Simulation of Condensed Matter:
Session in memory of Prof. Dr. Kurt Binder

NIC Köln, April 21, 2023

Kurt Binder (1944-2022)

computer simulations in condensed matter physics:
Monte-Carlo simulation, statistical physics of phase transitions,
finite-size scaling, physics of glasses, interfaces and polymers

2007 -	fellow, Gutenberg Forschungskolleg, Universität Mainz
1983 - 2012	Professor for Theoretical Physics, Universität Mainz
1977 - 1983	Director, Institute for Solid State Research, Jülich
1974 - 1977	Professor, Universität des Saarlandes

2018 - 2020	vice chair, scientific council of NIC
2012 - 2017	vice chair, steering committee of GCS
2012 - 2017	chair, scientific council of NIC
2011	vice chair, scientific council of NIC
2010 - 2012	member, scientific steering committee of PRACE
1987 - 1992	member, scientific council of HLRZ, Jülich

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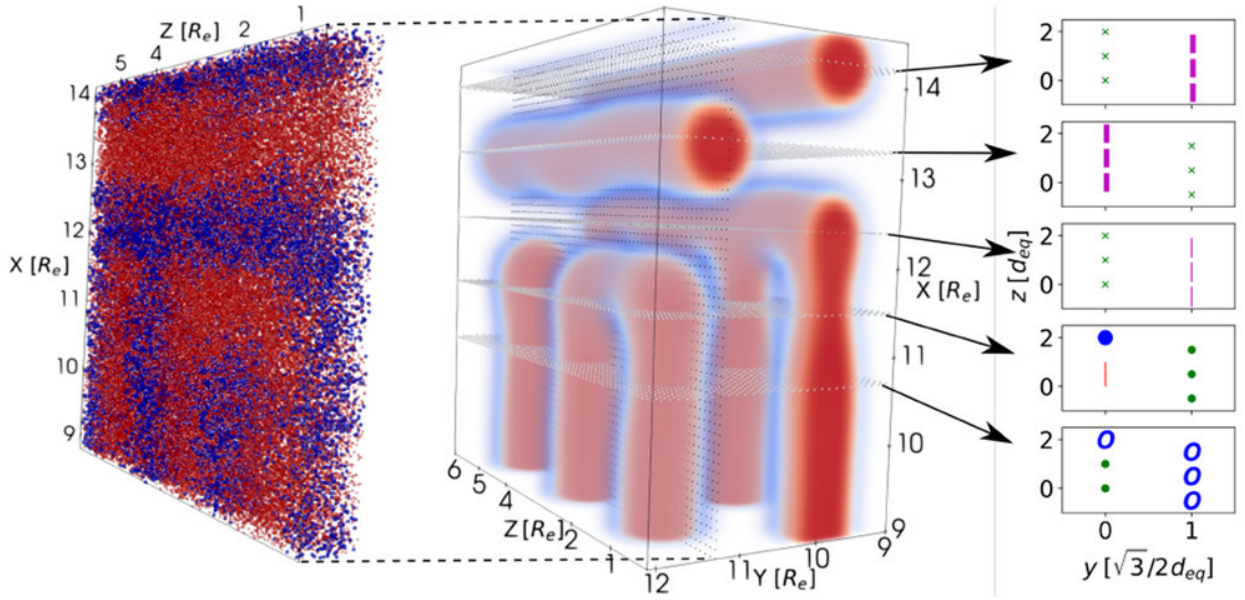
some awards:
2020 Polymer Physics Prize (APS)
2009 Lennard-Jones Lecture Award (RSC)
2007 Boltzmann Medaille (IUPAC)
2003 Staudinger-Dürrer-Prize (ETH Zürich)
2001 Berni Alder CECAM Preis
1993 Max Planck Medaille (DPG)

Kurt Binder's group (around 1998)

Multiscale modeling of grain-boundary motion in cylinder-forming block copolymers

Niklas Blagojevic and Marcus Müller



thanks to:
Gregor Ibbeken,
Ludwig Schneider, *Oliver Dreyer* (Hereon)

Müller, *Prog. Polym. Sci.* **101**, 101198 (2020)
Müller, Abetz, *Chem. Rev.* **121**, 14189 (2021)
Dreyer, Ibbeken, Schneider, Blagojevic, Radjabian, Abetz, Müller, *Macromolecules* **55**, 7564 (2022)
Blagojevic, Müller, *ACS Polymers AU* 3, 96 (2023)

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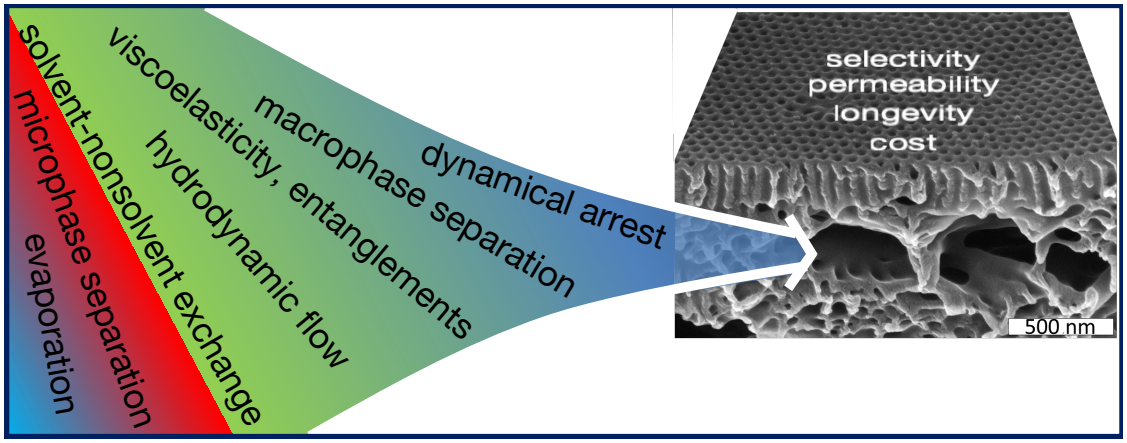
Institut für Theoretische Physik

Köln, April 21, 2023

EISA and NIPS in a diblock copolymer film

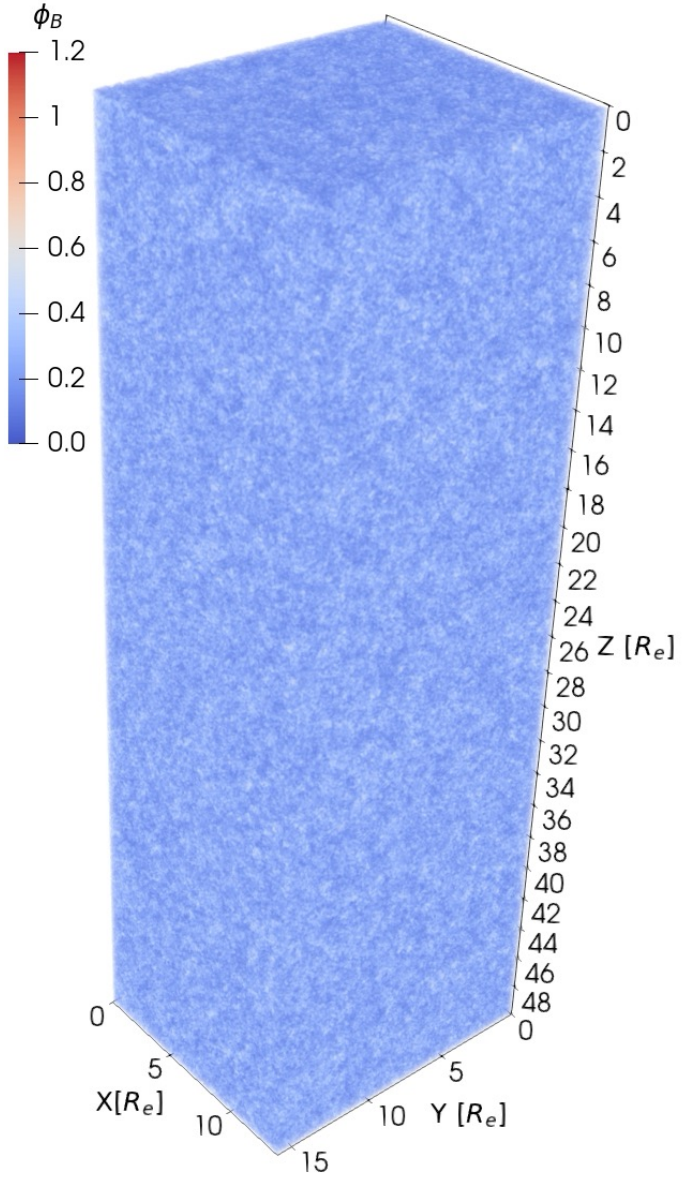


Müller, Abetz, *Chem. Rev.* **121**, 14189 (2021)

techniques: particle-based simulation
and continuum model

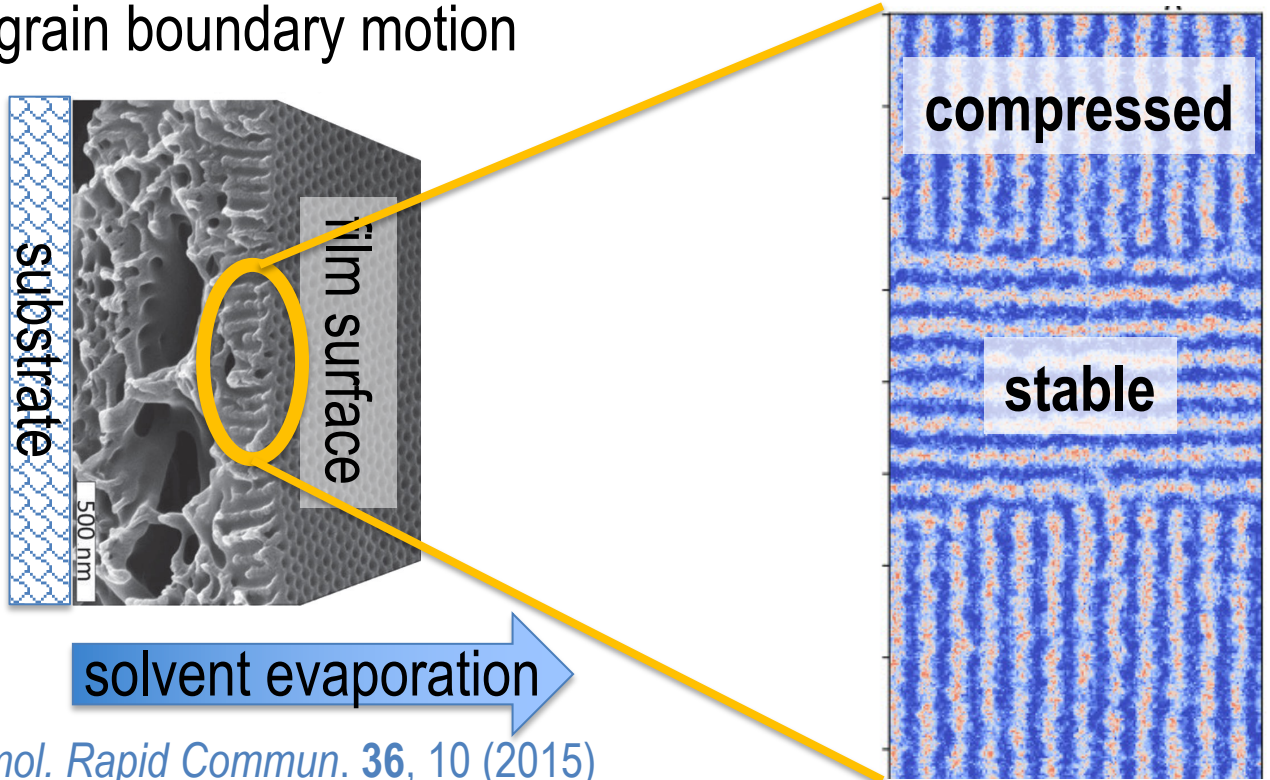
question:

- how to fabricate perpendicular cylinders?
- role of solvent selectivity and evaporation rate
- mechanism of structure formation



solvent evaporation from a diblock copolymer film

- solvent evaporates and polymer density at the film surface increases
  ➡ skin formation
- microphase separation commences at film surface (EISA)
  domains of cylinders with different orientations form
- as the solvent evaporates further, the film thickness shrinks
  ➡ anisotropic deformation of domains results in grain coarsening
  via grain boundary motion

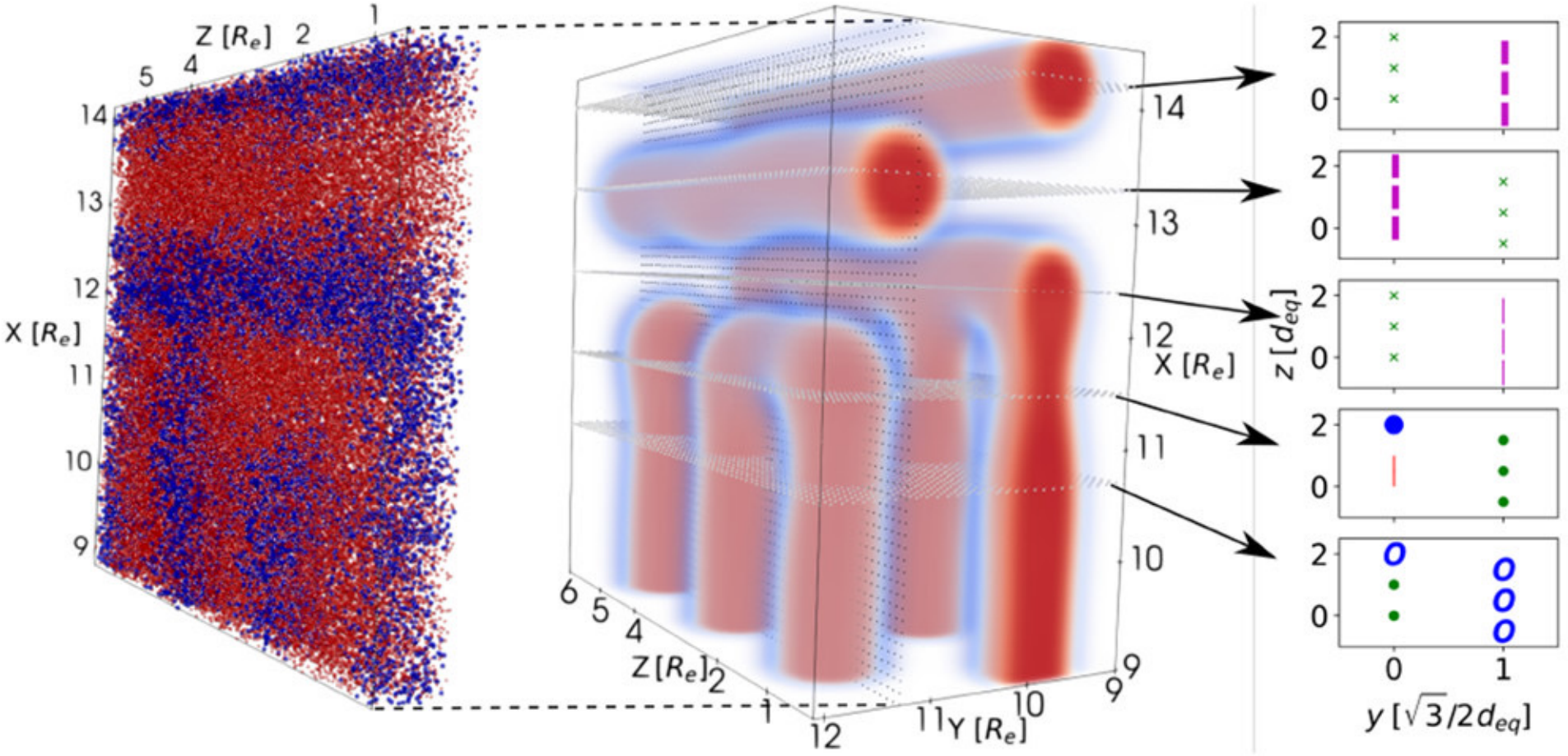


Abetz, *Macromol. Rapid Commun.* **36**, 10 (2015)

grain-boundary motion

system: cylinder-forming diblock copolymer χN=35, f=1/4, N=64
two grains with orthogonal orientation, one is only metastable

particle simulation ➡ continuum model / MFEP ➡ kMC model



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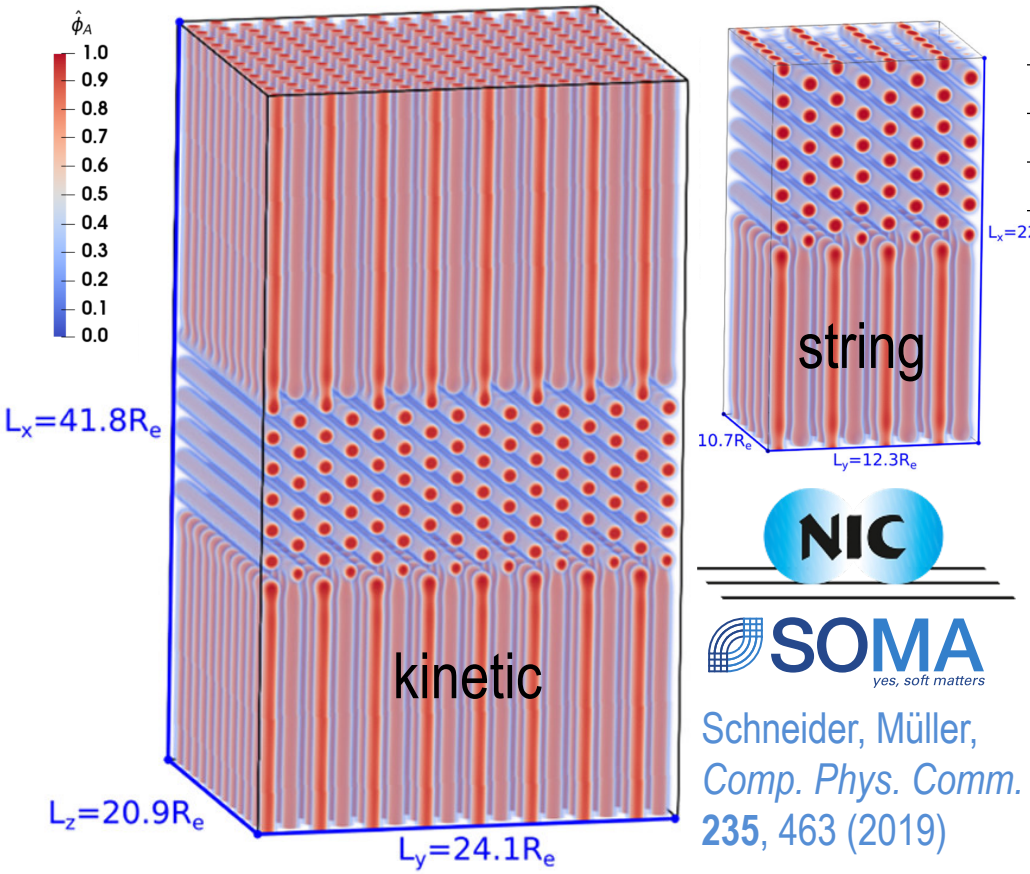


System	$L_x \cdot L_y \cdot L_z$ $[R_e^3]$	d_{eq} $[R_e]$	$\sqrt{\bar{N}}$
Single-grain	$5 \cdot 12.3 \cdot 10.7$	1.78	750
String	$22.0 \cdot 12.3 \cdot 10.7$	1.78	1300
Kinetic	$41.8 \cdot 24.1 \cdot 20.9$	1.74	60 & 90

typically 10^8 segments

NIC

SOMA
yes, soft matters

Schneider, Müller,
Comp. Phys. Comm.
235, 463 (2019)

choice of invariant degree of polymerization $\sqrt{\bar{N}} = \rho R_e^3 / N$:

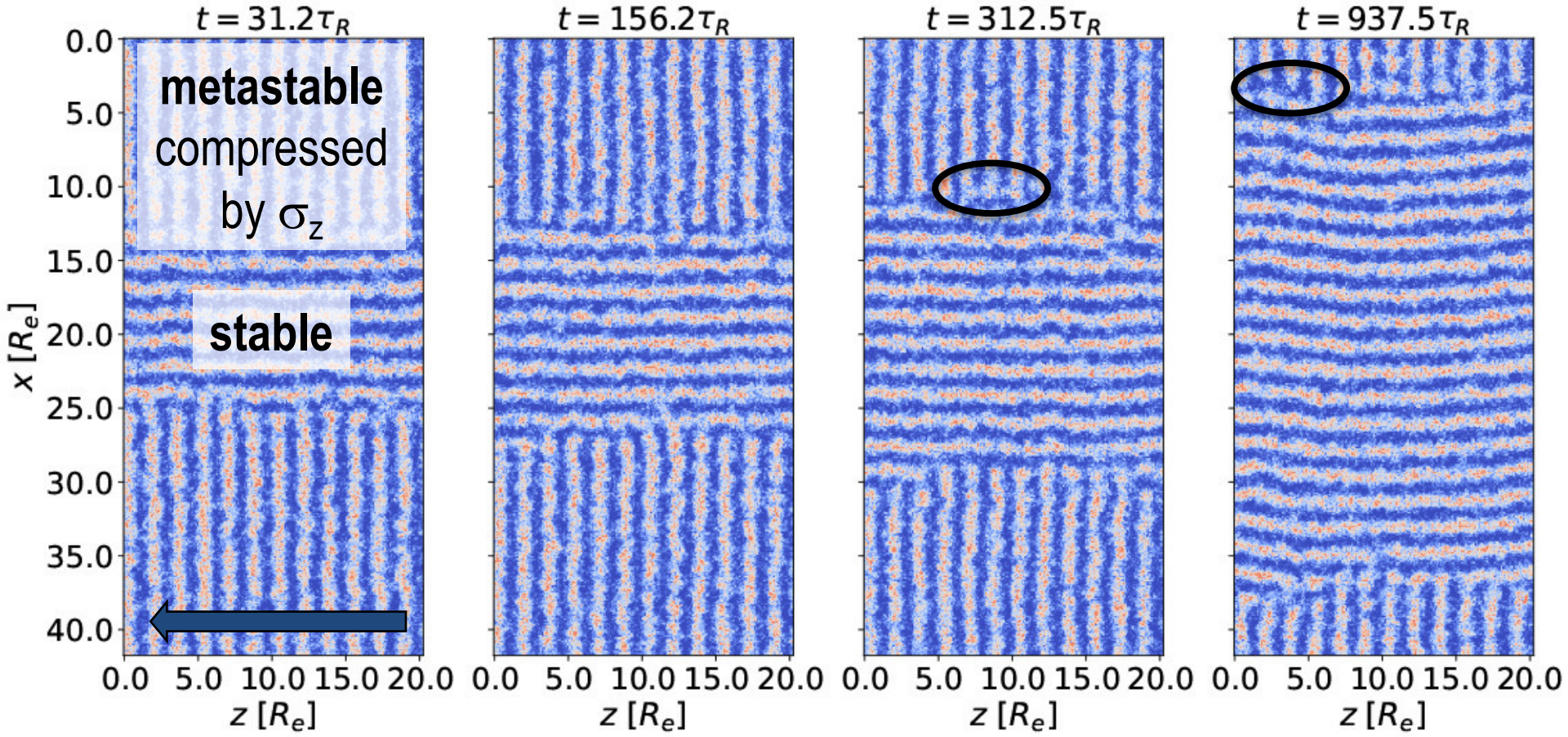
- small enough so that system overcomes free-energy barriers $\Delta F \sim \sqrt{\bar{N}} k_B T$
- large enough to suppress density fluctuations

compression, σ_z, along *z*-direction distorts one grain and thereby increases its free energy ➡ deterministic motion of grain boundary

kinetics of grain-boundary motion

main processes involved in grain-boundary motion (topological changes):

- fusion of heads of perpendicular cylinders with/to parallel cylinders
- rupture of junction between perpendicular and parallel cylinders



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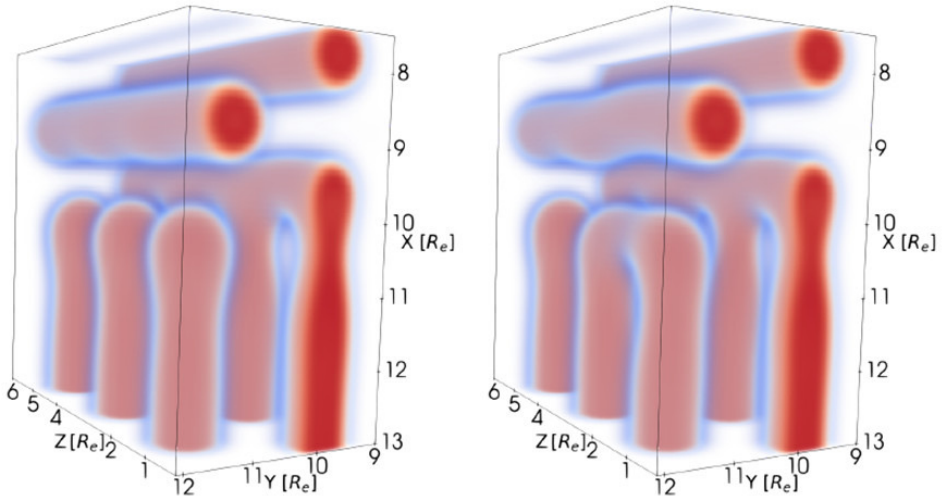

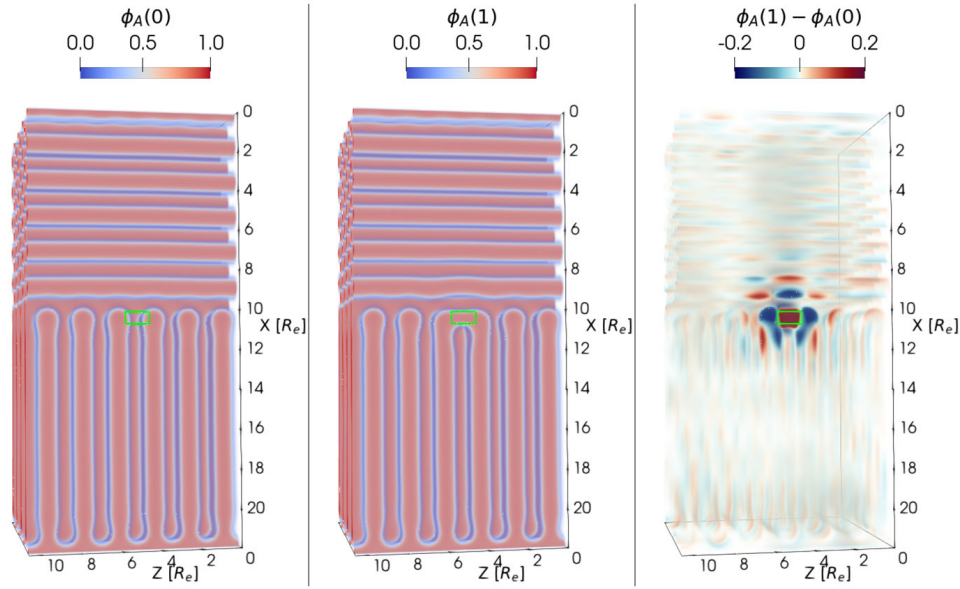

long-range strain field around defect:

- large system size necessary
- dependence of free-energy barrier on environment

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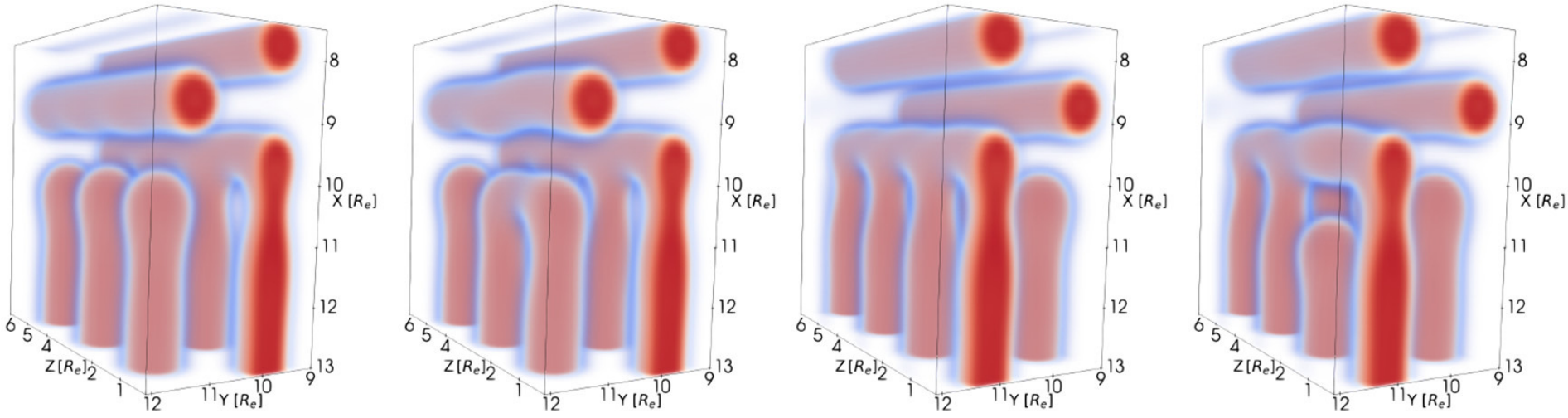
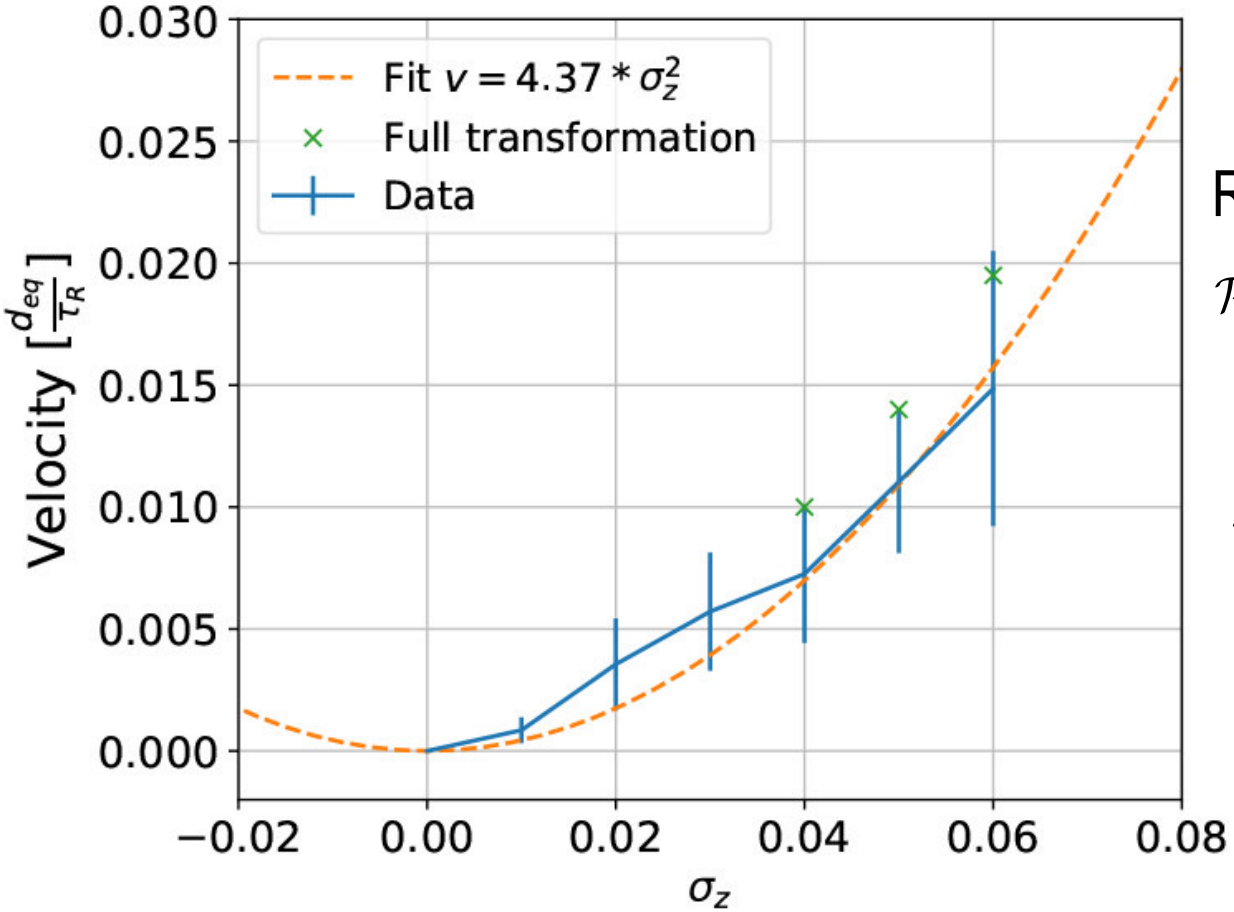


velocity of grain boundary at $\sqrt{\bar{N}} = 65$

fast motion at small invariant degree of polymerization $\sqrt{\bar{N}} = \rho R_e^3 / N$

grain-boundary velocity ~ free-energy difference $\Delta f \sim \sigma_z^2$



Rayleighian:

$$\mathcal{R} = \dot{F} + \frac{1}{2}\Sigma T$$

$$= -\Delta f A v + \frac{1}{2} A \zeta v^2 \rightarrow \min$$

$$v = \Delta f / \zeta$$

study sequence of topological changes and concomitant free-energy barriers that are required for grain-boundary motion

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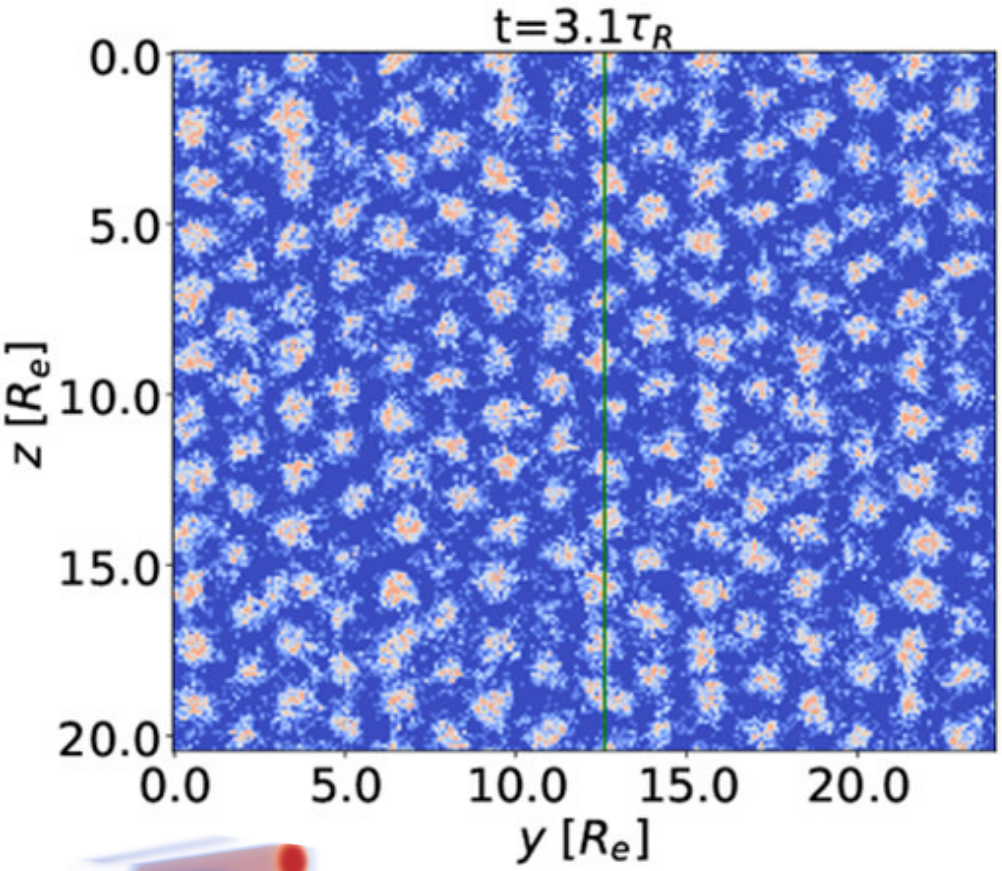
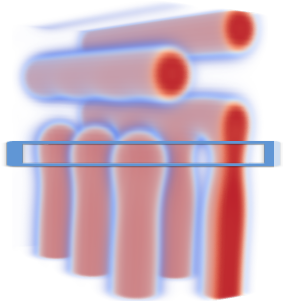
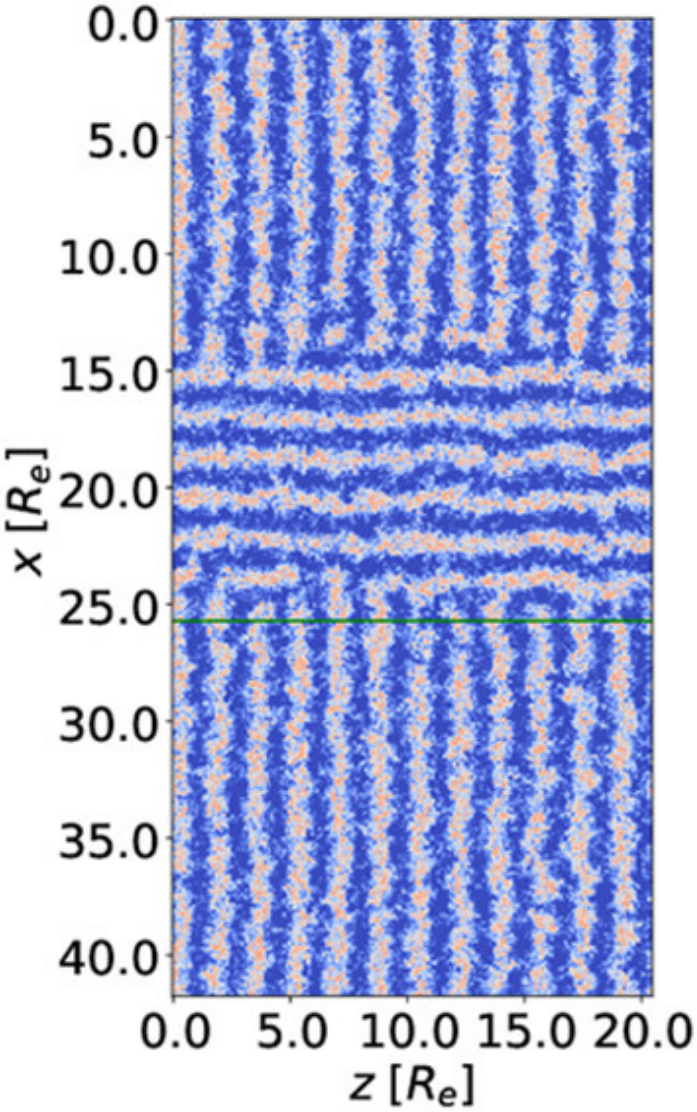
sequence of topology changes, correlated in space and time





cylinder heads and junctions



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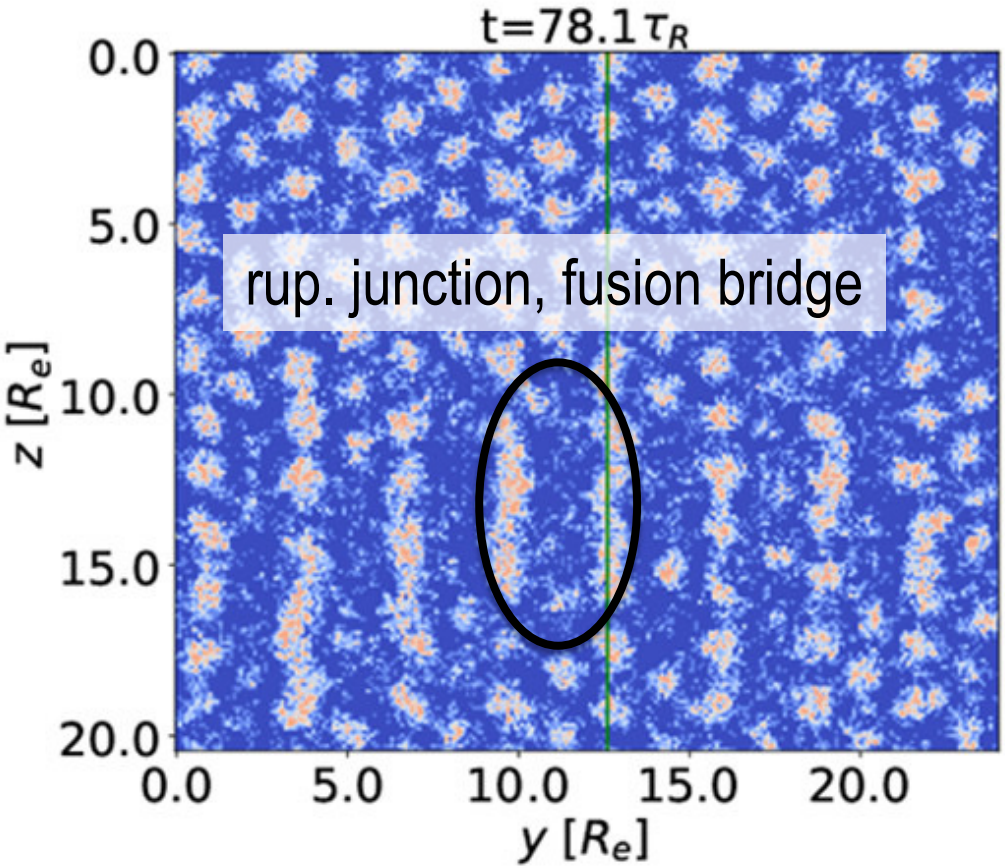
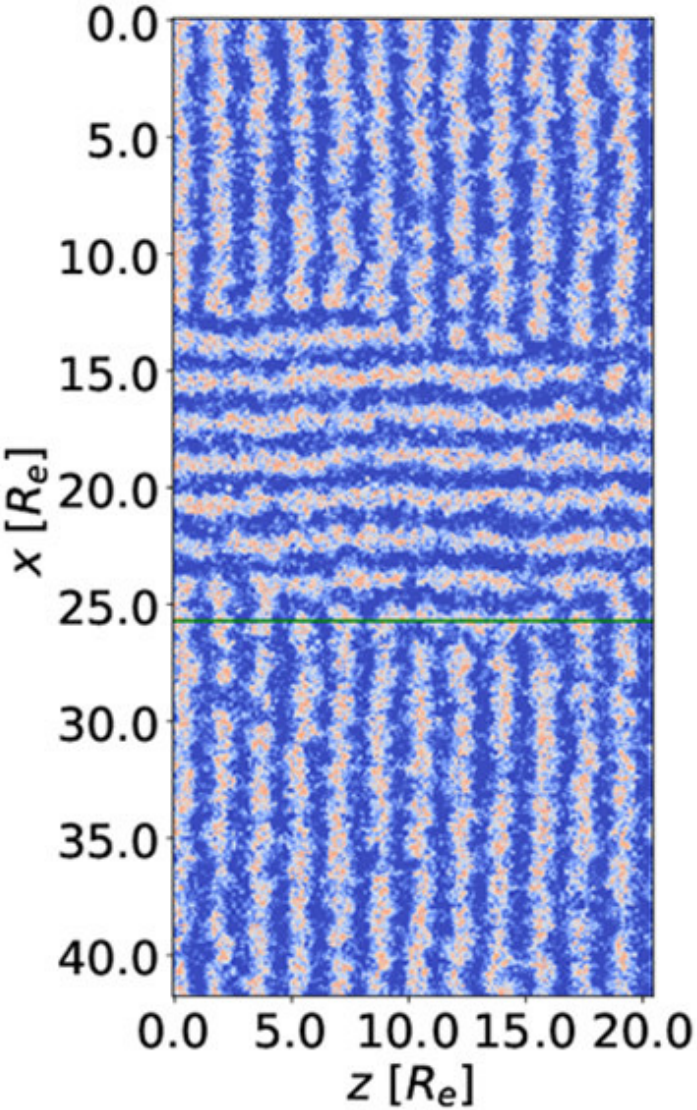
sequence of topology changes, correlated in space and time





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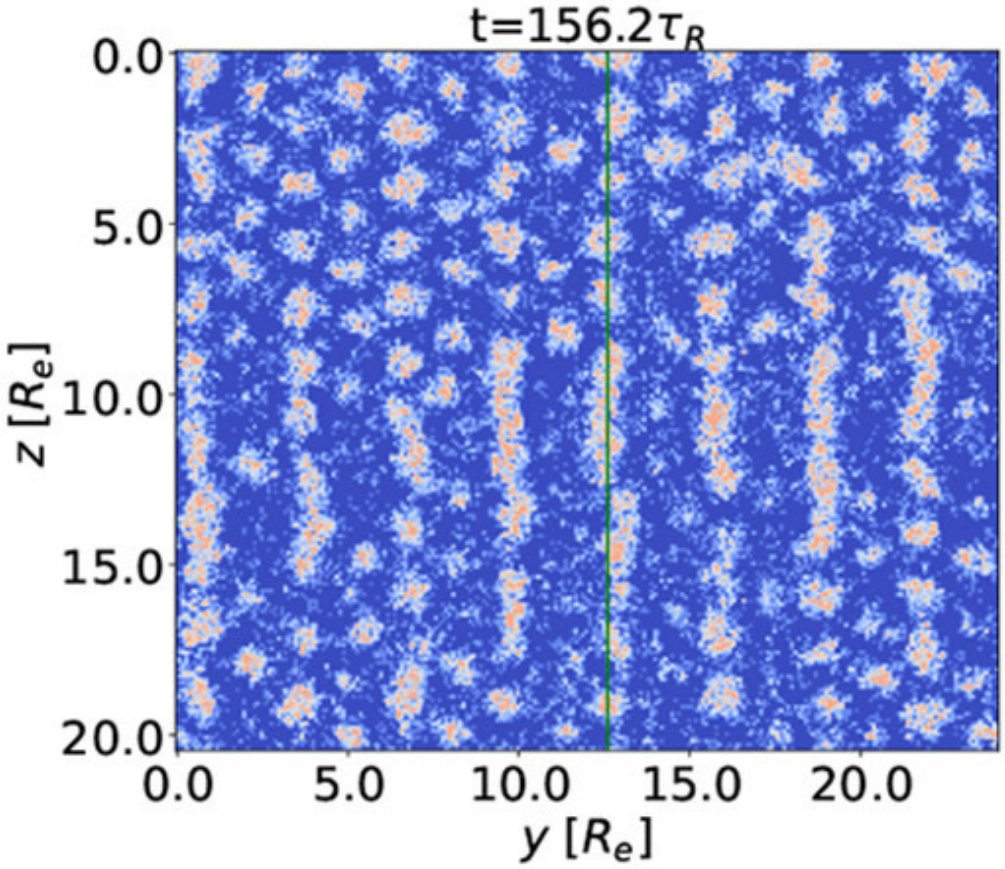

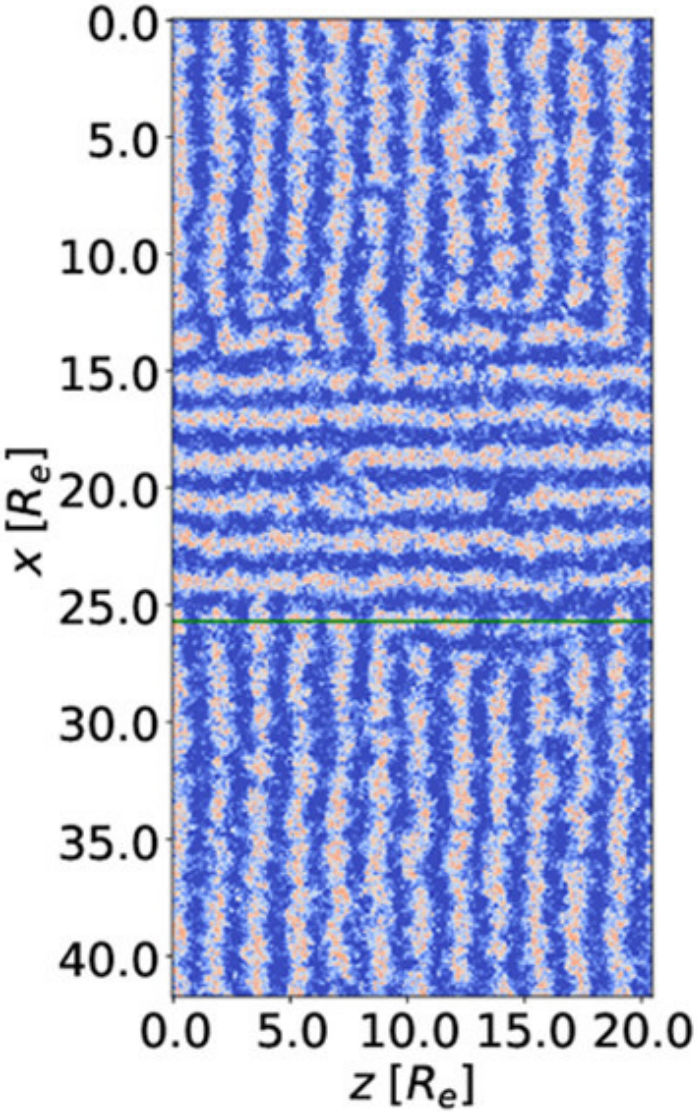

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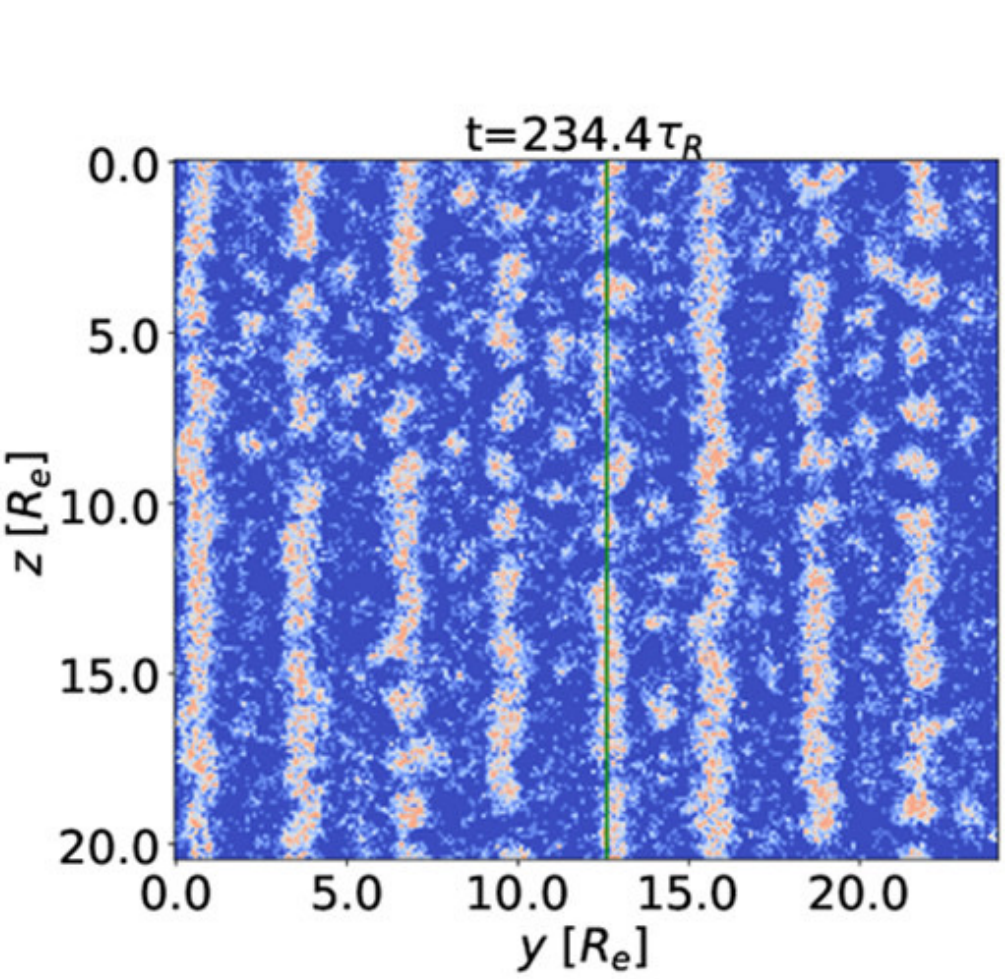

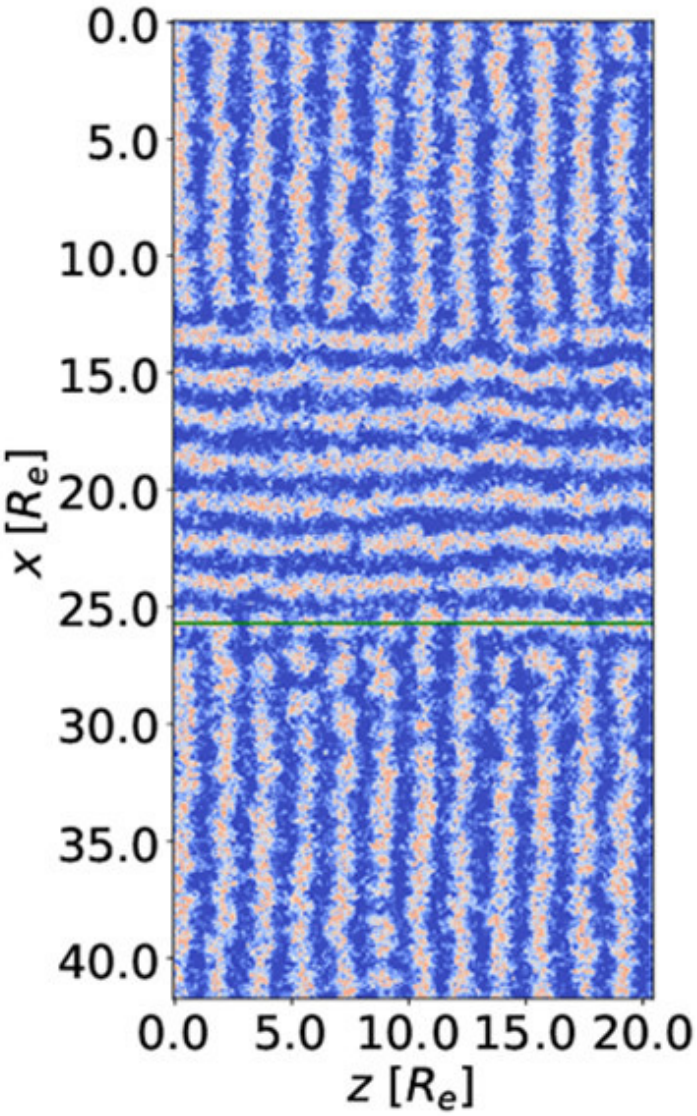

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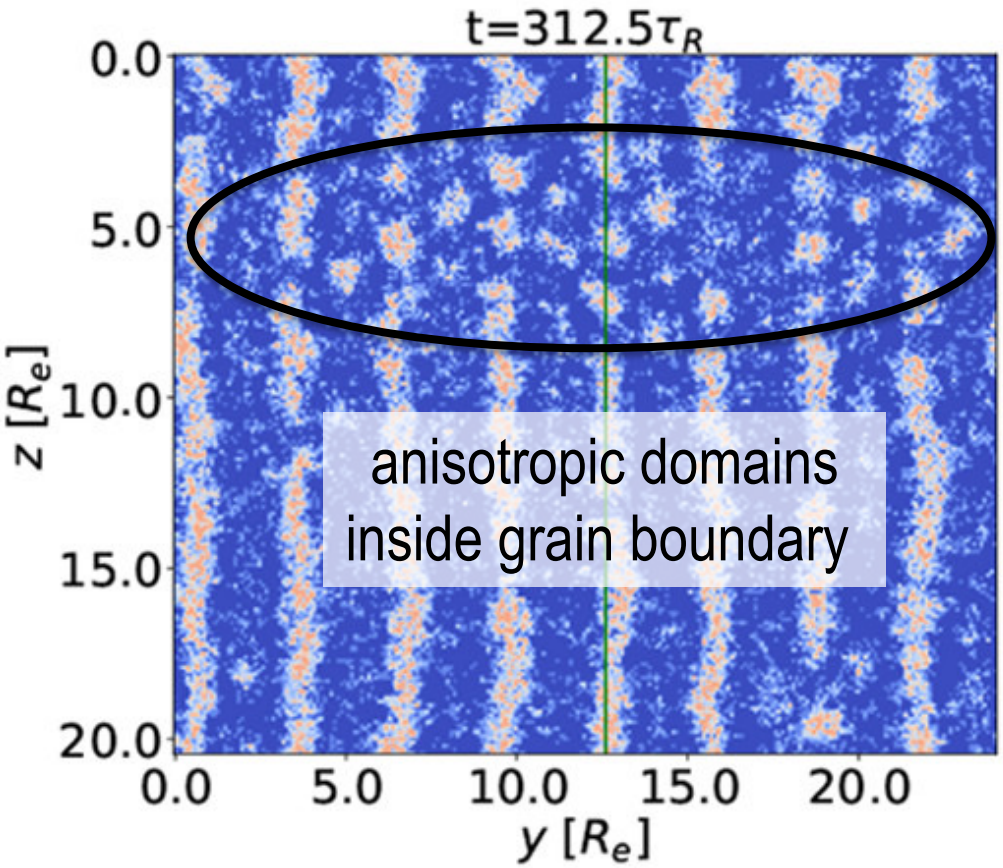

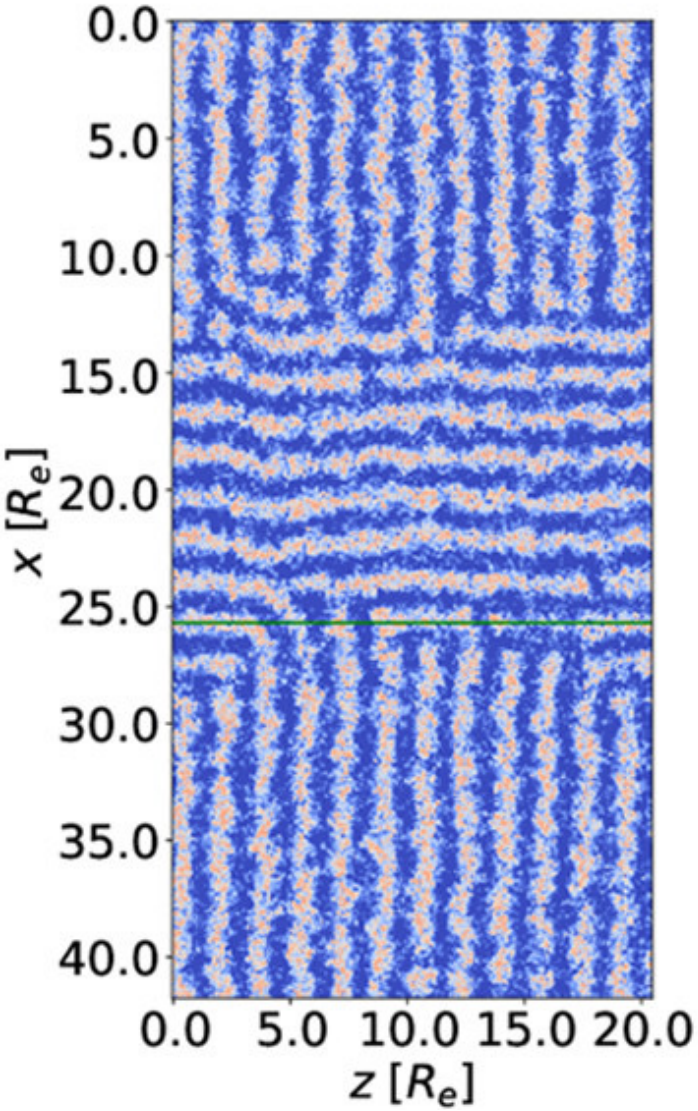

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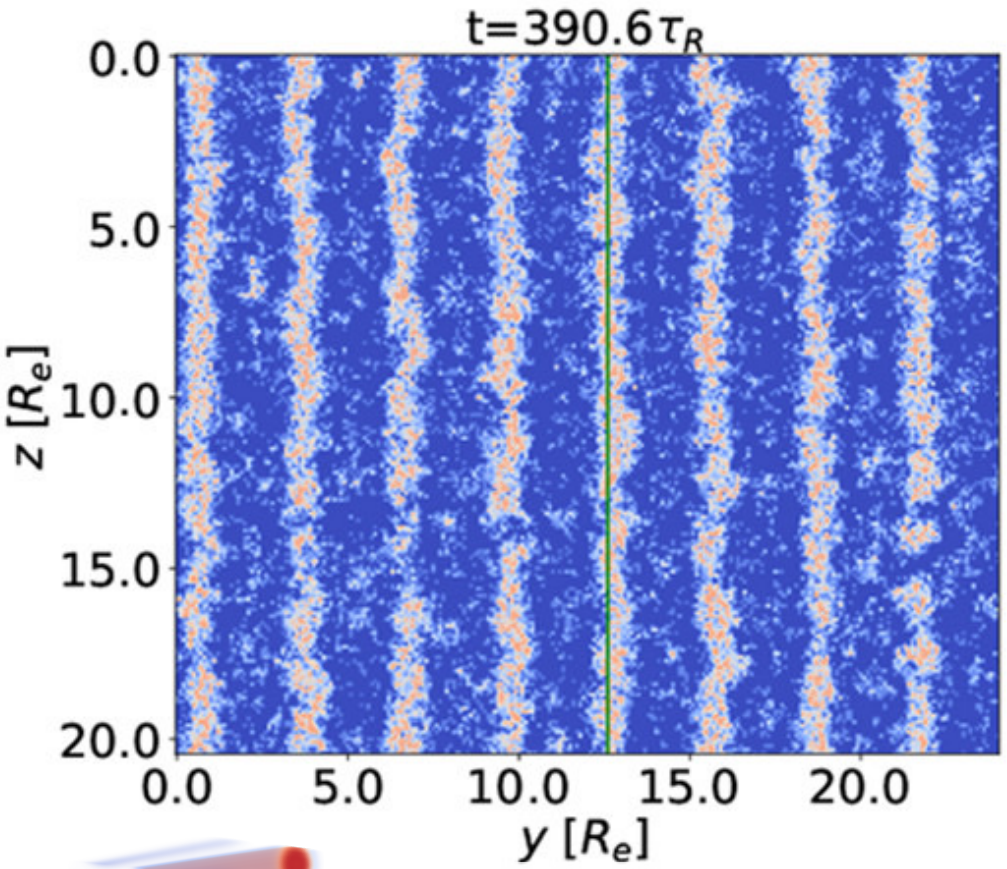
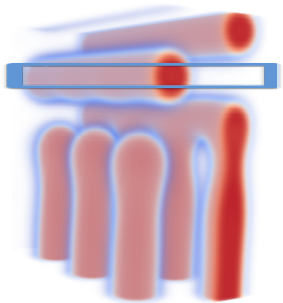
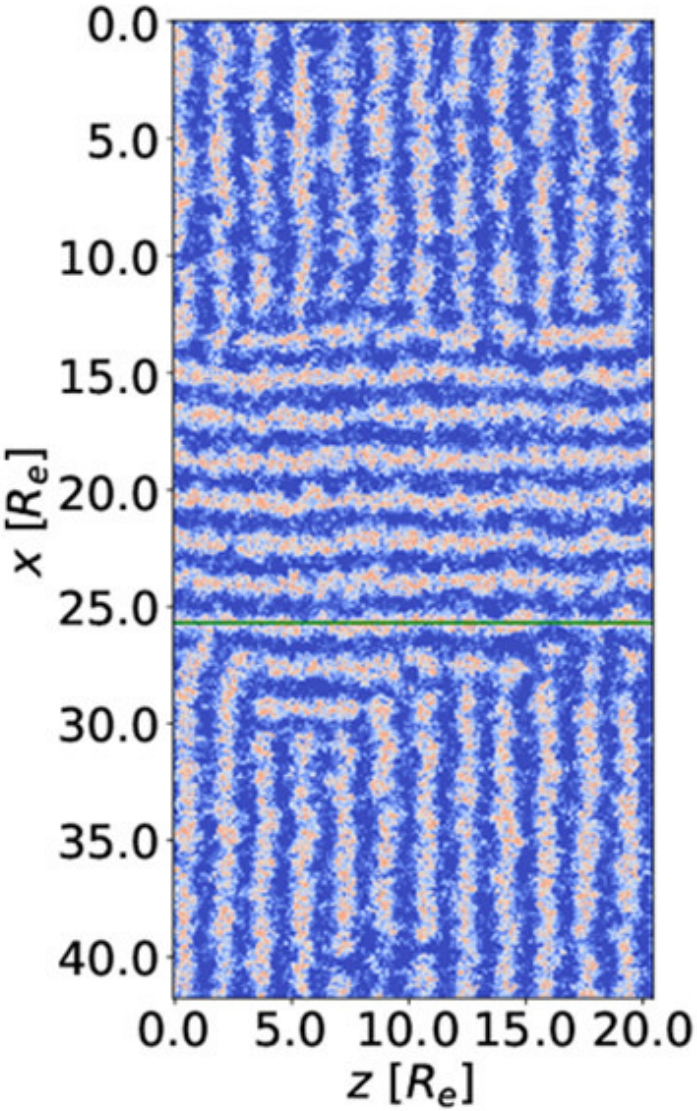




cylinders with stable orientation



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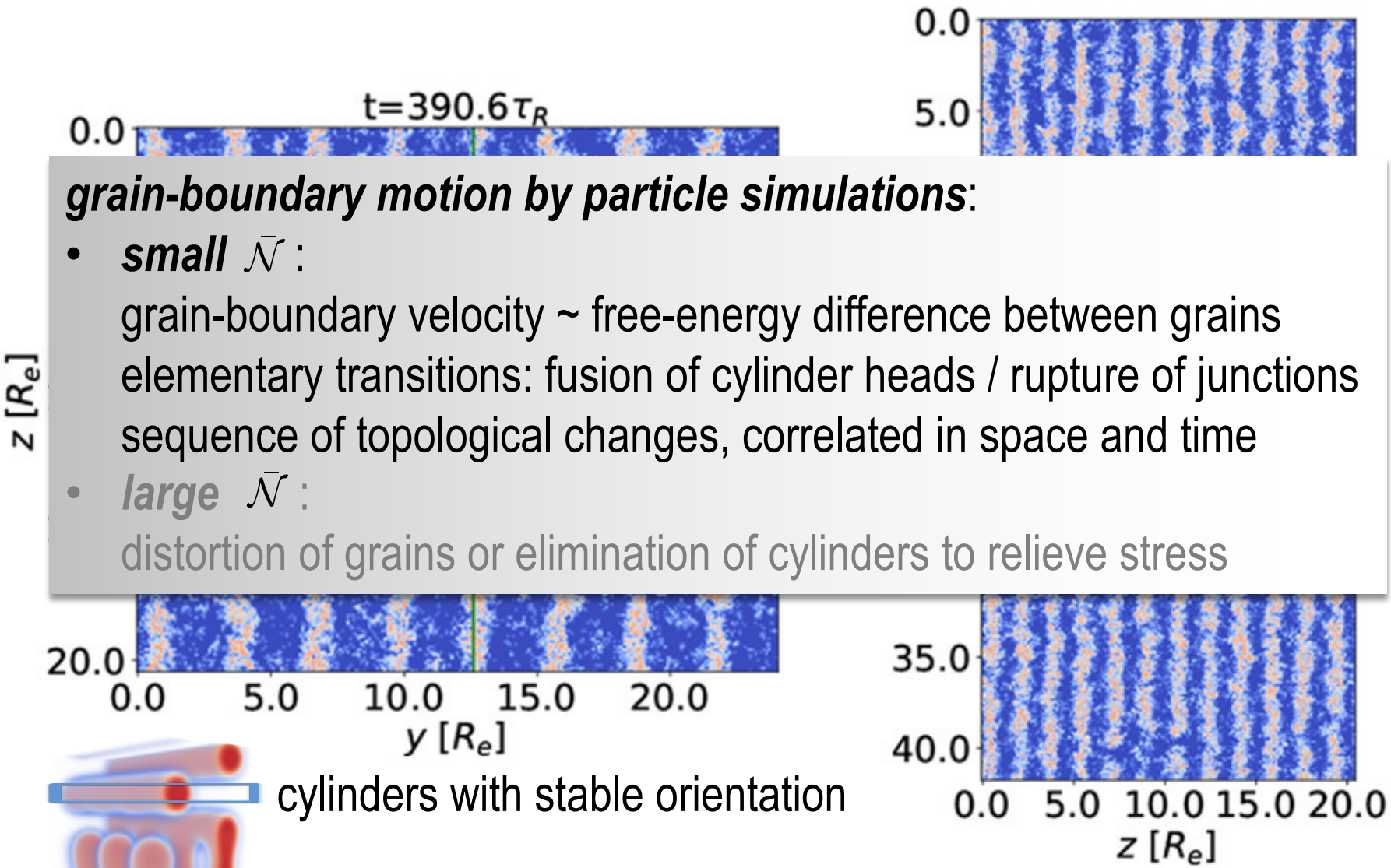
sequence of topology changes, correlated in space and time



grain-boundary motion by particle simulations:

- ***small*** $\bar{\mathcal{N}}$:
  grain-boundary velocity ~ free-energy difference between grains
  elementary transitions: fusion of cylinder heads / rupture of junctions
  sequence of topological changes, correlated in space and time
- ***large*** $\bar{\mathcal{N}}$:
  distortion of grains or elimination of cylinders to relieve stress

cylinders with stable orientation

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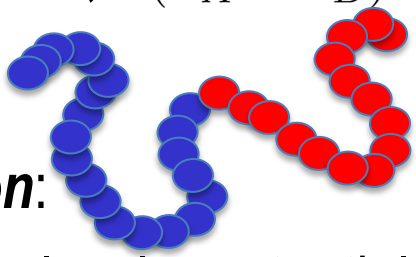
from particle simulation to continuum description

degrees of freedom:

particle coordinates, $N(n_A + n_B)$

$\{\mathbf{R}\} = \mathbf{R}(s)$



model definition:

intra- and intermolecular potentials

(here: soft, coarse-grained model, SCMF)

single-chain dynamics

(here: Rouse dynamics)

segmental friction, γ

order parameters

segment composition field (and density)

$m(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$

$\rho(\mathbf{r}) = \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) \approx \rho_0$ (not $\rho(\{\mathbf{R}\})$)

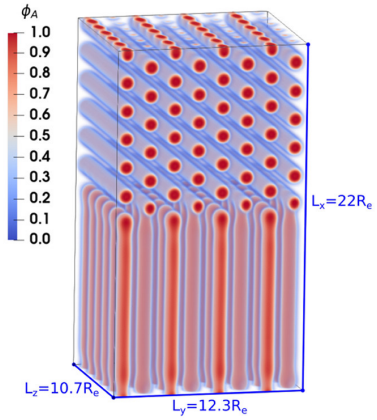
free-energy functional, $\mathcal{F}[m]$

(SCFT, Ohta-Kawasaki)

model-B dynamics

(Hohenberg & Halperin)

Onsager coefficient



projection: $\hat{\phi}_A(\mathbf{r}|\{\mathbf{R}\}_i)\text{“}=\text{”}\frac{1}{\rho_0}\sum_{i=1}^{n}\sum_{s=1}^{fN}\delta(\mathbf{r}-\mathbf{R}_i(s))$

$$\frac{\mathcal{F}[m]}{k_\mathrm{B}T} = -\ln\int \mathcal{D}[\{\mathbf{R}\}_i]e^{-\mathcal{H}/k_\mathrm{B}T}\delta\left[m-\hat{m}(\mathbf{r}|\{\mathbf{R}\}_i)\right]$$

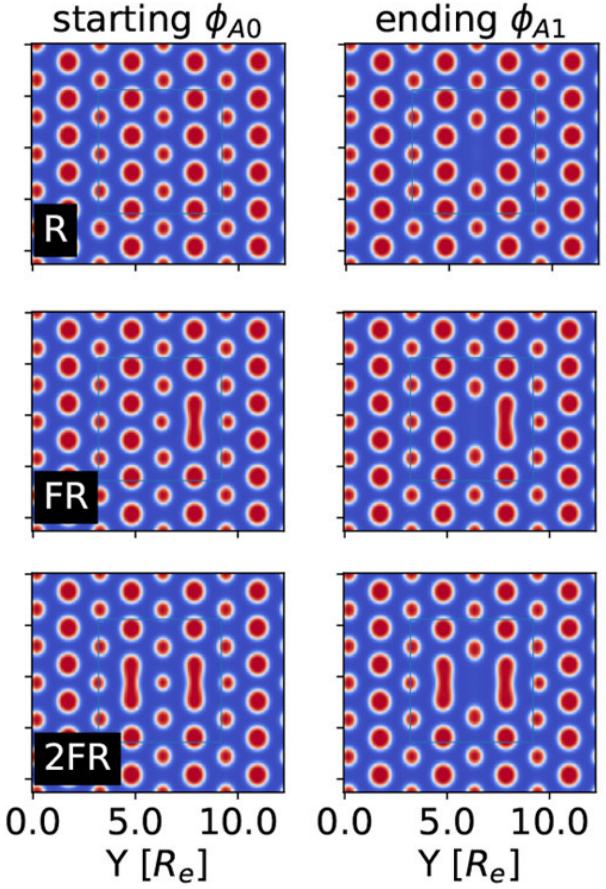
challenge:

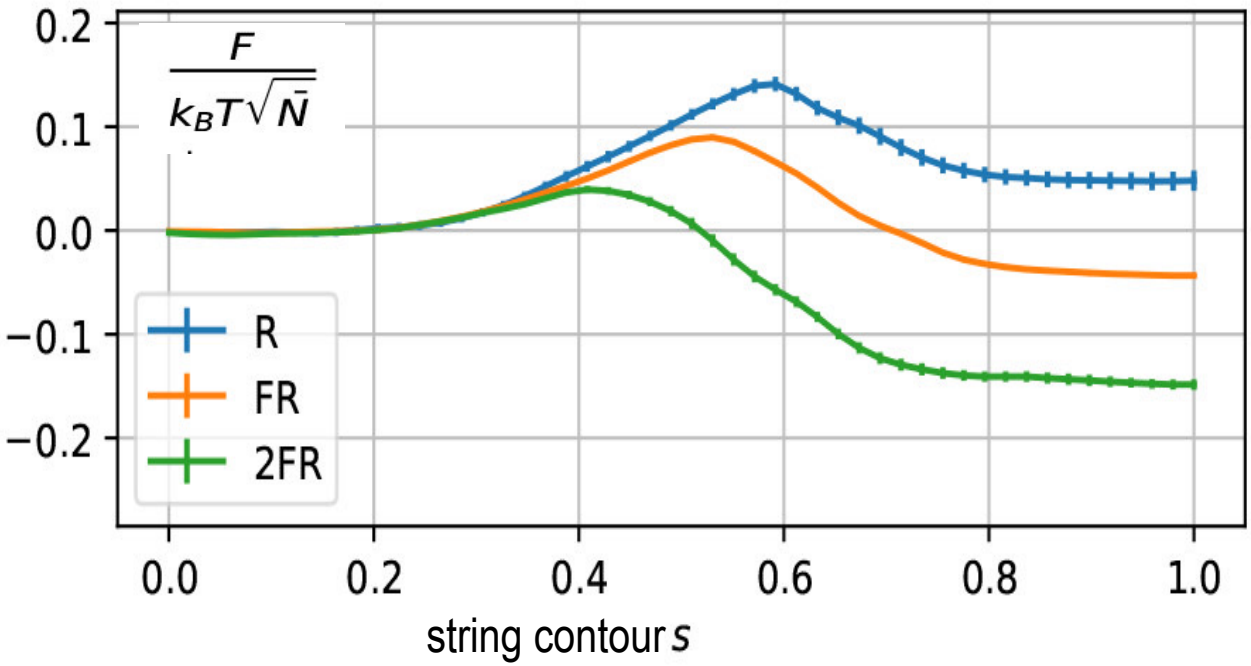
- sampling of free-energy differences or chemical potential ➡ $\mu[m](\mathbf{r}) = \frac{\delta\mathcal{F}[m]}{\delta m(\mathbf{r})}$
- construction of reversible paths (reaction coordinates)

MFEP of fusion and rupture transitions

- identify minimal set of 18 transitions (fusion/rupture in different environments)
- obtain chemical potential by field-theoretic umbrella sampling
- calculate the Minimum Free-Energy Path (MFEP) via string method

E, Ren, Vanden-Eijnden, *J. Chem. Phys.* **126**, 164103 (2007)





➡ free-energy difference and barrier depend on local environment (spatiotemporal correlation)

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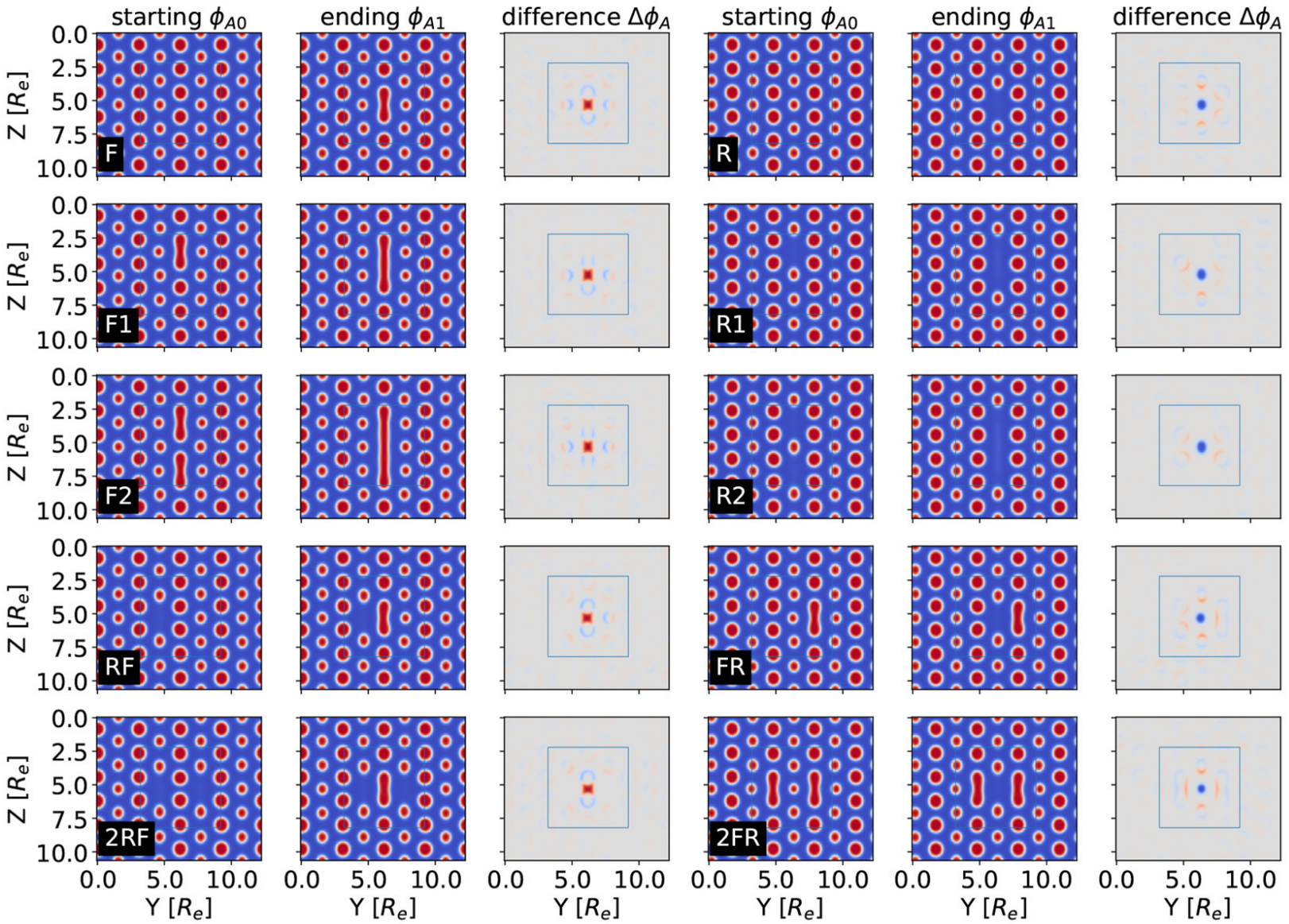
MFEP of 10 fusion and rupture transitions



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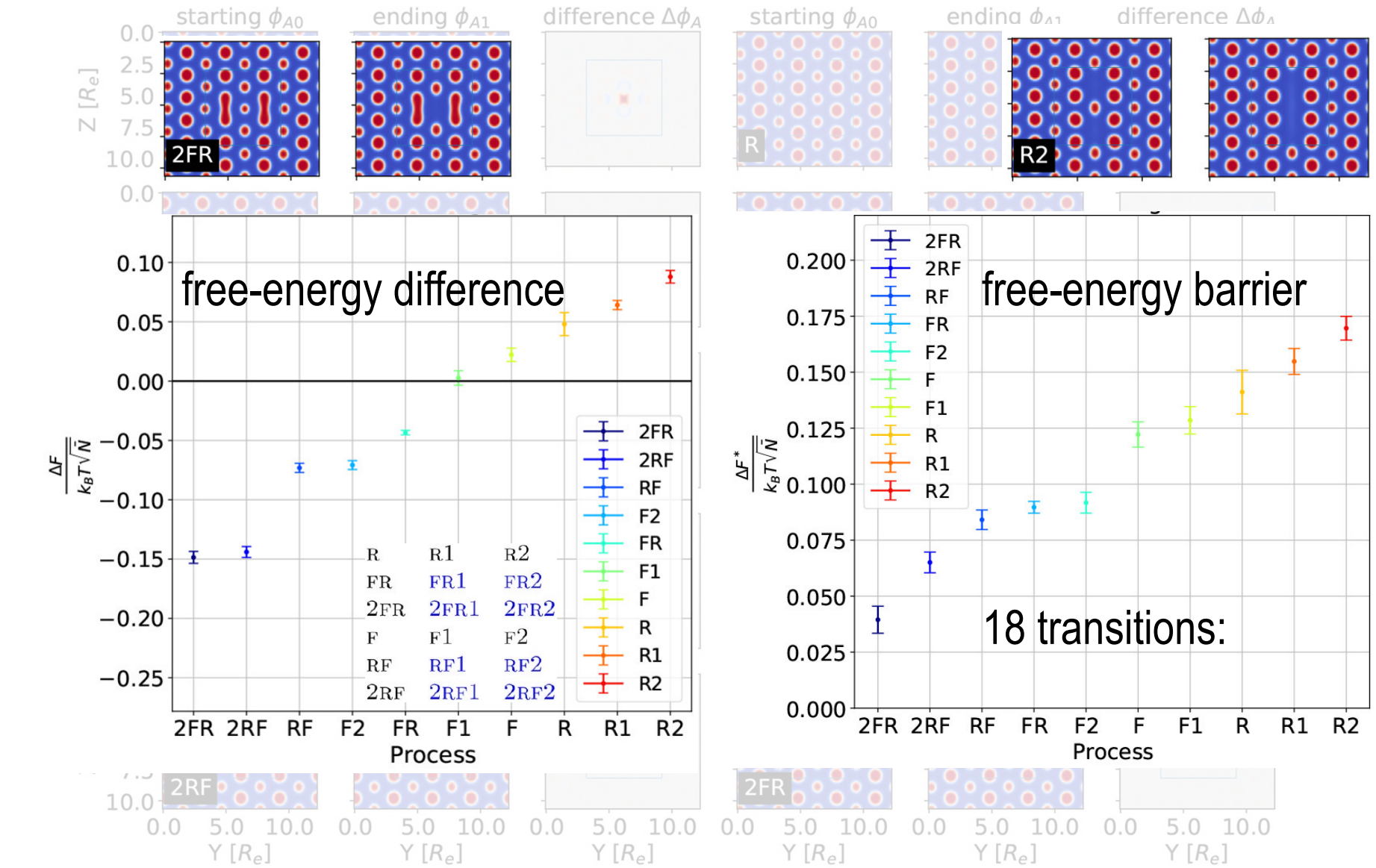
MFEP of fusion and rupture transitions



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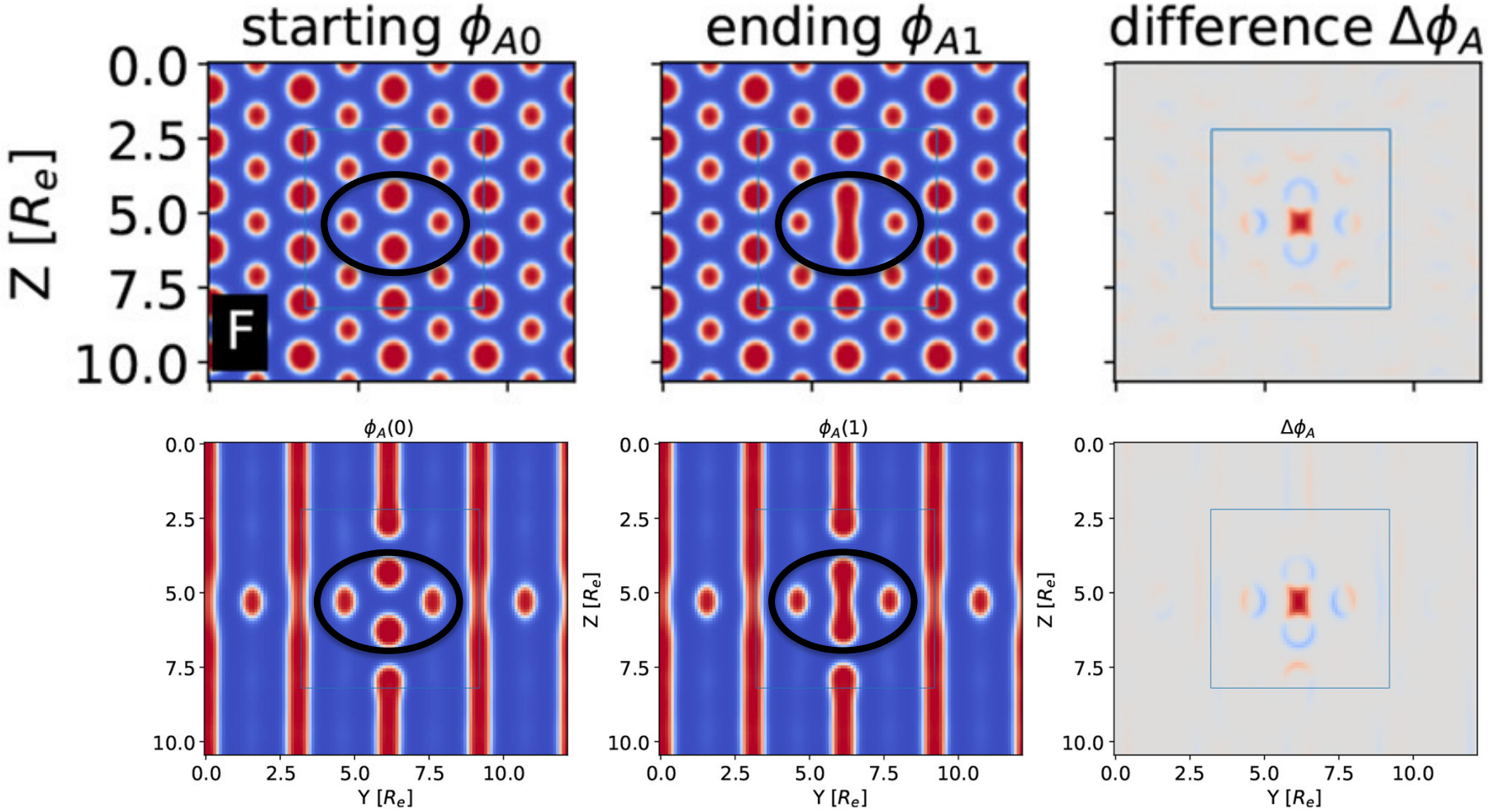
MFEP of fusion and rupture transitions

question: Do 18 transitions suffice to capture the environment dependence?



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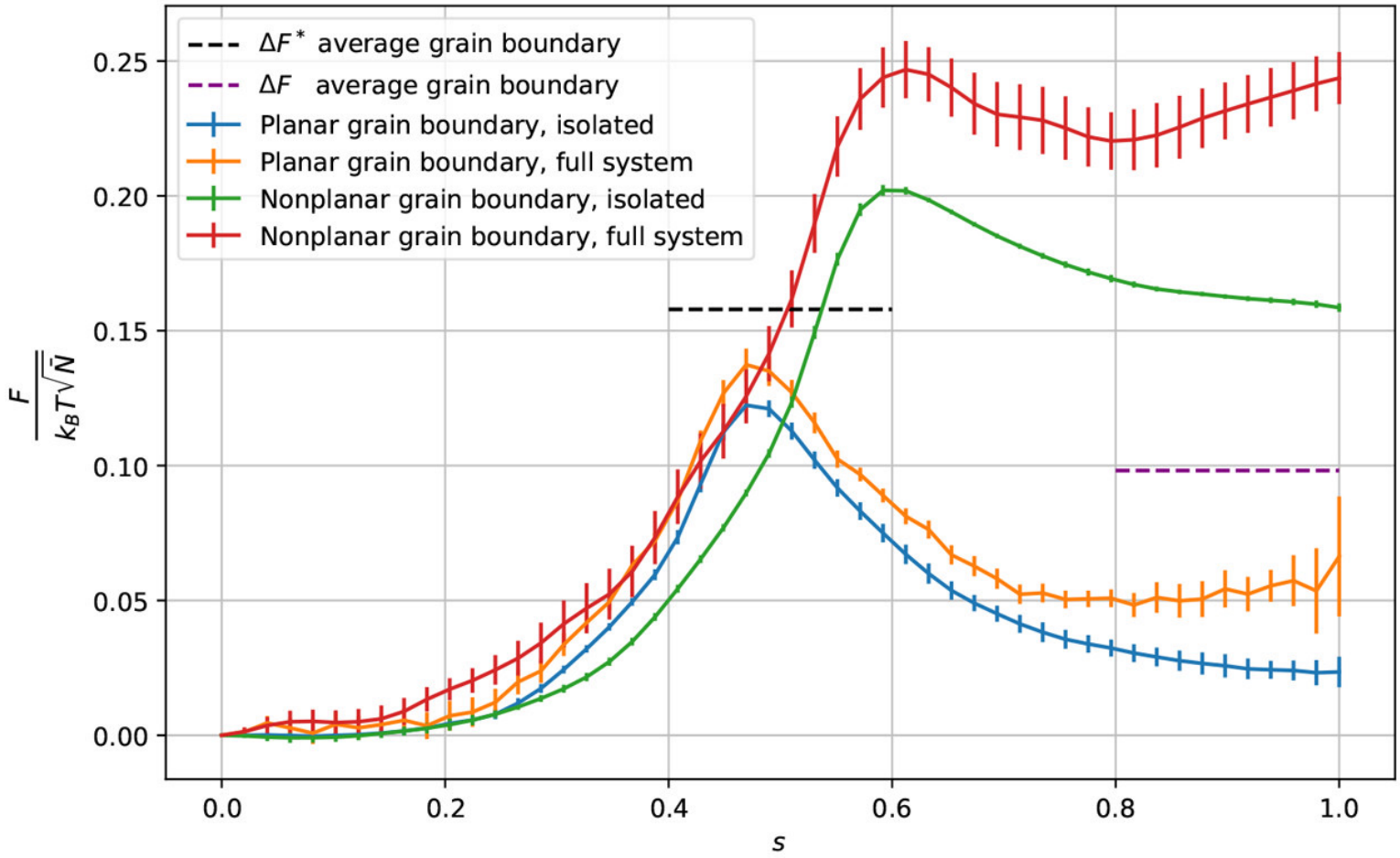
MFEP of fusion and rupture transitions

question: Do 18 transitions suffice to capture the environment dependence?

answer: unfortunately, no



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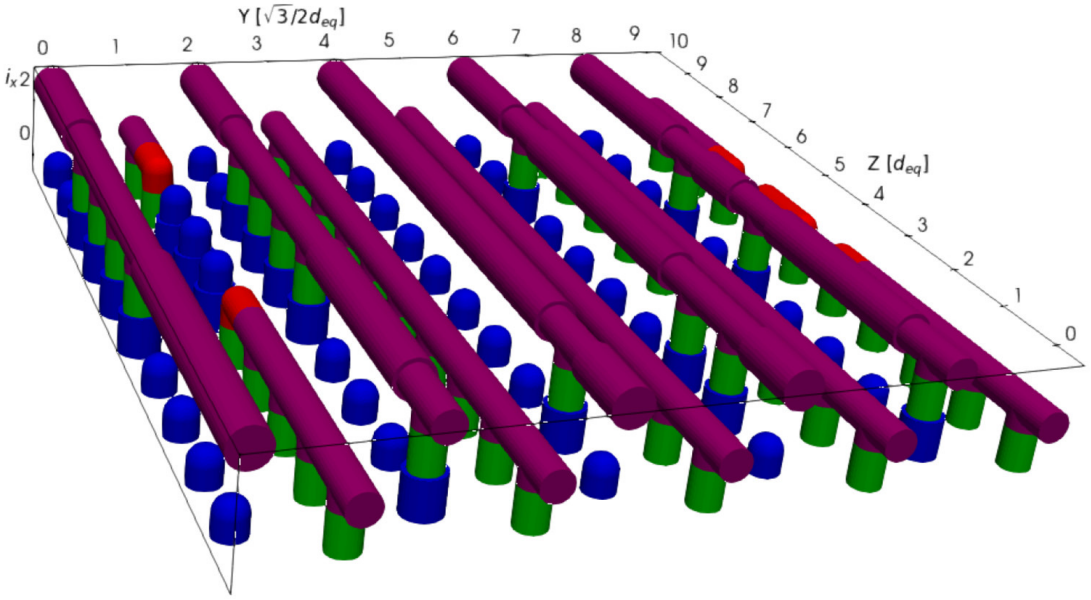
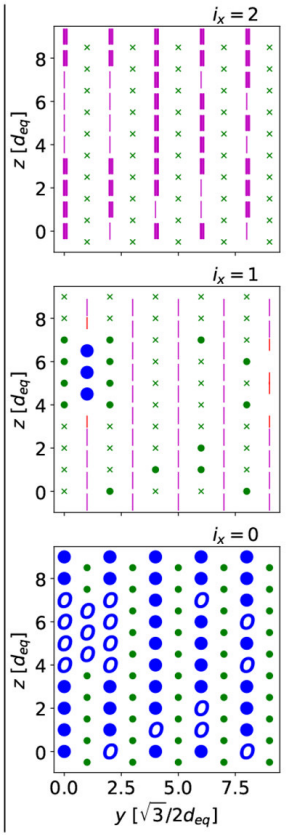
Monte-Carlo simulation of grain-boundary motion

model: describe diblock copolymer morphology by 7 states on a lattice

state	icon	may transition to
(1) parallel inner cylinder		
(2) perpendicular inner cylinder		
(3) cylinder head		
(4) bridge center		
(5) junction		
(6) void		
(7) bridge end		



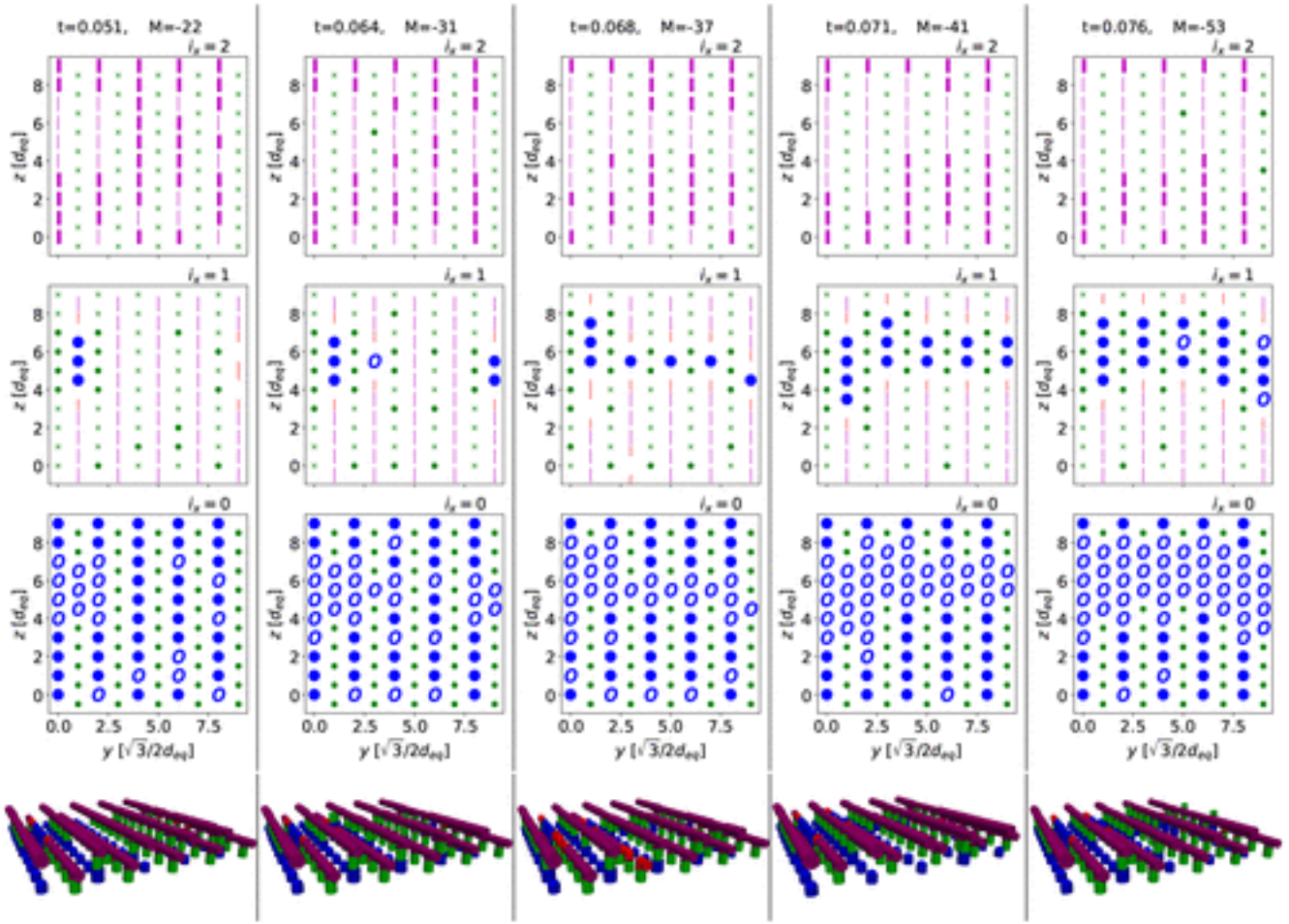


Blagojevic, Müller, *ACS Polymers AU* 3, 96 (2023)

Monte-Carlo simulation of grain-boundary motion

model: describe diblock copolymer morphology by 7 states on a lattice
and use consistent transition rates from MFEP + optimization

nucleation of an anisotopic cluster at $t=0.051\tau_{kMC}$ $\Delta t=0.02\tau_{kMC}\approx 10^6$ MCS



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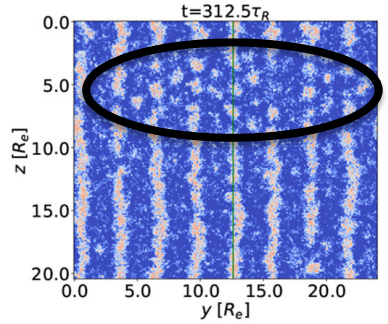
Monte-Carlo simulation of grain-boundary motion

anisotopy of clusters in grain boundary



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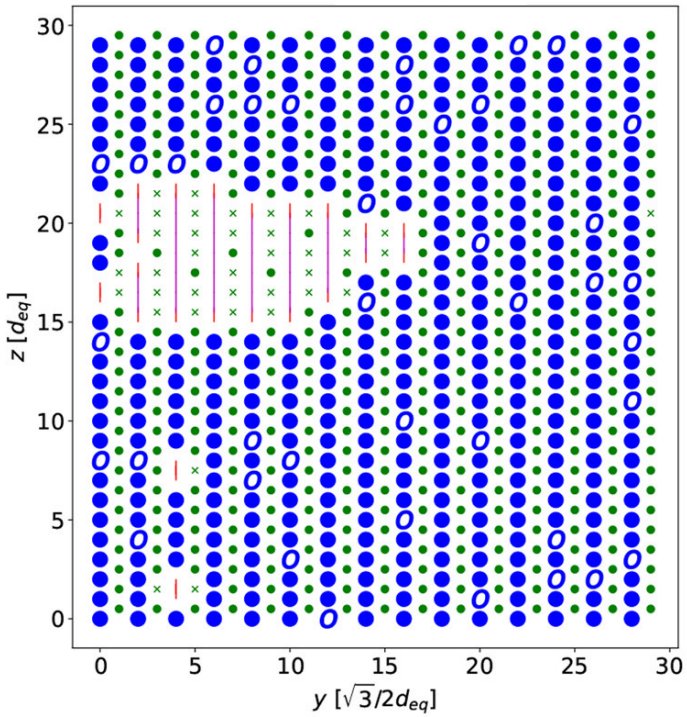
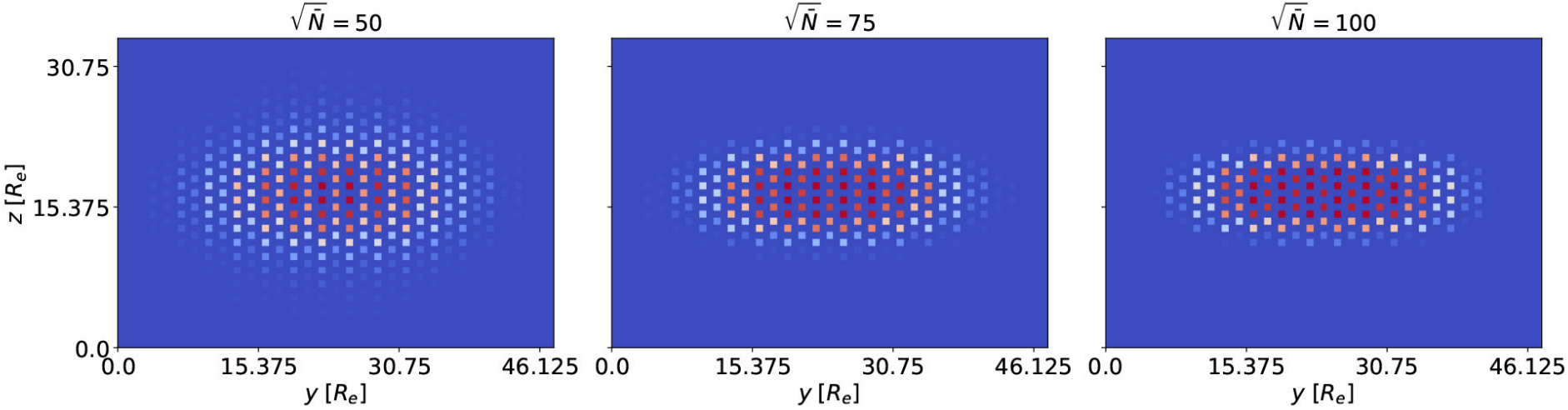
yes, soft matters





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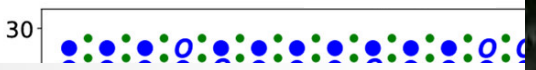
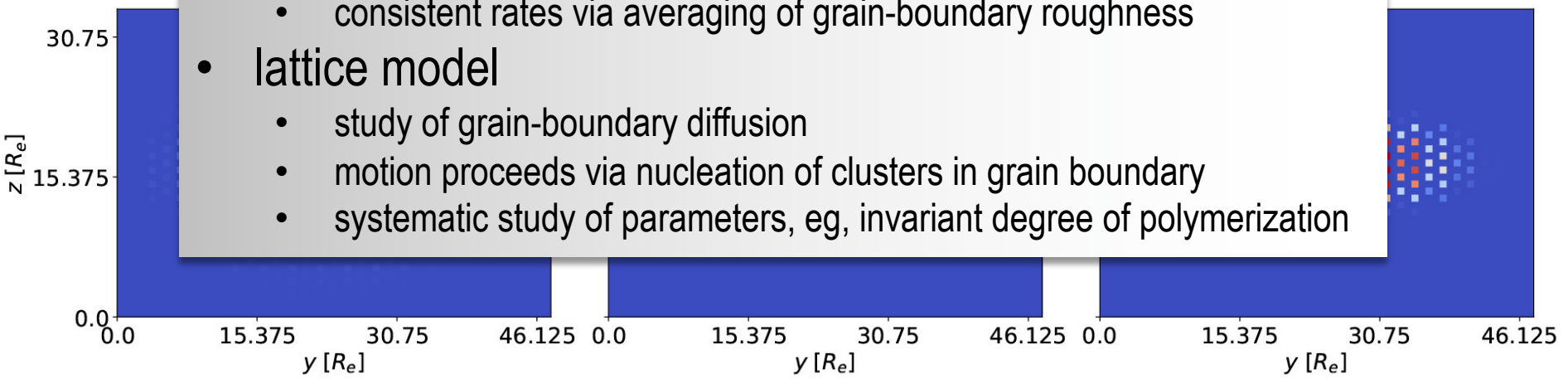
Monte-Carlo simulation of grain-boundary motion

anisotopy of clusters in grain boundary



multiscale modelling of grain-boundary motion:

- triple-scale modelling:
  particle simulation – MFEP – MC of lattice model
- particle simulation:
  - grain-boundary velocity ~ free-energy difference between grains
  - class of transitions: fusion of cylinder heads and rupture of junctions
  - sequence of topological changes, correlated in space and time
- continuum model and MFEP
  - free-energy differences and barriers
  - free-energy profiles of transitions depend on environment
  - consistent rates via averaging of grain-boundary roughness
- lattice model
  - study of grain-boundary diffusion
  - motion proceeds via nucleation of clusters in grain boundary
  - systematic study of parameters, eg, invariant degree of polymerization



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