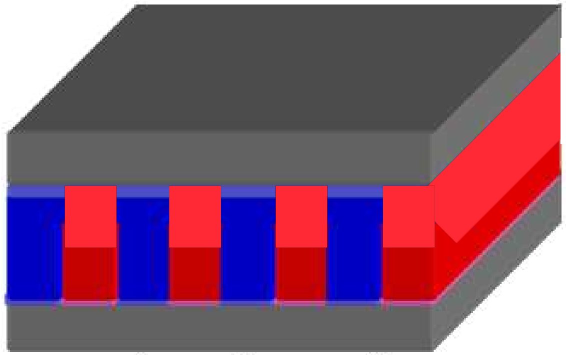
Liu, Ramirez-Hernandez, Yoshida, Nygard, Satapathy, Bunk, de Pablo, Nealey, PRL 108, 065502 (2012)

question: location of the grain boundary ?

➡ control of three-dimensional morphology

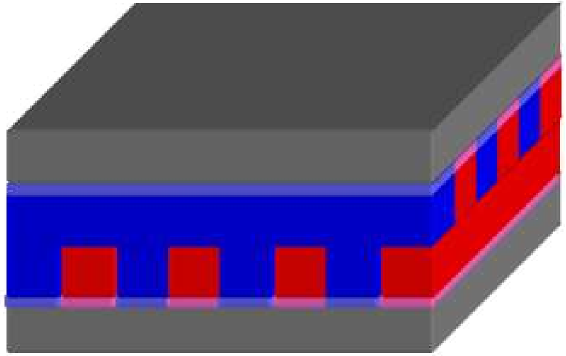
analogy between behavior of twist grain boundary and wetting in a film with strictly anti-symmetric boundaries (interface localization-delocalization)
control via geometric parameters of the system

interface localization delocalization-transition



localized state:

twist-grain boundary localized close top or bottom surface (partial wetting)



delocalized state:

twist-grain boundary fluctuates around the center of the film (repelled by both surfaces, complete wetting)

➡ use position, *x*, of grain boundary as order parameter

mesoscopic free energy:

$$\frac{\Delta F(x)}{A} = \gamma_{\mathrm{b}}(\Lambda) + \gamma_{\mathrm{t}}(\Lambda) + \gamma(\alpha)$$

surface and interface tensions (Young)

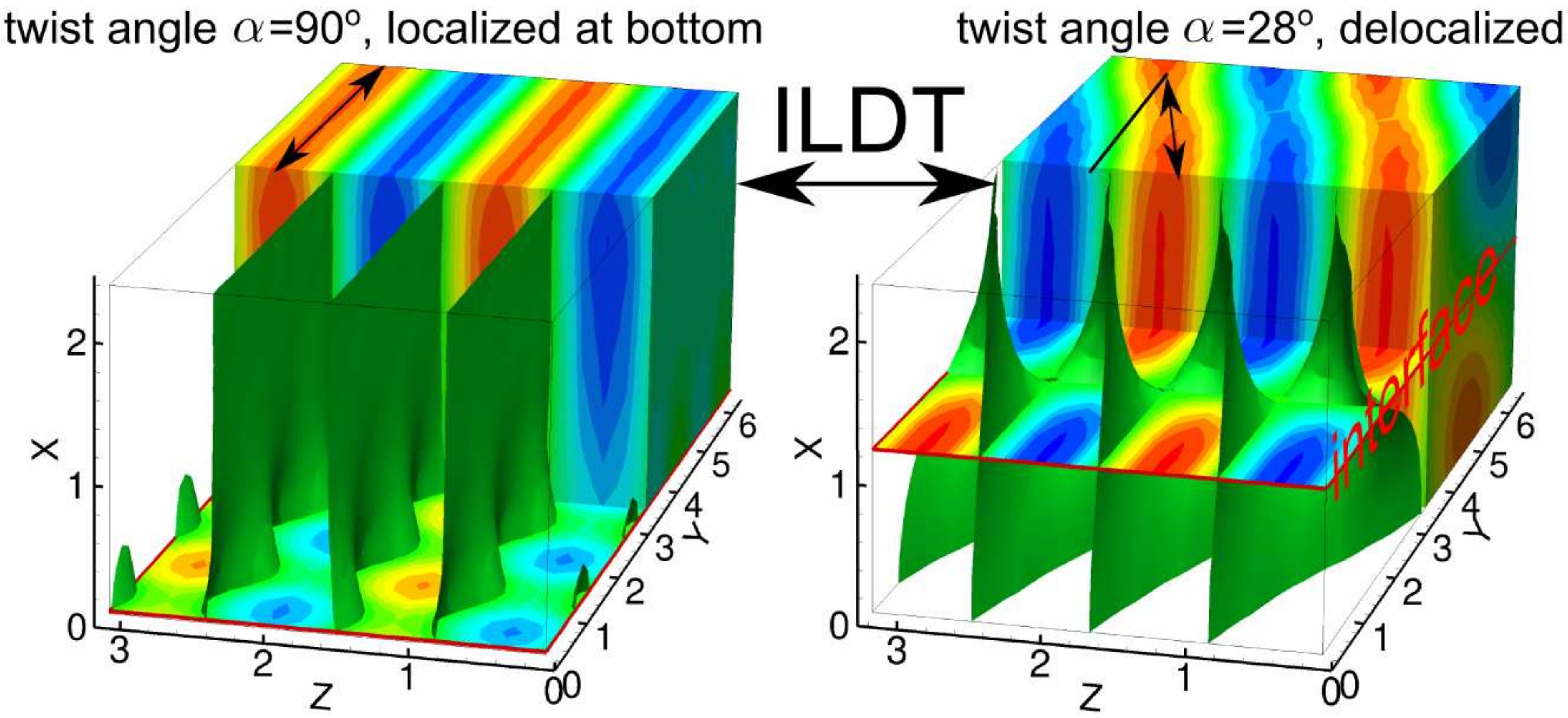
$$+ \frac{1}{2} B(\lambda_{\mathrm{b}} - \lambda_0)^2 x + \frac{1}{2} B(\lambda_{\mathrm{t}} - \lambda_0)^2 (D - x)$$

stretch/compression (μ)

$$+ g_{\mathrm{b}}(x) + g_{\mathrm{t}}(D - x)$$

short-range interface potential due to distortion

interface localization delocalization-transition



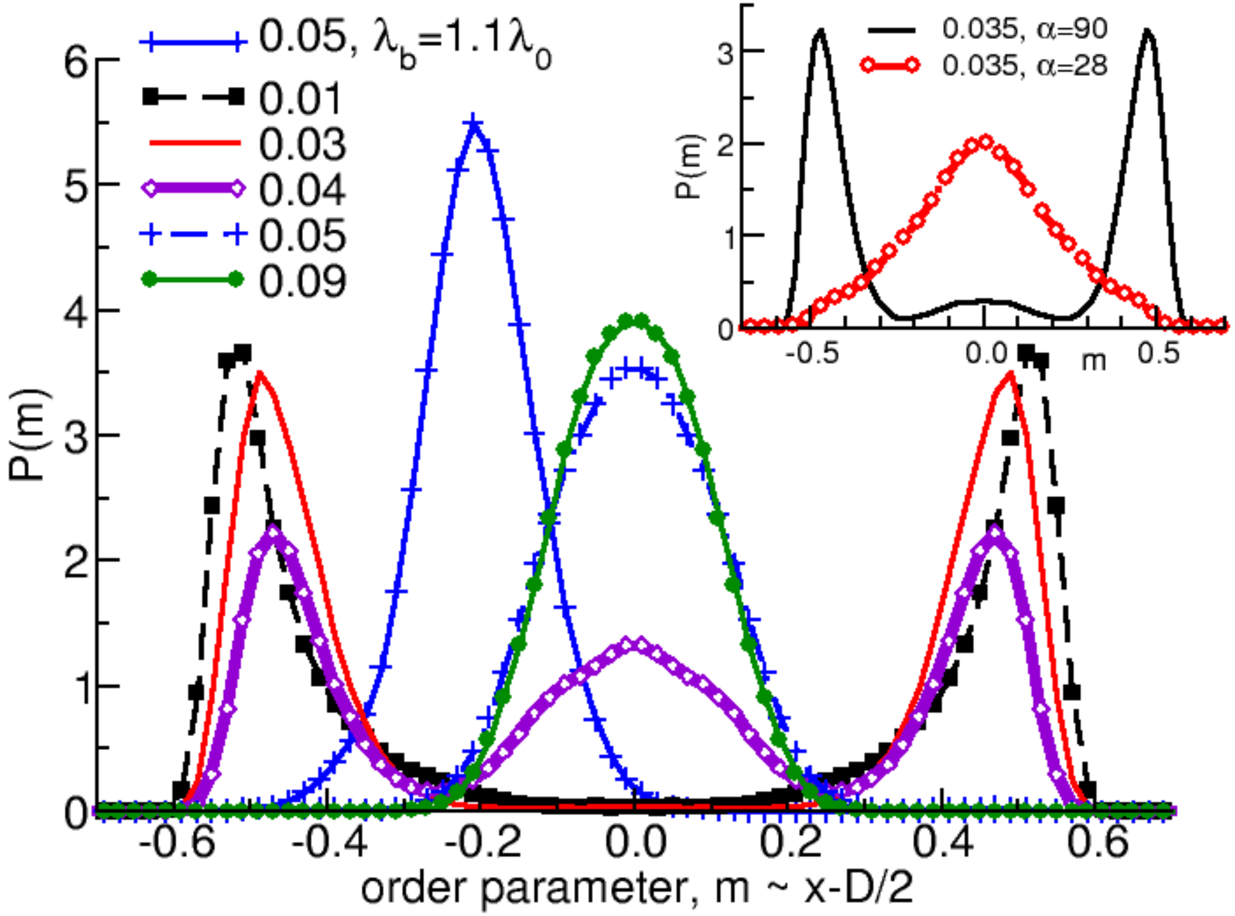
twist angle α=90°, localized at bottom

twist angle α=28°, delocalized

$$\frac{\Delta F(x)}{A} = \gamma_{\mathrm{b}}(\Lambda) + \gamma_{\mathrm{t}}(\Lambda) + \gamma(\alpha)$$
$$+ \frac{1}{2}B(\lambda_{\mathrm{b}} - \lambda_0)^2 x + \frac{1}{2}B(\lambda_{\mathrm{t}} - \lambda_0)^2 (D - x)$$
$$+ g_{\mathrm{b}}(x) + g_{\mathrm{t}}(D - x)$$

Müller, PRL in press

interface localization delocalization-transition

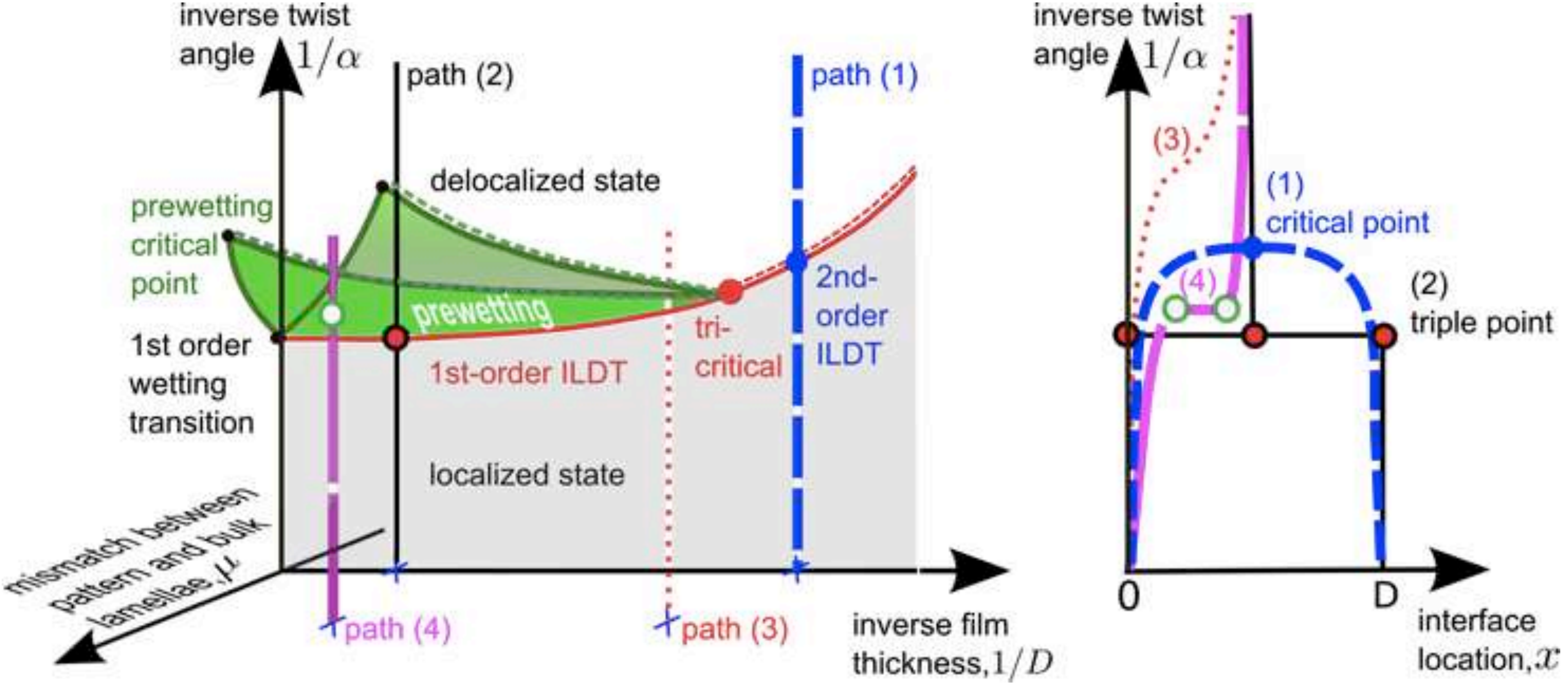


$$\frac{\Delta F(x)}{A} = \gamma_b(\Lambda) + \gamma_t(\Lambda) + \gamma(\alpha) + \frac{1}{2}B(\lambda_b - \lambda_0)^2 x + \frac{1}{2}B(\lambda_t - \lambda_0)^2(D-x) + g_b(x) + g_t(D-x)$$

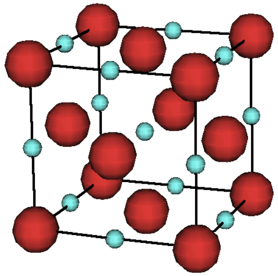
$D = 2.468R_{e0}$, $L_y = 2L_z = 2\lambda_0$

Müller, PRL in press

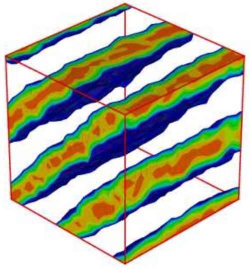
interface localization delocalization-transition



- analogy between behavior of twist grain boundary and wetting in a film with strictly anti-symmetric boundaries (interface localization-delocalization)
- control via geometric parameters of the system ($T \sim 1/\alpha$ and $\mu \sim (\lambda-\lambda_0)^2$)

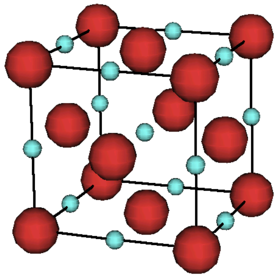


crystallization vs self-assembly

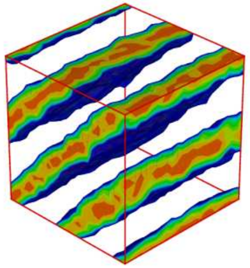


order parameter:

Fourier mode of density fluctuation ideal ordered state: ideal crystal (T=0) disordered state: ideal gas	Fourier mode of composition fluctuation SCFT solution homogeneous fluid/melt
ordered state: particles vibrate around ideal lattice positions	ordered phase: composition fluctuates around reference state (SCFT solution), but ***molecules diffuse*** (liquid)
Einstein crystal is reference state use thermodynamic integration wrt to uniform, harmonic coupling of particles to ideal position (Frenkel & Ladd)	***no simple reference state*** for self-assembled morphology



crystallization vs self-assembly



order parameter:

Fourier mode of density fluctuation — Fourier mode of composition fluctuation

ideal ordered state: ideal crystal (T=0) — SCFT solution

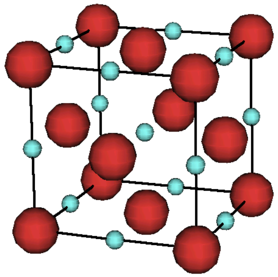
disordered state: ideal gas — homogeneous fluid/melt

ordered state: particles vibrate around ideal lattice positions

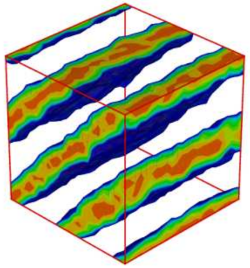
ordered phase: composition fluctuates around reference state (SCFT solution), but ***molecules diffuse*** (liquid)

free energy per molecule N $k_B T$
relevant free-energy differences 10^{-3} $k_B T$

➡ absolute free energy must be measured with a relative accuracy of 10^{-5}



crystallization vs self-assembly



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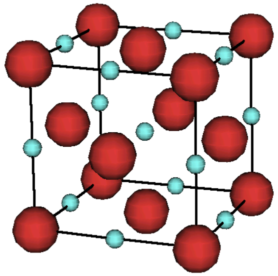
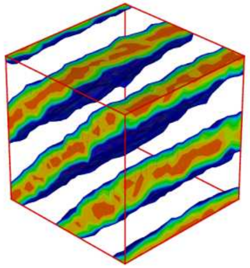
free energy per molecule N $k_B T$
relevant free-energy differences 10^{-3} $k_B T$

➡ absolute free energy must be measured with a relative accuracy of 10^{-5}
measure free energy differences by **reversibly transforming one structure into another** (10^{-3} relative accuracy needed)



crystallization vs self-assembly



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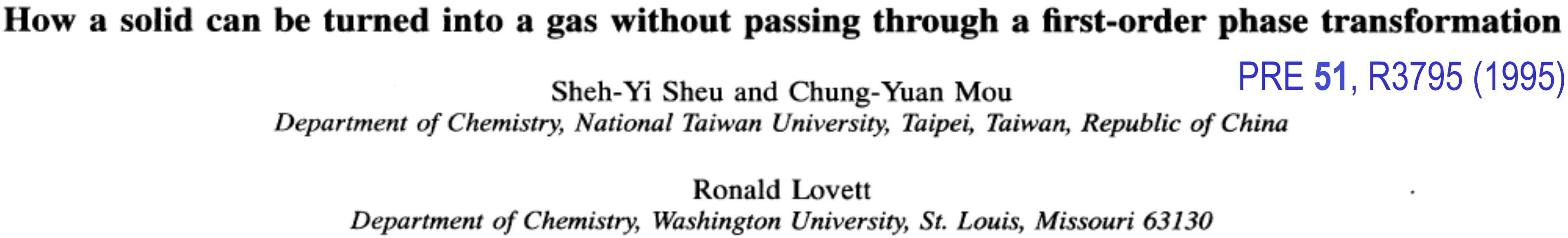


How a solid can be turned into a gas without passing through a first-order phase transformation

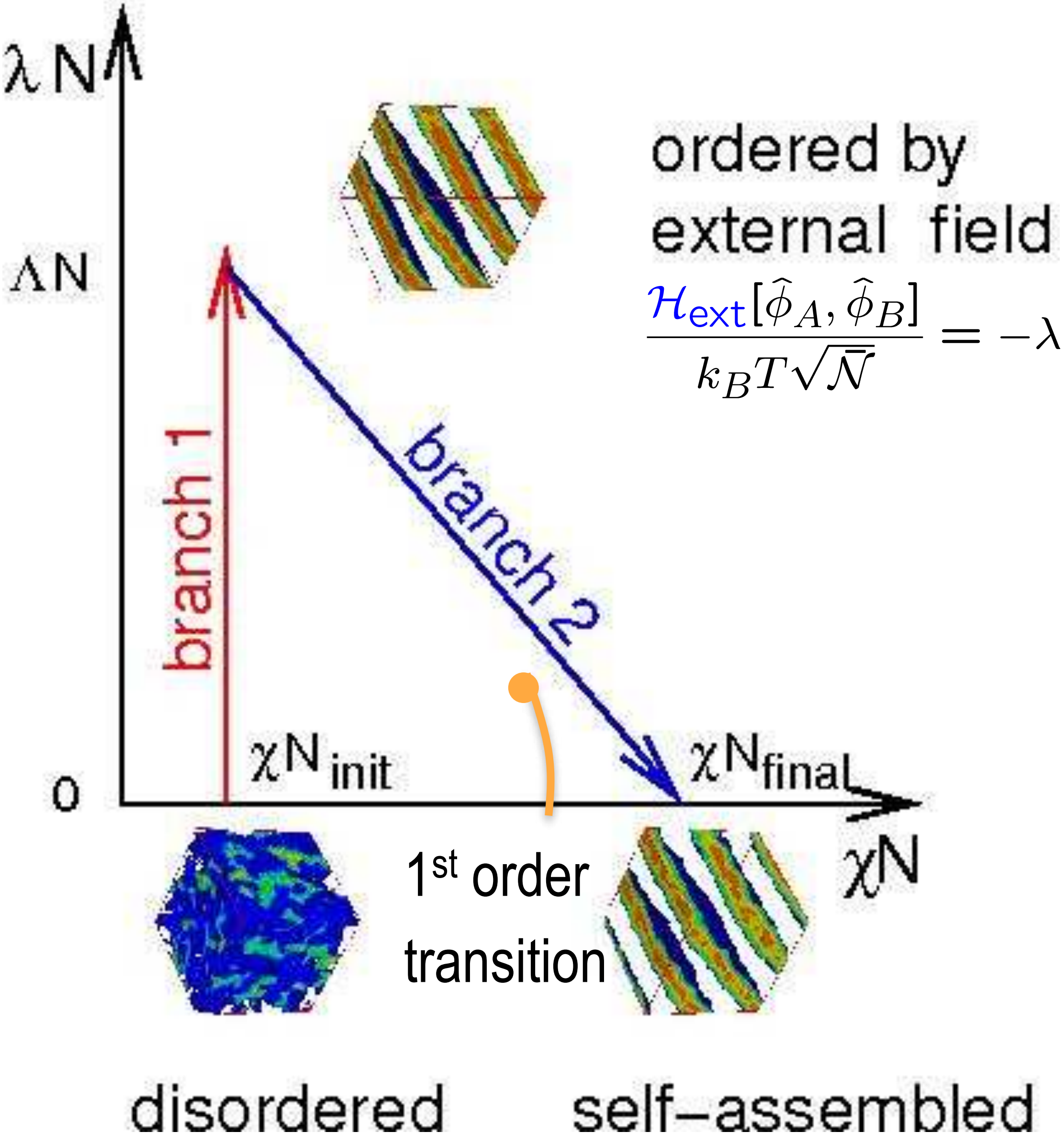
Sheh-Yi Sheu and Chung-Yuan Mou
Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Ronald Lovett
Department of Chemistry, Washington University, St. Louis, Missouri 63130

PRE **51**, R3795 (1995)

see also Grochola, JCP **120**, 2122 (2004)

calculating free energy differences



intermediate state:
independent chains in static, external field (SCFT)

$$\frac{\mathcal{H}_{\text{ext}}[\hat{\phi}_A,\hat{\phi}_B]}{k_BT\sqrt{\bar{\mathcal{N}}}} = -\lambda N \int \frac{\mathrm{d}^3\mathbf{r}}{R_{\text{eo}}^3}\, h(\mathbf{r}) \left[\hat{\phi}_A(\mathbf{r}) - \hat{\phi}_B(\mathbf{r})\right]$$

branch 1:
“non-interacting
= no collective phenomena”

branch 2:
ideally: no structural change
condition for ordering field

$\bar{\mathcal{N}} = 14\,884,\ V = (4.88R_{\text{e}})^3$

$n = 13\,241,\ N = 32$

$\Delta L = 0.19675R_{\text{e}}$

Müller, Daoulas, JCP **128**, 024903 (2008)

free energy difference via TDI

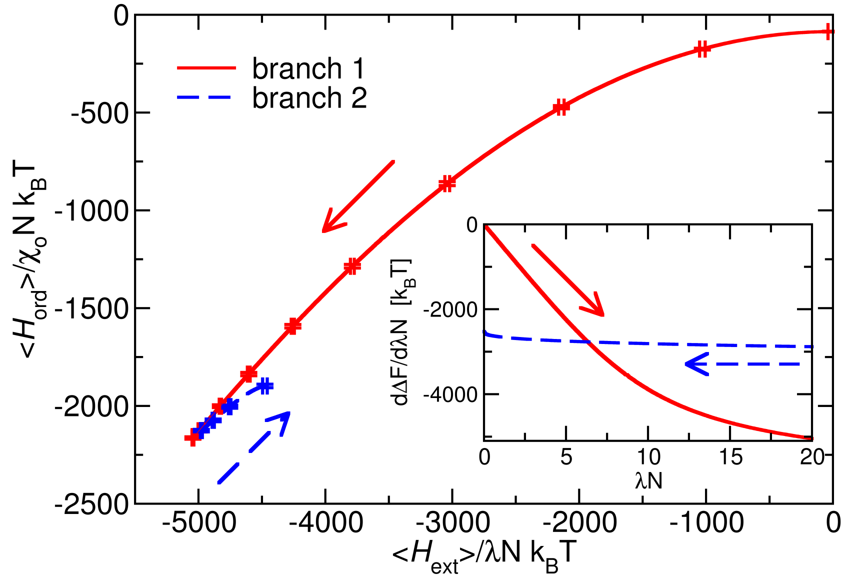
$$\mathcal{H}_{\text{nb}} = \mathcal{H}_{\text{liq}} + \mathcal{H}_{\text{ord}} + \mathcal{H}_{\text{ext}}$$

$$\frac{\mathcal{H}_{\text{ord}}}{nk_BT} = -\chi_{\text{o}} N f_{\text{ord}}[\phi] \quad \text{with} \quad \phi = \phi_A - \phi_B$$

$$\frac{\mathcal{H}_{\text{ext}}}{nk_BT} = -\frac{\lambda N}{V} \int_V \mathrm{d}^3\mathbf{r}\; h(\mathbf{r})\phi(\mathbf{r})$$

$$F = -k_BT \ln \int \mathcal{D}[\{r\}]\, \exp\left[-\frac{\mathcal{H}_{\text{b}} + \mathcal{H}_{\text{liq}} + \mathcal{H}_{\text{ord}} + \mathcal{H}_{\text{ext}}}{k_BT}\right]$$

$$\frac{\partial F}{\partial \lambda N} = -k_BT \frac{\int \mathcal{D}[\{r\}]\, -\frac{1}{k_BT}\frac{\partial \mathcal{H}_{\text{ext}}}{\partial \lambda N} \exp\left[-\frac{\mathcal{H}_{\text{b}}+\mathcal{H}_{\text{liq}}+\mathcal{H}_{\text{ord}}+\mathcal{H}_{\text{ext}}}{k_BT}\right]}{\int \mathcal{D}[\{r\}]\, \exp\left[-\frac{\mathcal{H}_{\text{b}}+\mathcal{H}_{\text{liq}}+\mathcal{H}_{\text{ord}}+\mathcal{H}_{\text{ext}}}{k_BT}\right]} = \left\langle \frac{\mathcal{H}_{\text{ext}}}{\lambda N} \right\rangle$$



optimal choice of external field (Sheu et al):

structure does not change along 2nd branch

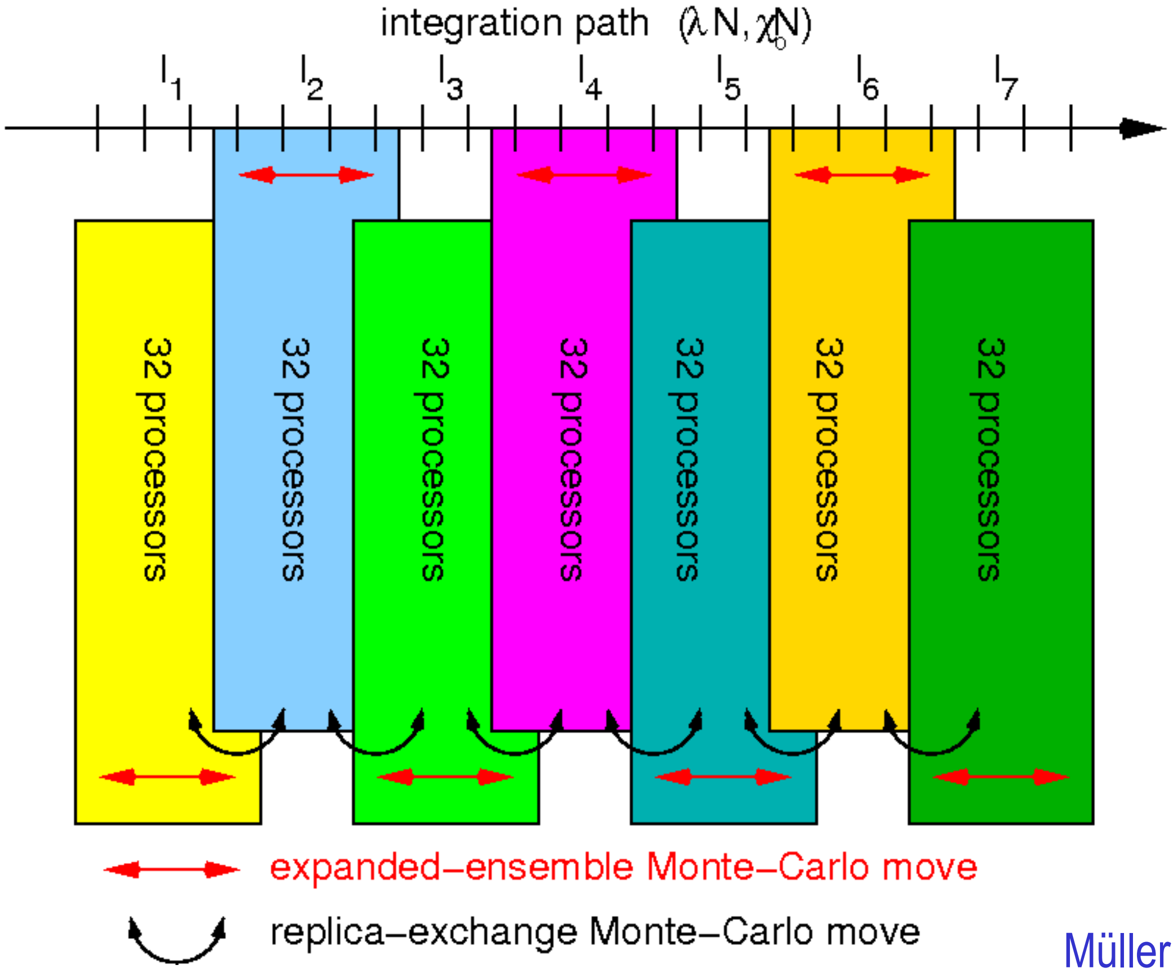
$$-\lambda N h_{\text{eff}}(\mathbf{r}) = \frac{V}{nk_BT}\left(\frac{\delta \mathcal{H}_{\text{ord}}}{\delta\phi(\mathbf{r})} + \frac{\delta \mathcal{H}_{\text{ext}}}{\delta\phi(\mathbf{r})}\right)$$

$$= -\lambda N h(\mathbf{r}) - \chi_{\text{o}} N \frac{\delta f_{\text{ord}}}{\delta\phi(\mathbf{r})}$$

SCFT: $\chi_{\text{o}} N(\lambda N) = \chi_{\text{o}} N(0) - 2\lambda N$

TDI vs expanded ensemble/replica exchange

$$\mathcal{Z} \sim \prod_{j=1}^{M_r} \sum_{\lambda_i N \in I_j} \frac{e^{\eta(\lambda_i N)}}{n!} \int \prod_{i=1}^{n} \mathcal{D}[\mathbf{r}_i(s)]\; e^{-\frac{\mathcal{H}_{\mathrm{b}}+\mathcal{H}_{\mathrm{liq}}+\mathcal{H}_{\mathrm{ord}}+\mathcal{H}_{\mathrm{ext}}}{k_B T}}$$



only replica exchange is impractical because one would need several 100 configurations

at initial stage, where weights are unknown ($\Delta F \sim 10^4 k_B T$), replica exchange guarantees more uniform sampling

expanded ensemble technique is useful because it provides an error estimate

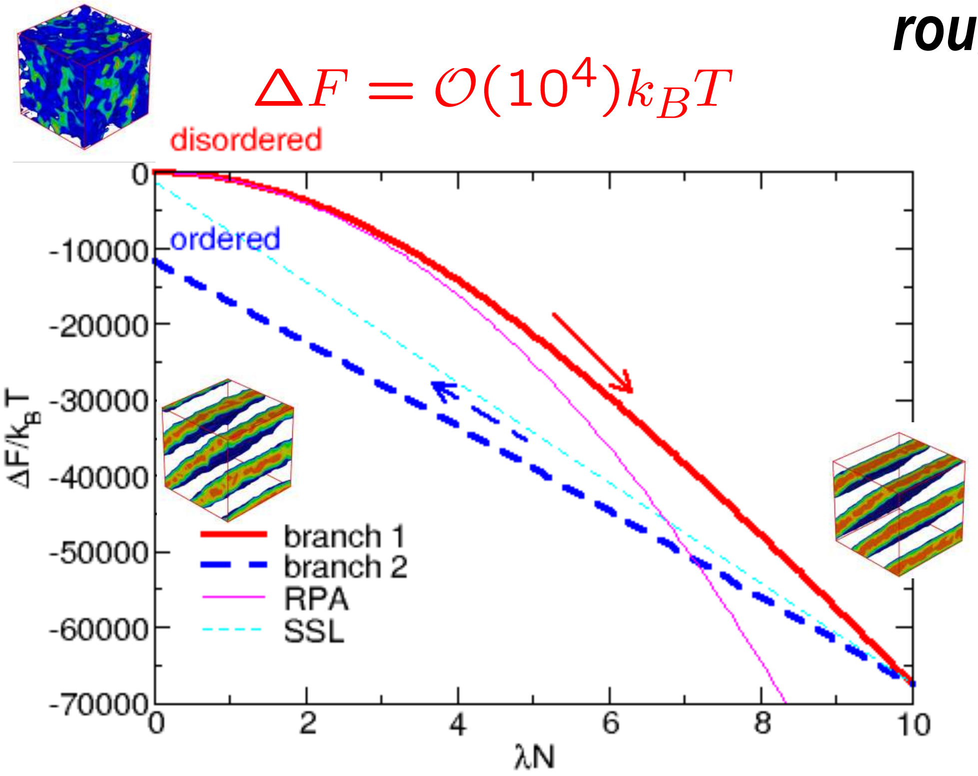
Müller, Daoulas, Norizoe, PCCP **11**, 2087 (2009)

accuracy of the method

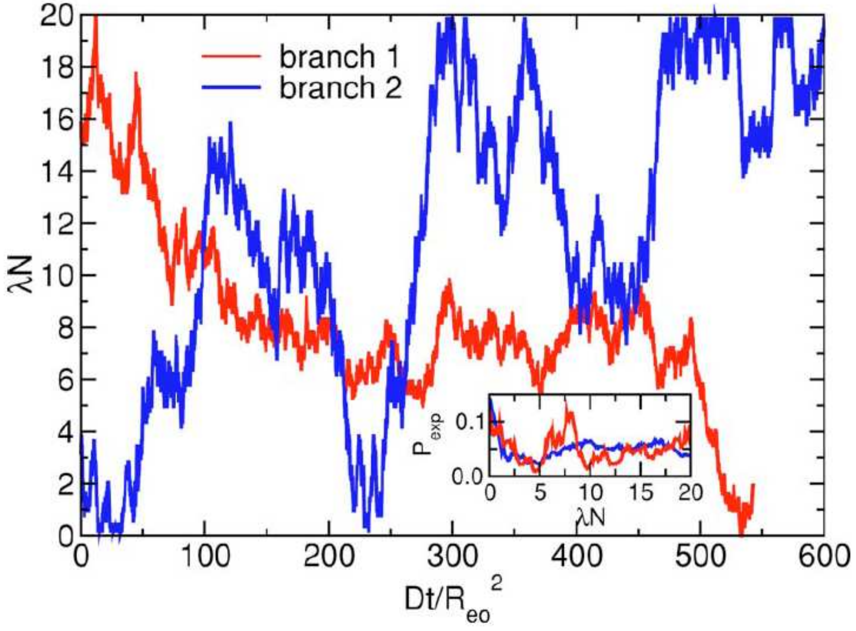
no kinetic barrier, ie no phase transition

roughly equal probability

$\Delta F = \mathcal{O}(10^4) k_B T$



$\delta \Delta F = \mathcal{O}(10^1) k_B T$



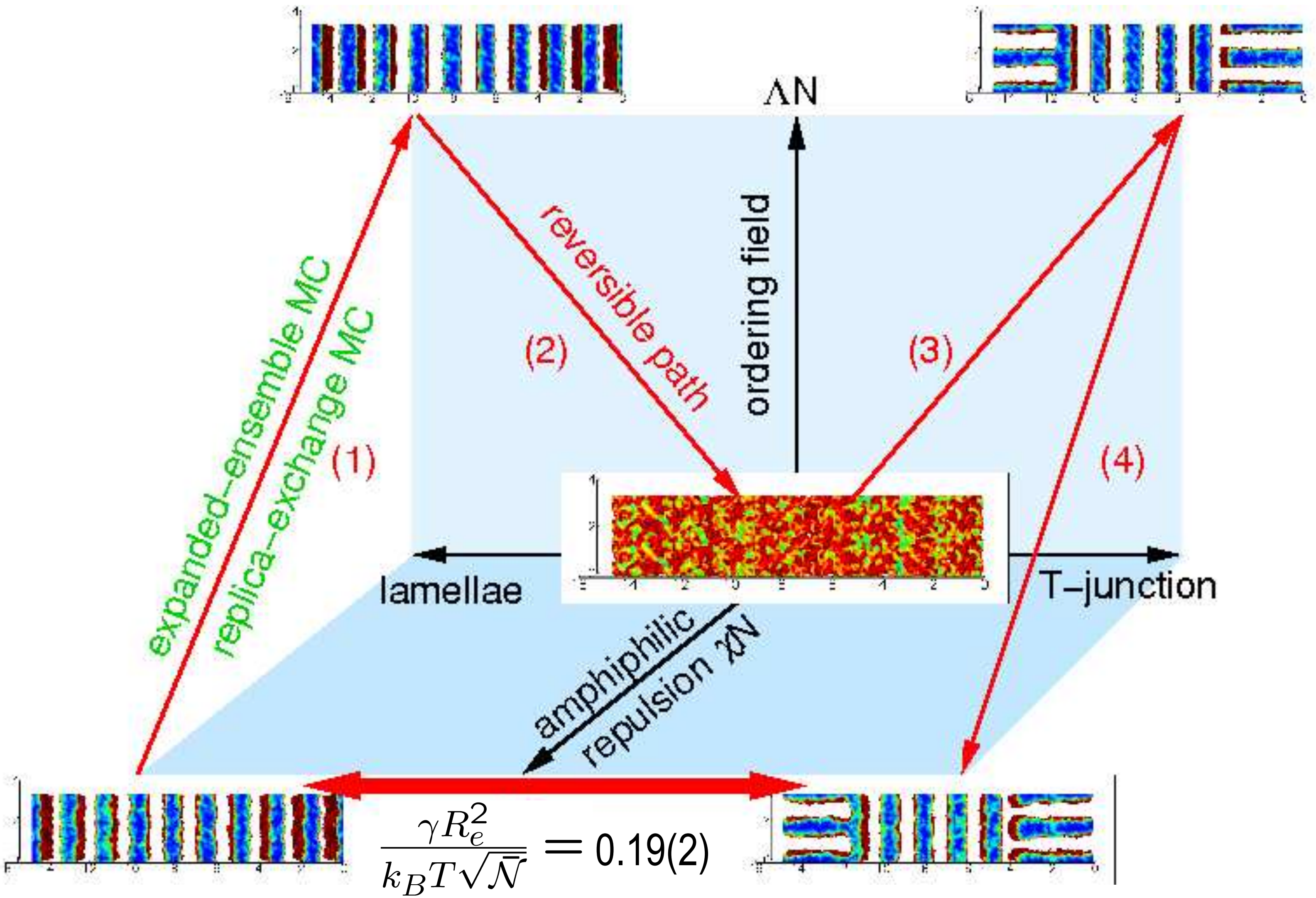
$$\Delta F_1 = \int_0^{\Lambda N} \mathrm{d}\lambda N \, \frac{\langle \mathcal{H}_{\mathrm{ext}} \rangle}{\lambda N} \bigg|_{\chi_o N_{\mathrm{init}}}$$

reweighting technique removes large free energy change along the path

probability distribution of reweighted simulation estimates accuracy

kinetics demonstrates the absence of first-order transition

free-energy calculations: grain boundaries

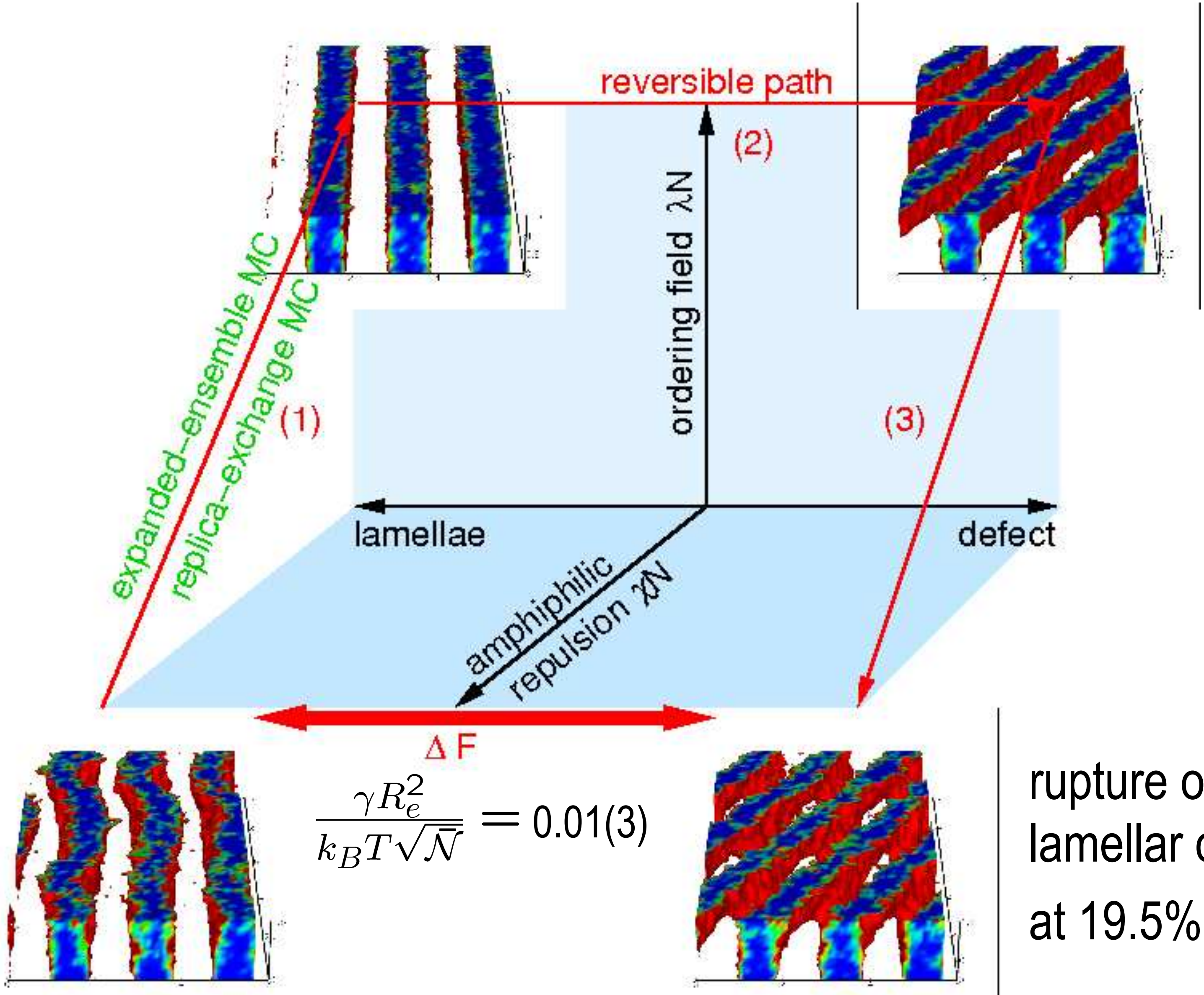


$$\frac{\gamma R_e^2}{k_B T\sqrt{\bar{\mathcal{N}}}} = 0.19(2)$$

SCF theory: $\frac{\gamma R_e^2}{k_B T\sqrt{\bar{\mathcal{N}}}} = 0.21$

Duque, Katsov, Schick, JCP **117**, 10315 (2002)
Müller, Daoulas, Norizoe, PCCP **11**, 2087 (2009)

reconstruction of soft morphology at patterned surface

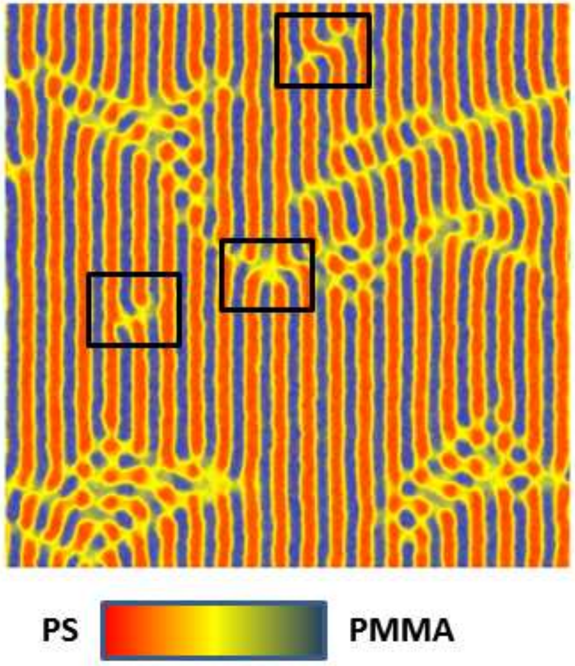


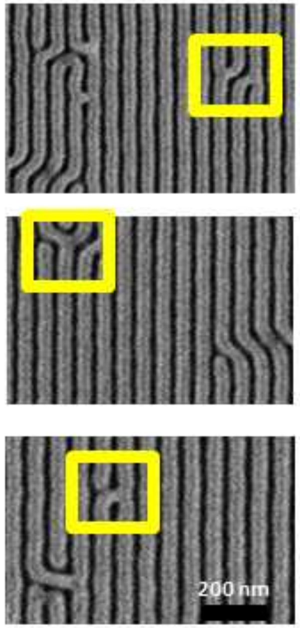
$$\frac{\gamma R_e^2}{k_B T \sqrt{\bar{\mathcal{N}}}} = 0.01(3)$$

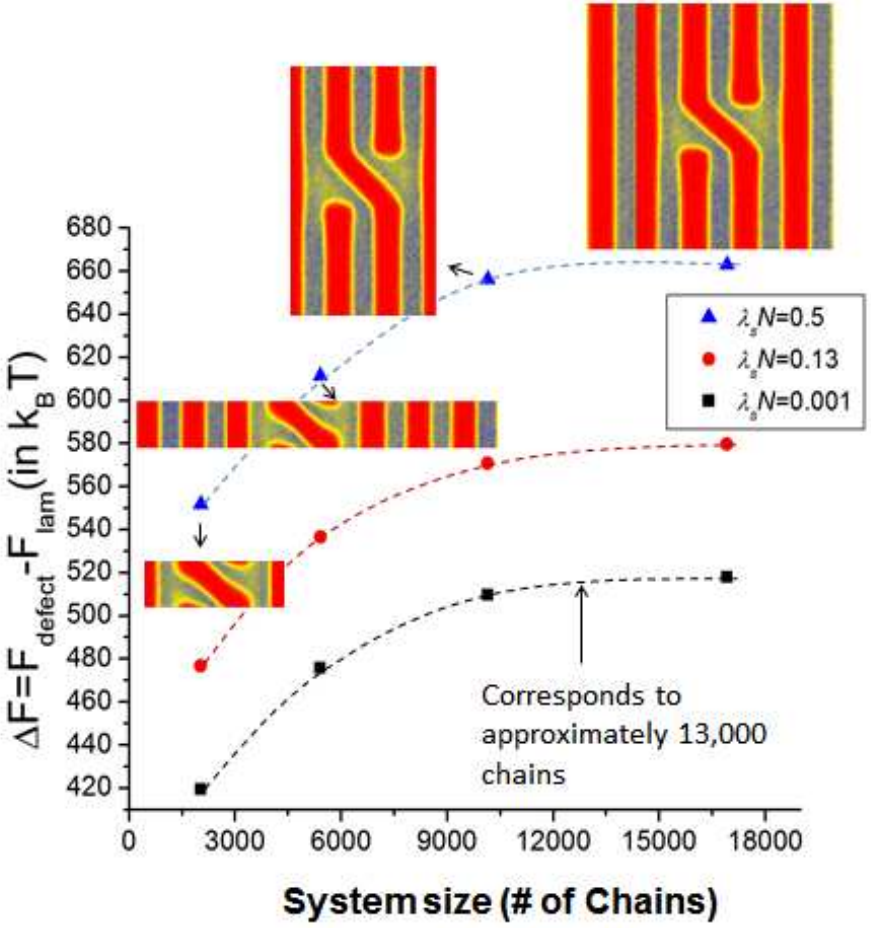
rupture of lamellar ordering at 19.5% stretch

Müller, Daoulas, Norizoe, PCCP **11**, 2087 (2009)

defect free energy for lamellar pattern replication







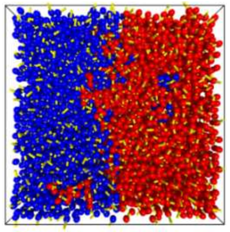
naïve estimate:

$$
\begin{aligned}
\Delta F &= \gamma A \\
&\approx \frac{\sqrt{\bar{N}}k_BT}{{R_{eo}}^2} \times 2L_sD_o \\
&\approx 128k_BT \times 3.6 = 460k_BT
\end{aligned}
$$

➡ **extremely small defect density in equilibrium**

Nagpal, Müller, Nealey, de Pablo, ACS Macro Letters **1**, 418 (2012)

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), ∞
$m(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$
$\rho(\mathbf{r}) = \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) \approx \rho_o$

model definition:

intra- and intermolecular potentials
(here: soft, coarse-grained model, SCMF)
single-chain dynamics
(here: Rouse dynamics)
segmental friction, ζ

free-energy functional, $\mathcal{F}_{\rm GL}[m(\mathbf{r})]$
(Ginzburg-Landau-de Gennes or Ohta-Kawasaki)
time-dependent GL theory
(model B according to Hohenberg & Halperin)
Onsager coefficient, $\Lambda(\mathbf{r} - \mathbf{r}')$

projection:

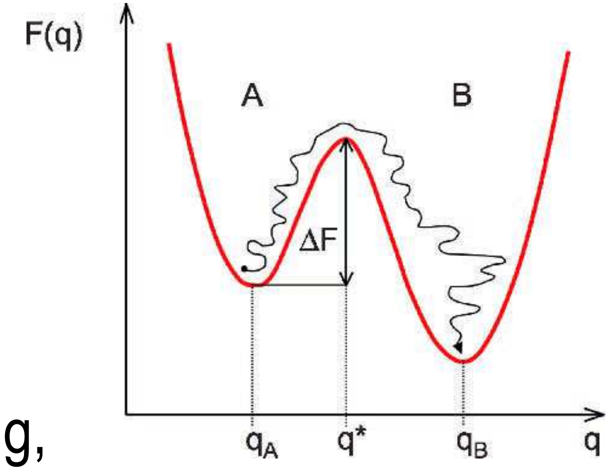
$$\hat\phi_A(\mathbf{r}) \text{“} = \text{”} \frac{1}{\rho_o} \sum_{i=1}^{n_A} \sum_{s=1}^{N} \delta\left(\mathbf{r} - \mathbf{r}_i(s)\right)$$

$$\frac{\mathcal{F}[m]}{k_BT} \equiv - \ln \int \mathcal{D}[\{\mathbf{r}_{i,s}\}]\, e^{-\frac{\mathcal{H}(\{\mathbf{r}_{i,s}\})}{k_BT}} \delta[m - (\hat\phi_A - \hat\phi_B)]$$

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

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, …

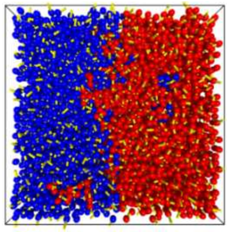
Dellago, Bolhuis, Adv. Polym. Sci **221**, 167 (2008)

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

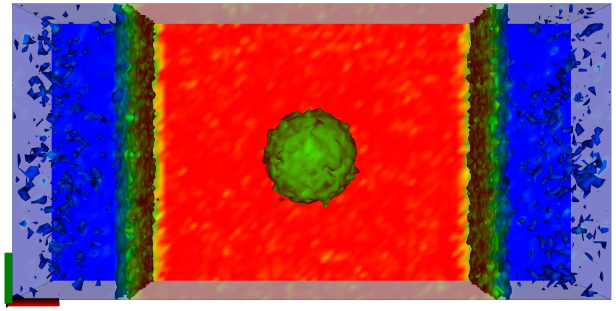
bonded interactions (stiff) $f_\mathrm{b} \sim \frac{k_BT}{b} \sim \frac{k_BT\sqrt{N}}{R_\mathrm{eo}}$

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

➡ **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 $\mu^\star = \frac{R_\mathrm{eo}}{R}\frac{\gamma^\star}{m_\mathrm{coex}}$

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

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

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

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\Delta_\mathrm{o}}{N\sqrt{\bar{N}}} = -\frac{2\pi}{\tau}(1-m^2_\mathrm{coex})\frac{\gamma {R_\mathrm{eo}}^2}{k_BT\sqrt{\bar{N}}}$$

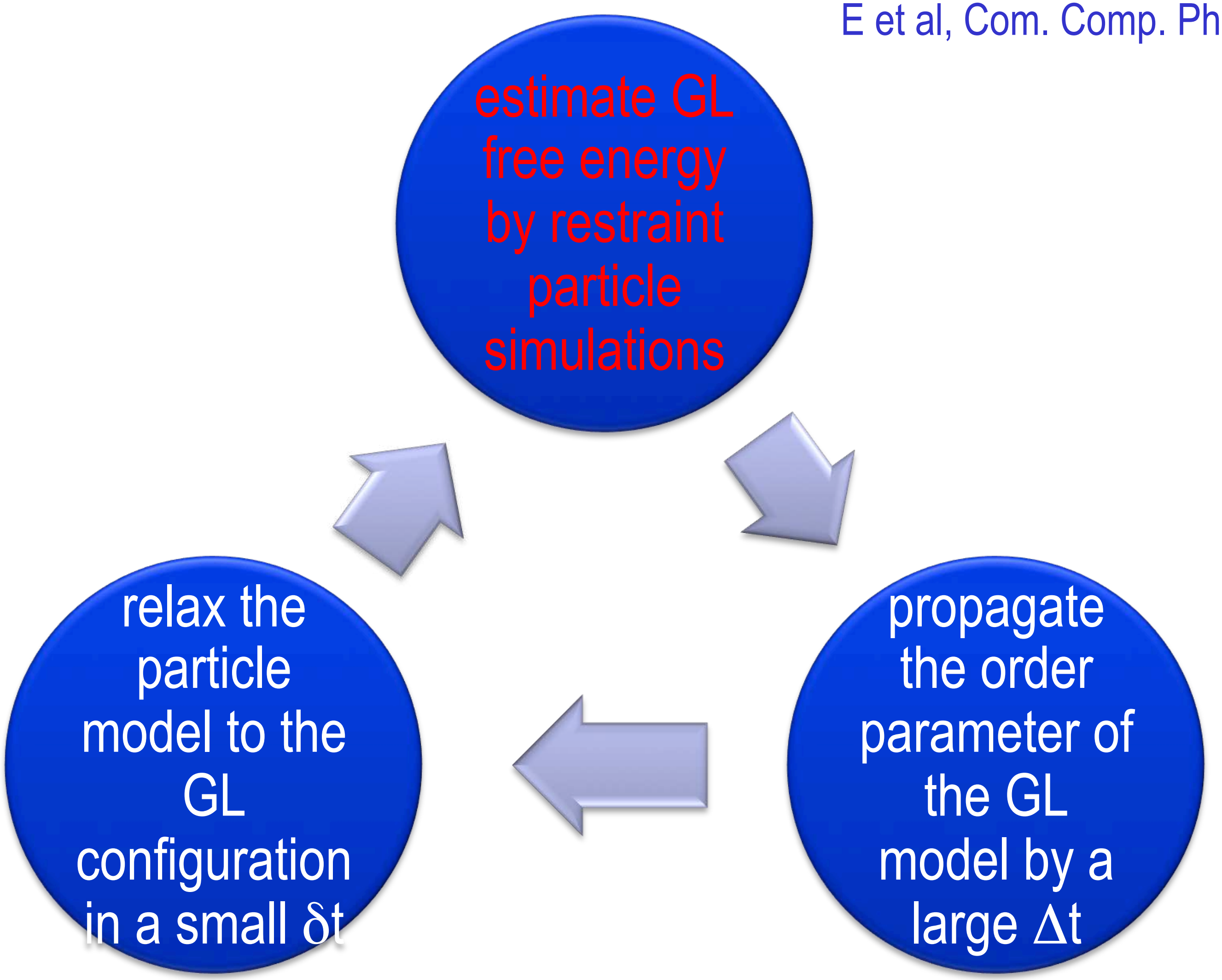
$$1-m_\mathrm{coex} \approx 2\exp(-\chi_\mathrm{o}N)$$

- 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)



estimate GL free energy by restraint particle simulations

propagate the order parameter of the GL model by a large Δt

relax the particle model to the GL configuration in a small δt

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, $m(\mathbf{r})$)

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

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

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

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

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

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

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

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

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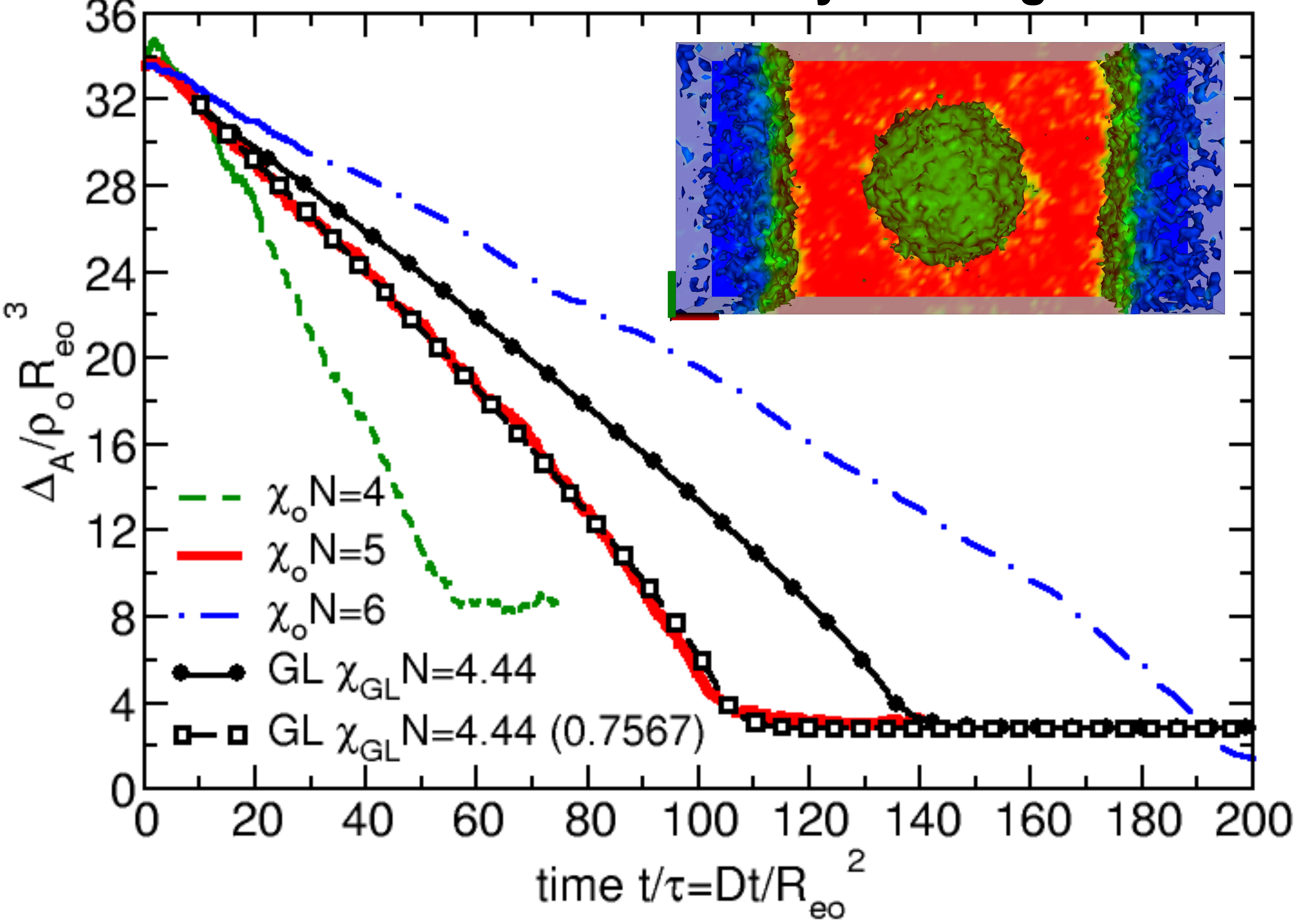
make an **Ansatz for the continuum description** with a few parameters $\{a_r\}, a_g$
determine parameters by comparing $\mu(\mathbf{r}|m)$ with result of Ansatz

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



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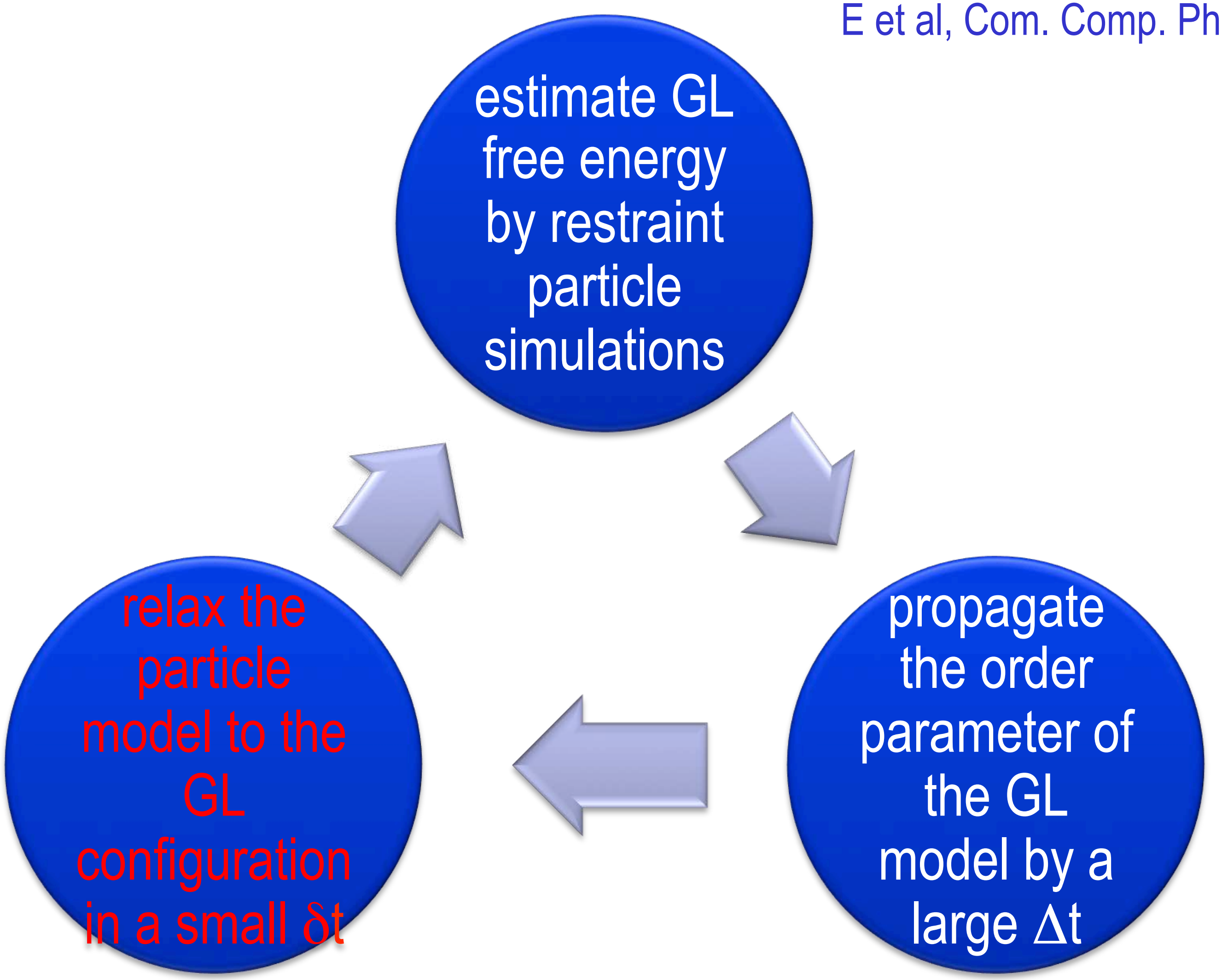
E et al, Com. Comp. Phys **2**, 367 (2007)



estimate GL free energy by restraint particle simulations

propagate the order parameter of the GL model by a large Δt

relax the particle model to the GL configuration in a small δt

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

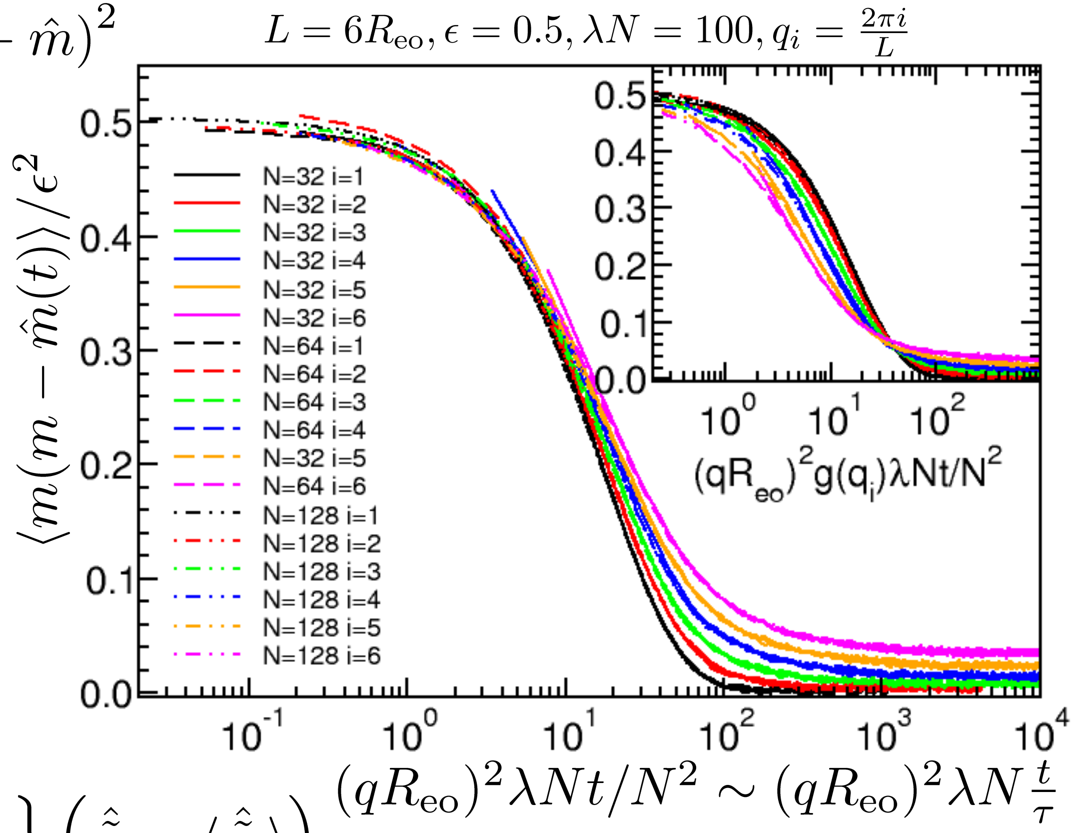
Onsager coefficient from relaxation of simulations

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

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

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



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

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

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

➡ constraint system exponentially relaxes towards $\langle \tilde{\hat{m}} \rangle = \frac{\tilde{m}}{1 + \frac{1}{2\lambda N h(\mathbf{q})}}$

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 $\lambda N \sim \frac{V\sqrt{N}}{R_{\mathrm{eo}}^3}$

forces due to the restraint must be smaller than the original forces that dictate the intrinsic kinetics of the particle model

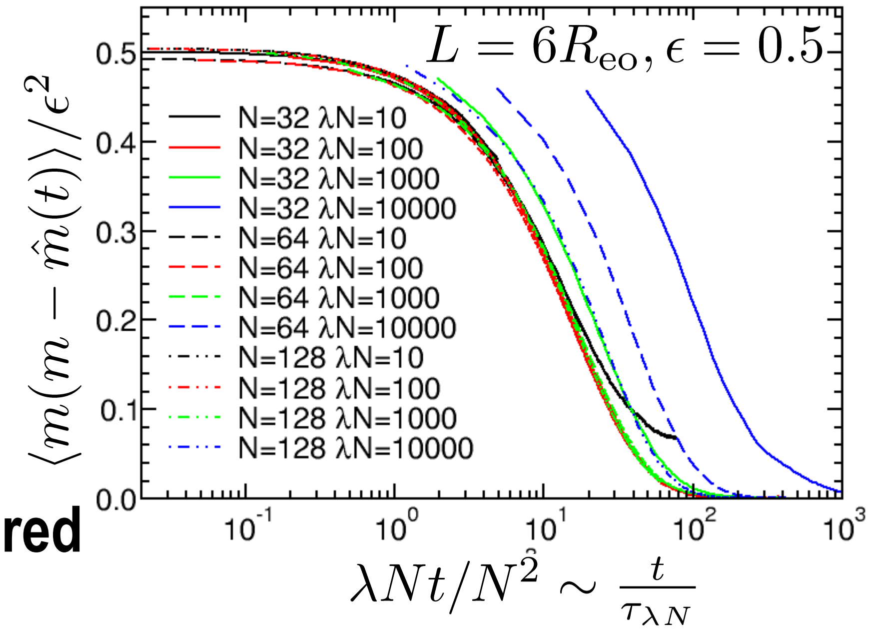
bonded force per segment $f_{\mathrm{b}} \sim \frac{k_B T}{b} \sim \frac{k_B T \sqrt{N}}{R_{\mathrm{eo}}}$

non-bonded, thermodynamic force $f_{\mathrm{nb}} \sim \frac{k_B T \chi}{w} \sim \frac{k_B T \chi N}{R_{\mathrm{eo}}} N^{-1}$

restraint force $f_{\lambda N} \sim \frac{k_B T \lambda}{\Delta L} \sim \frac{k_B T \lambda N}{R_{\mathrm{eo}}} N^{-1/2}$

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

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

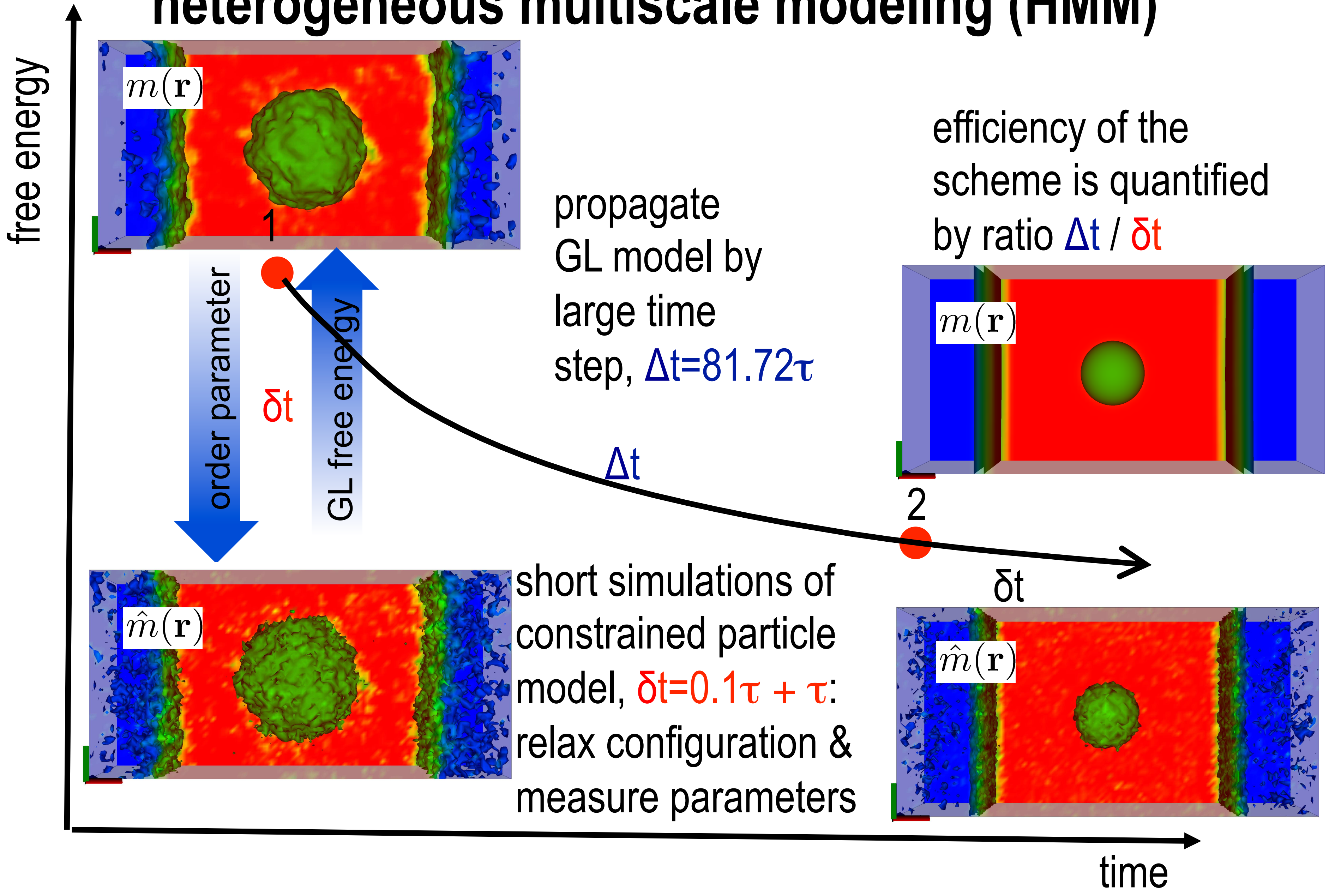


➡

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

➡ **additional relaxation τ may be required**

heterogeneous multiscale modeling (HMM)

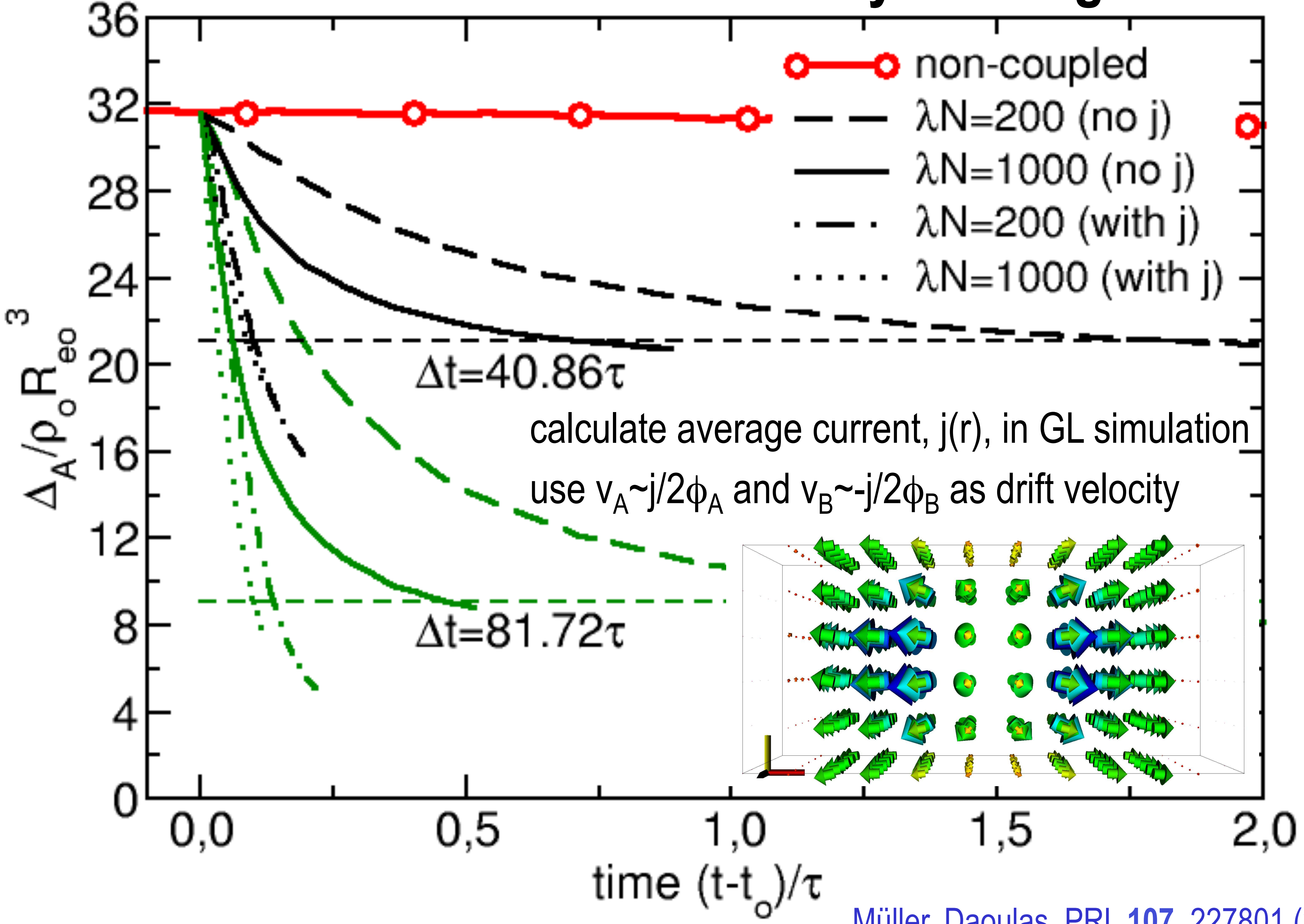


propagate
GL model by
large time
step, Δt=81.72τ

efficiency of the
scheme is quantified
by ratio Δt / δt

short simulations of
constrained particle
model, δt=0.1τ + τ:
relax configuration &
measure parameters

numerical results: Lishitz-Slyozov regime

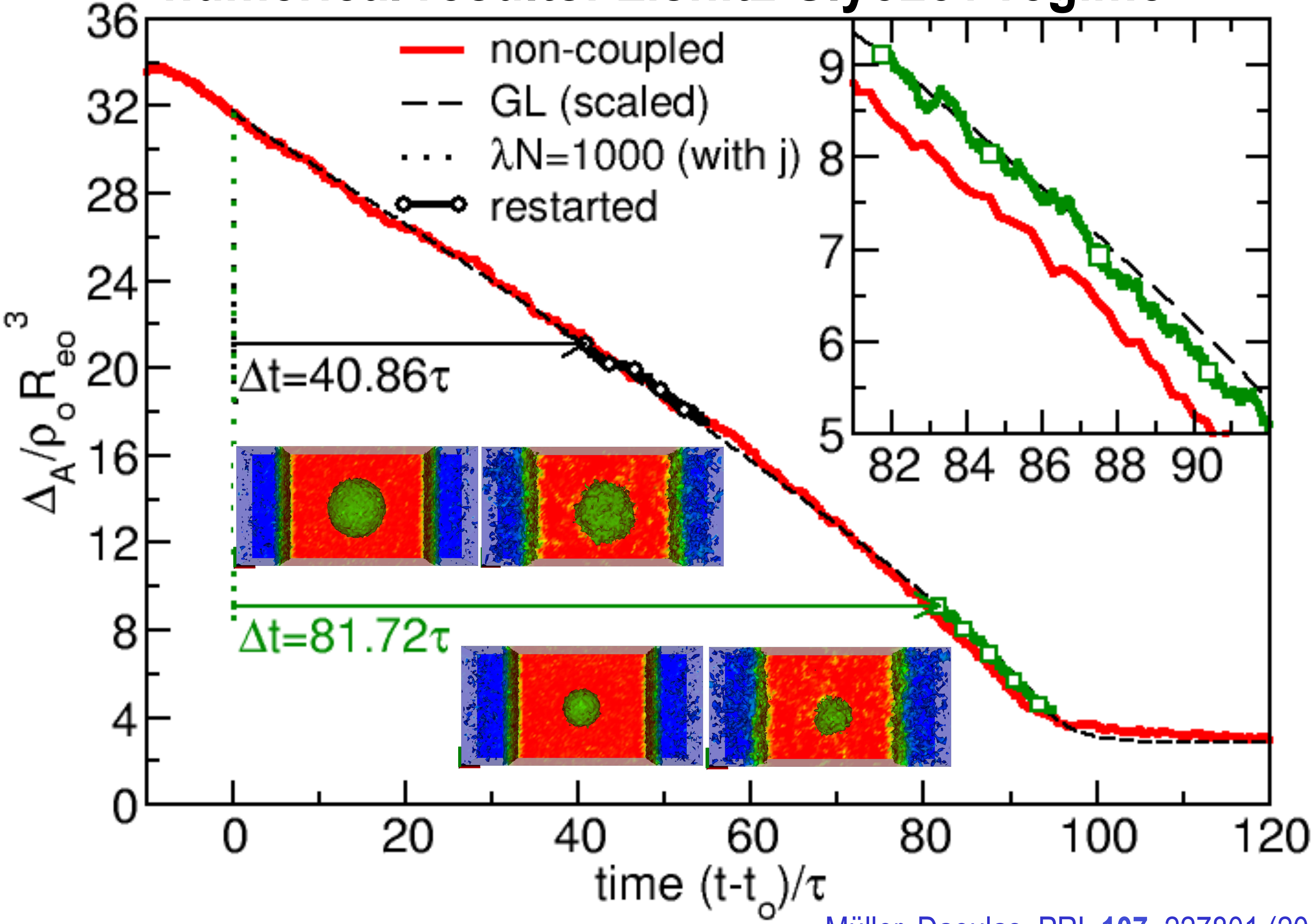


calculate average current, j(r), in GL simulation

use $v_A \sim j/2\phi_A$ and $v_B \sim -j/2\phi_B$ as drift velocity

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

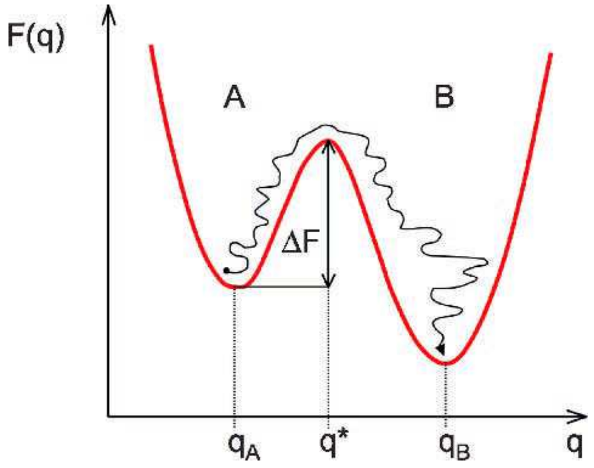
numerical results: Lishitz-Slyozov regime



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

b) collective transformation between morphologies

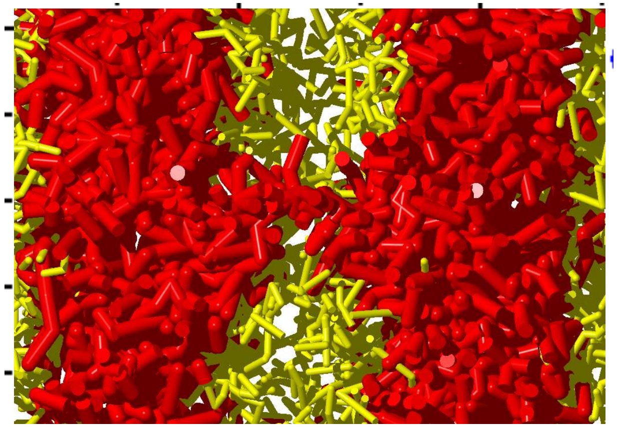
problem: find a **physical reversible path**
that identifies the barrier to stalk formation



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)

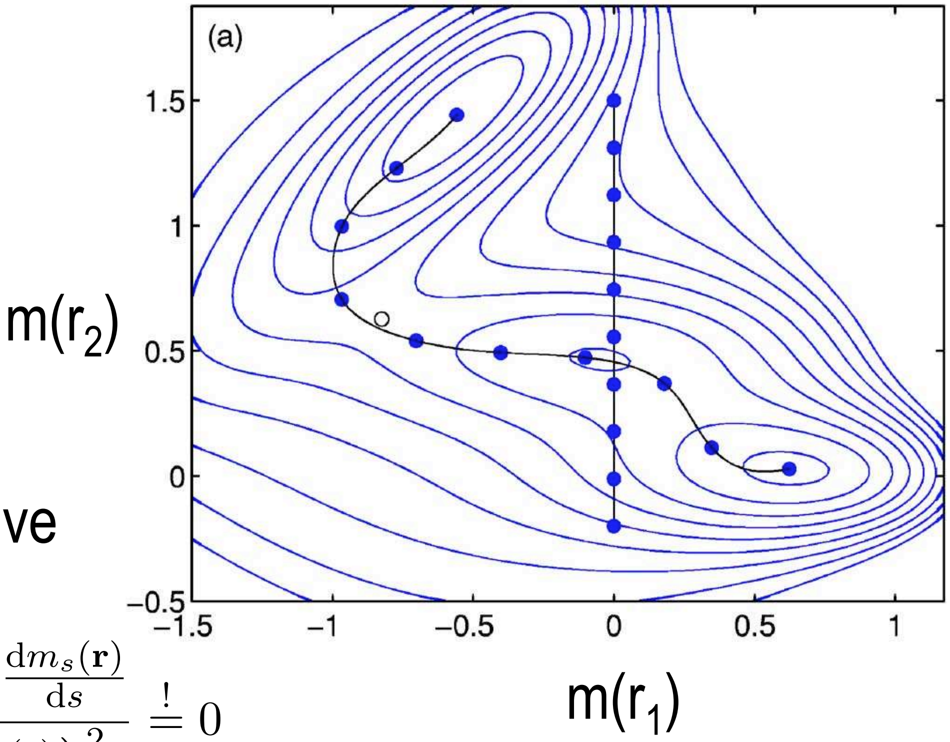
find minimal free-energy path (MFP) in high-dimensional “coordinate” space (for functional $\mathcal{F}[m]$ on collocation lattice)

➡ 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

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

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

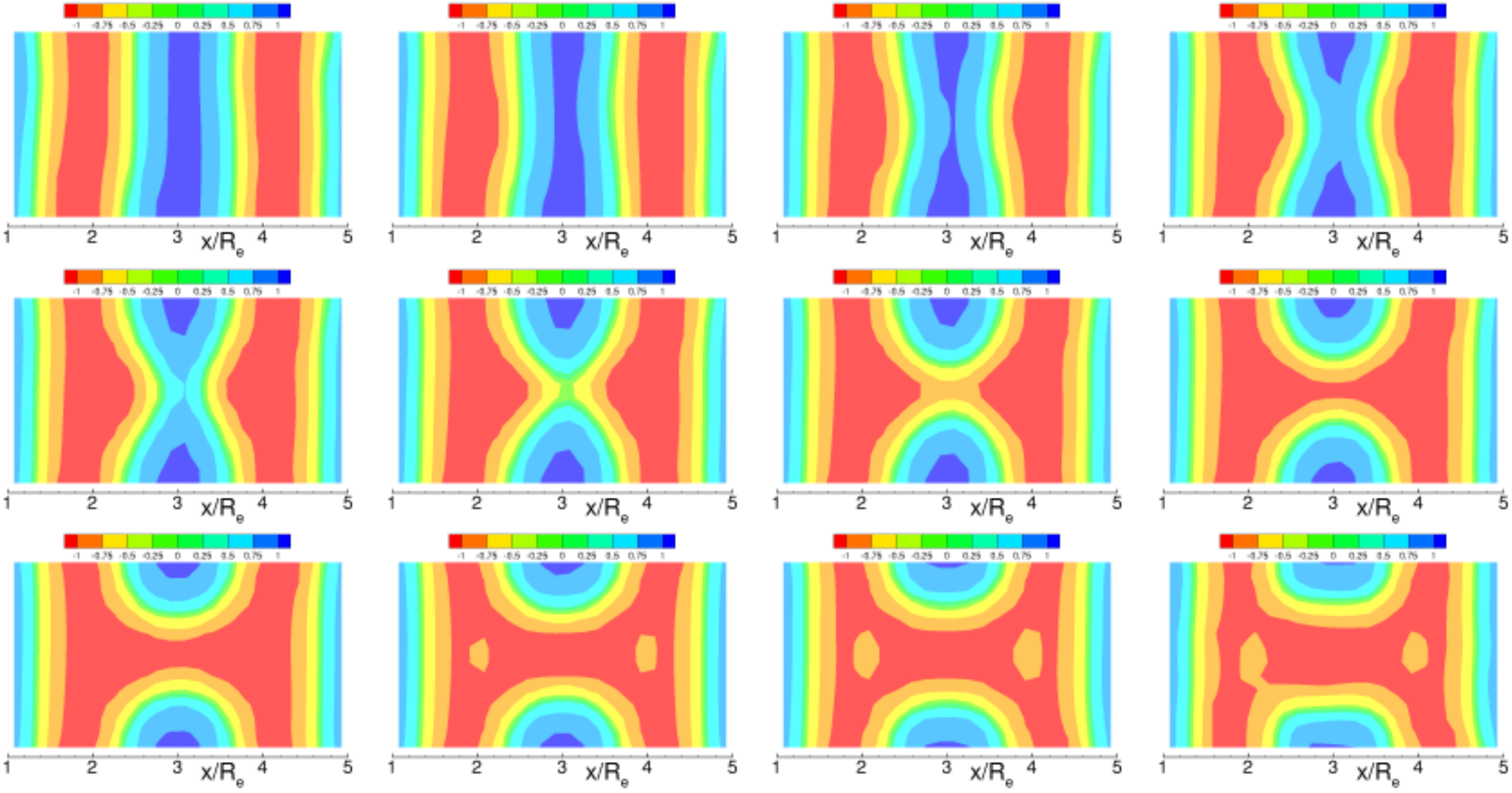
evolve each morphology $m_s(\mathbf{r})$ as to minimize the free energy

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

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

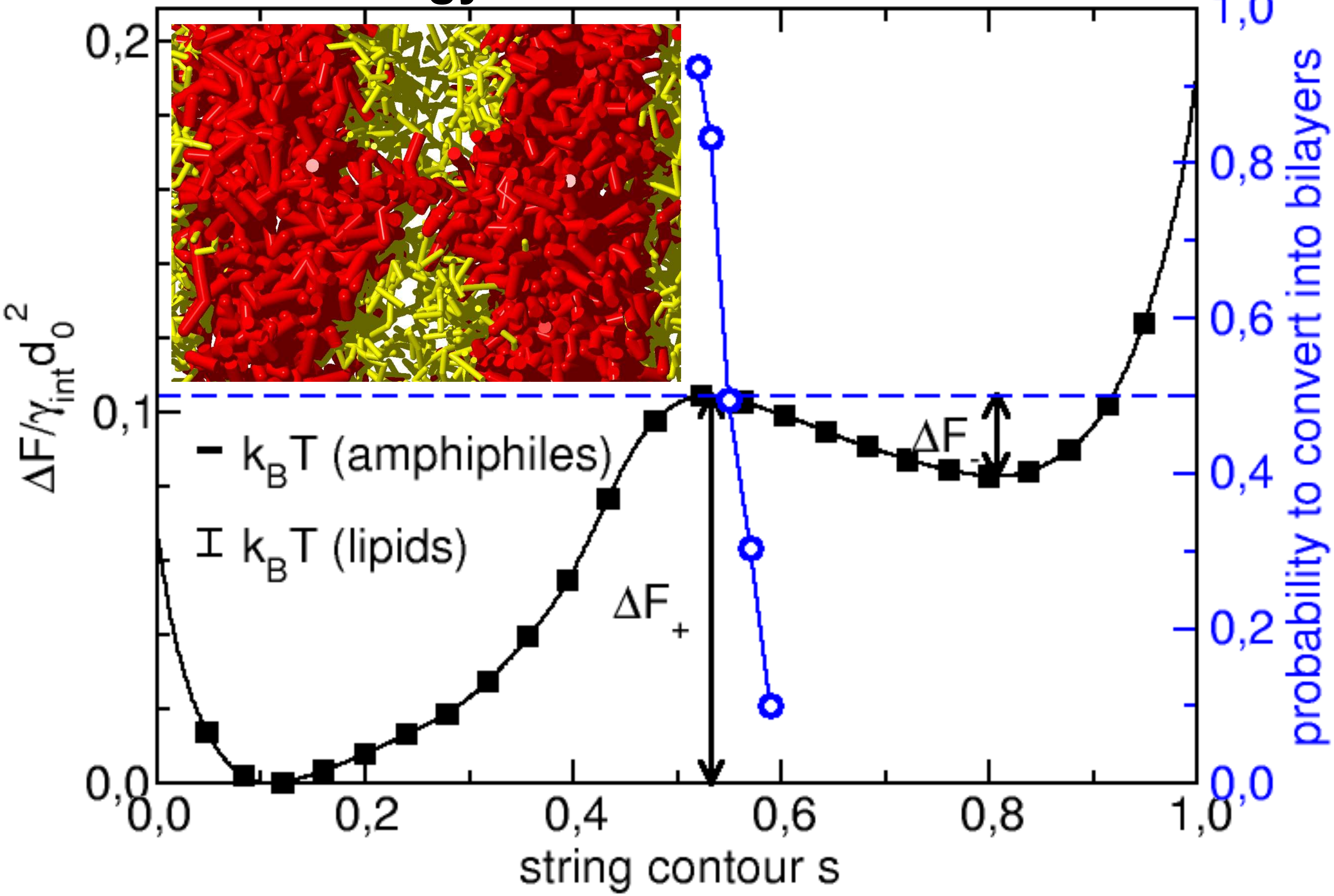
E, Ren, Vanden-Eijnden, JCP **126**, 164103 (2007)
Maragliano, Vanden-Eijnden. Chem. Phys. Lett., **446**, 182 (2007)

string of morphologies for stalk formation



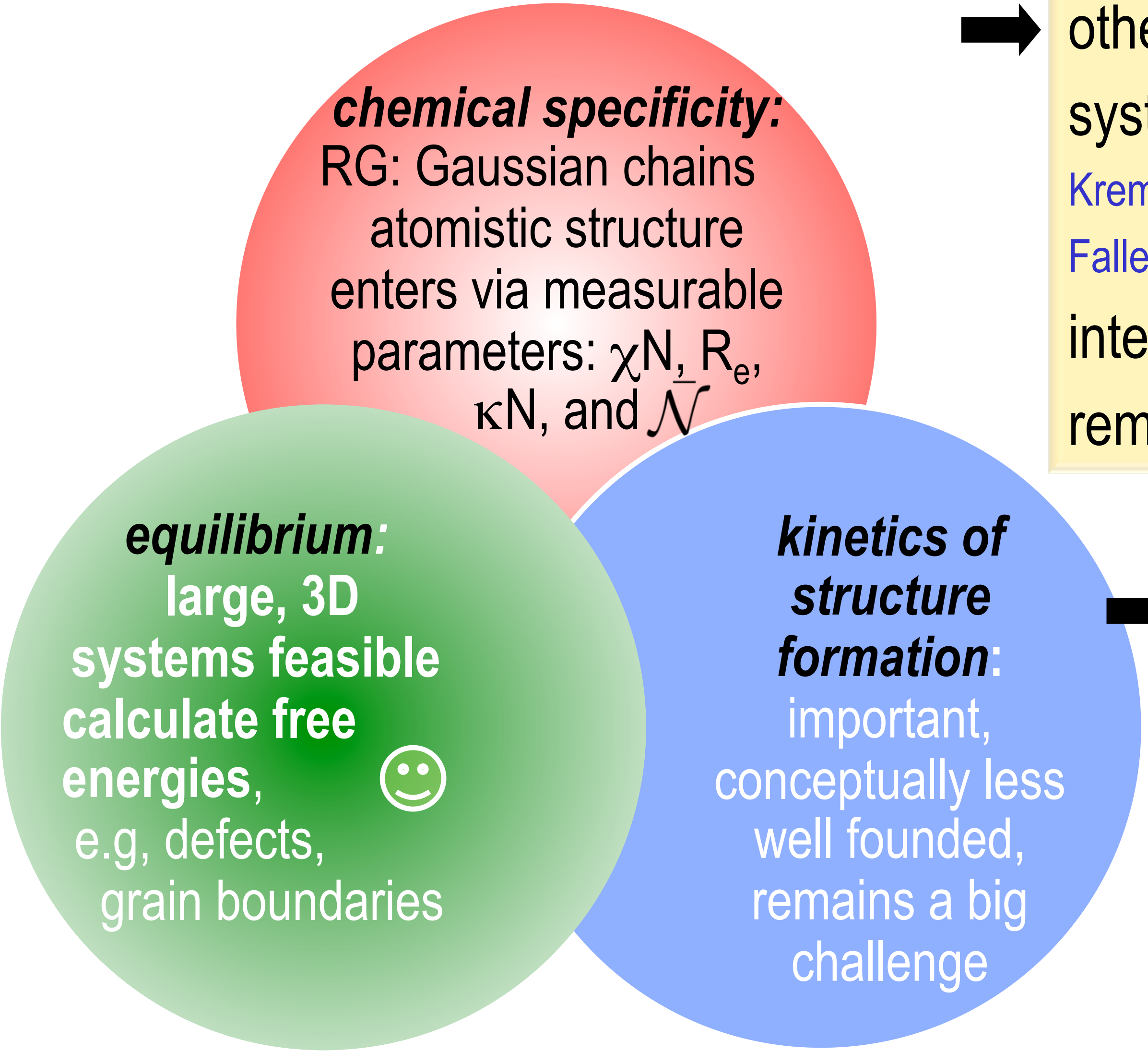
Müller, Smirnova, Marelli, Fuhrmans, Shi, PRL **108**, 228103 (2012)

free-energy barrier for stalk formation



Müller, Smirnova, Marelli, Fuhrmans, Shi, PRL **108**, 228103 (2012)

Mesoscopic and Monte Carlo Simulations



chemical specificity:
RG: Gaussian chains
atomistic structure
enters via measurable
parameters: χN, R_e,
κN, and $\bar{\mathcal{N}}$

equilibrium:
large, 3D
systems feasible
calculate free
energies, ☺
e.g, defects,
grain boundaries

kinetics of structure formation:
important,
conceptually less
well founded,
remains a big
challenge

→ other topologies, e.g., combs

systematic coase-graining

Kremer, Müller-Plathe, Paul,
Faller, Klein, Marrink, Voth

intermolecular interactions

remain challenging, $\chi \sim 10^{-3}\, k_BT$

→ thermostats

Kremer, Espanol

crossability due

soft interactions

Likhtman, Briels

HMM

thanks to **Kostas Daoulas, Yuliya Smirnova, An-Chang Shi,**
Juan de Pablo / Paul Nealey

Moscow, July 18, 2012