

Modeling of Semi-batch Emulsion Copolymerization: Fast Hybrid Monte Carlo Kinetic Model and Particle-based Model of Coagulation and Fouling



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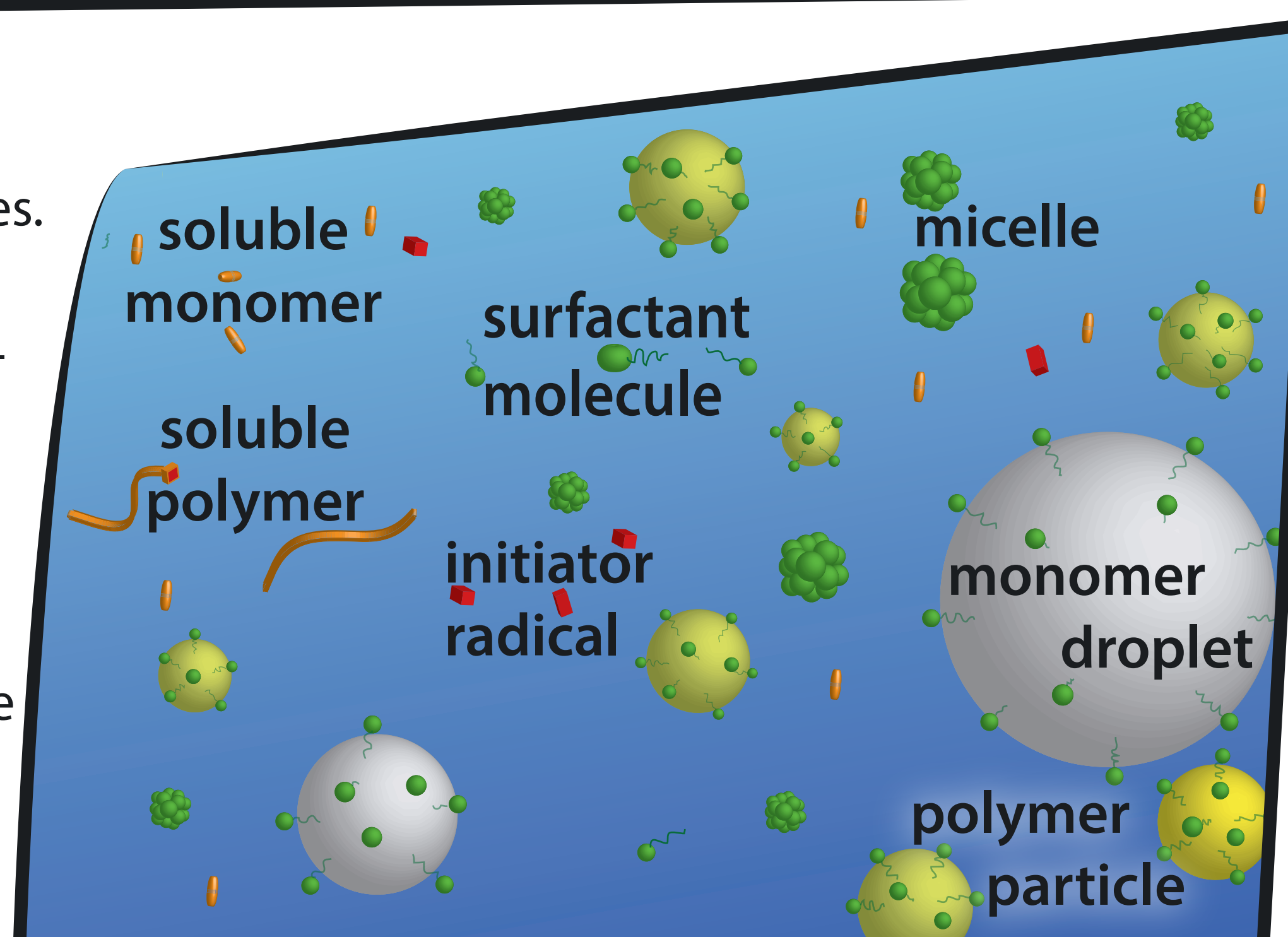
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RECOBA Project

- ☆ Intensification of industrial semi-batch processes.
- ☆ Mathematical model for on-line control must:
 - ★ Provide **robust predictions** in a sufficient agreement with experimental data.
 - ★ Calculate the process trajectory and product properties **very quickly** for on-line control.
- ☆ Mathematical model for process safety:
 - ★ Is intended to provide constraints for the safe operation of a reactor.
 - ★ The main task is to prevent fouling and the formation of coagulum.



Hybrid Monte Carlo Model

- ☆ Control model predicting the process trajectory and polymer properties is divided into two parts:
 - ★ **Deterministic Process model** covers concentration development of 4 monomers in different phases and solid content in latex.
 - ★ **Monte Carlo model** uses Process model data, and predicts full molecular weight distribution and chains molecular architecture.

Particle-based Model

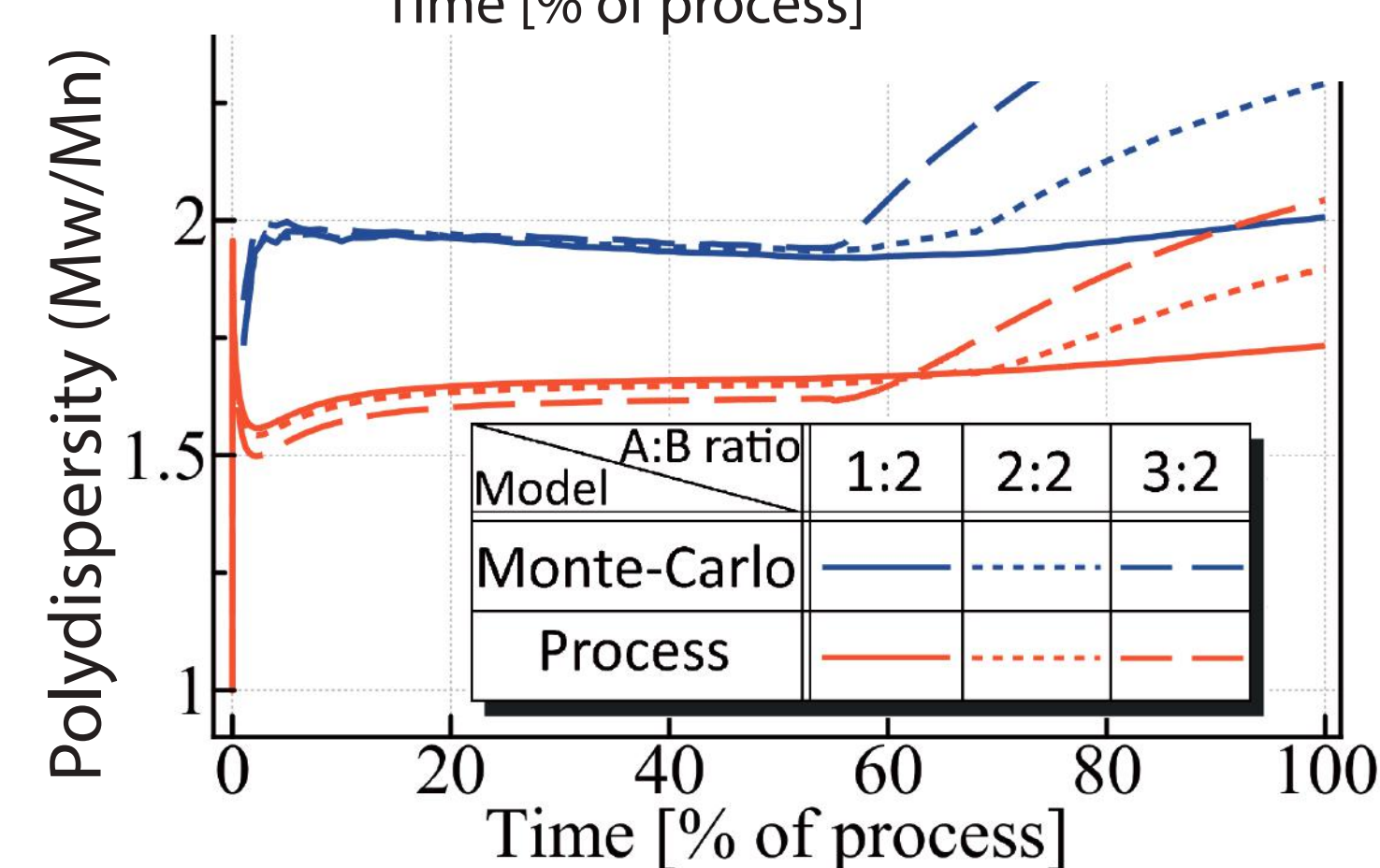
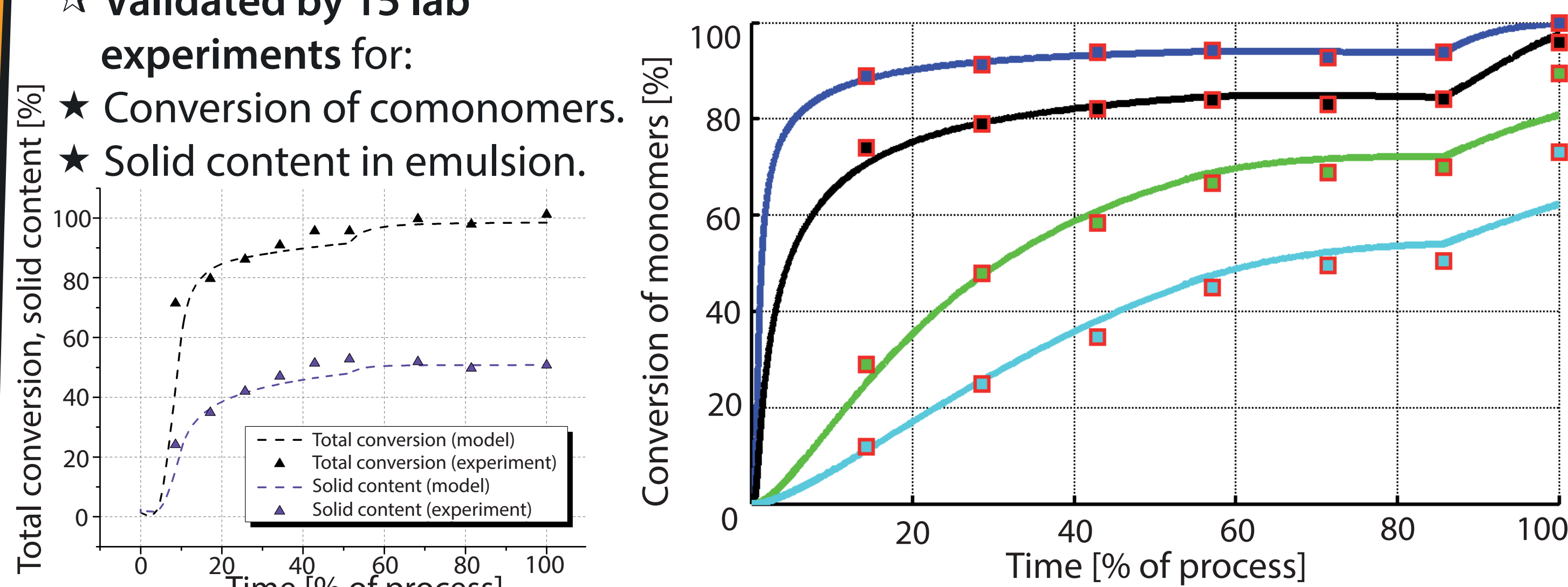
- ☆ Describes the dynamic behavior of a colloidal dispersion. It takes into account all relevant forces acting on particles.

Model Assumptions & Structure

- ☆ Amount of monomers dissolved in incompatible phase can be neglected [3], leading to **Emulsion** copolymerization (M1 + M2) in **polymer** phase running **Solution** copolymerization (M3 + M4) in **aqueous** phase simultaneously.
- ☆ Model is coded as a system of ODE and is based on the following equations [4]:
 - ★ Material balance of all non-polymeric species in appropriate phases.
 - ★ Material balance of radicals in aqueous and polymer phase.
 - ★ Copolymerization kinetics includes initiation, propagation and termination.
 - ★ Heat balance of the reaction mixture and of the cooling jacket.

Validated by 15 lab experiments for:

- ★ Conversion of comonomers.
- ★ Solid content in emulsion.

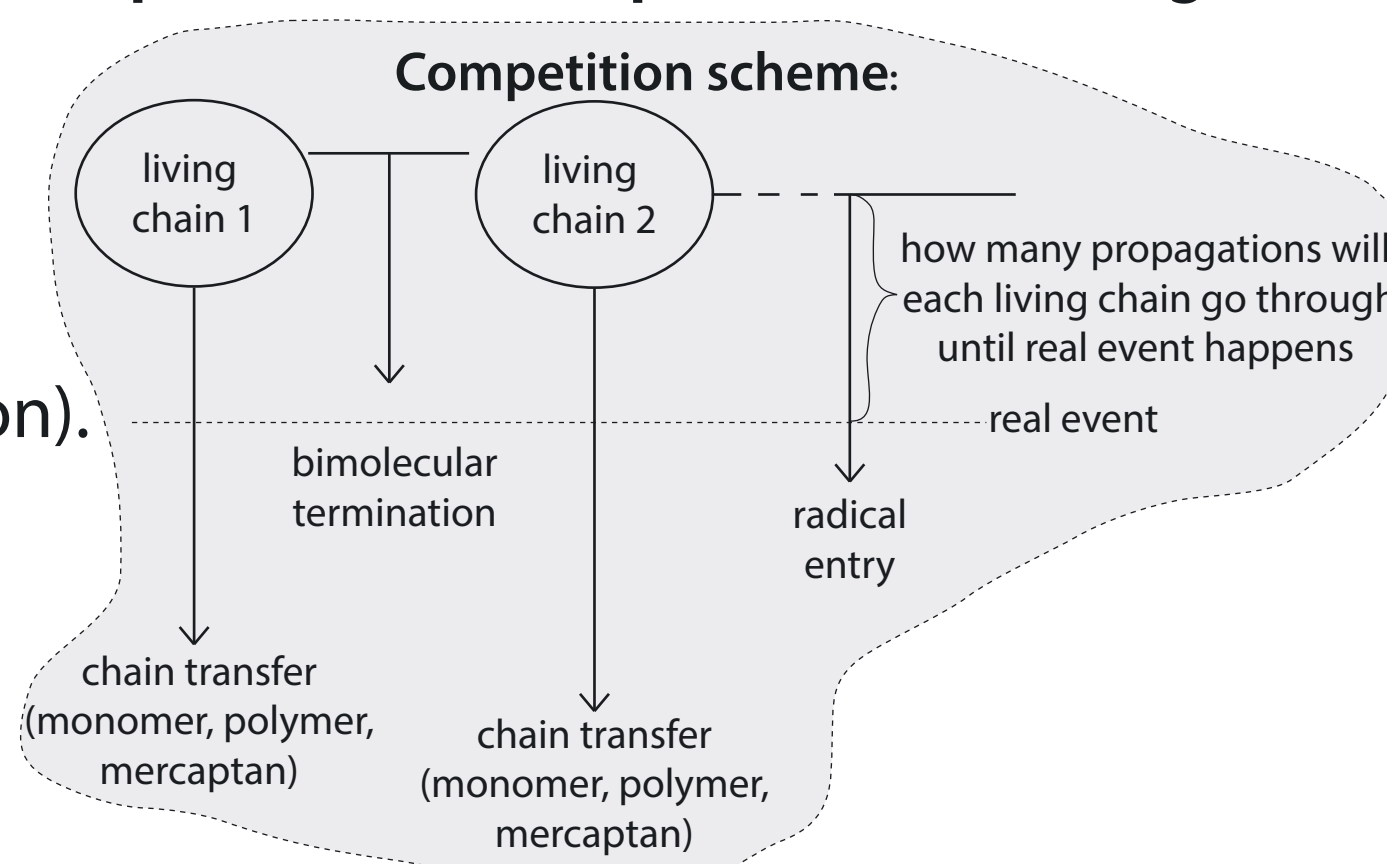
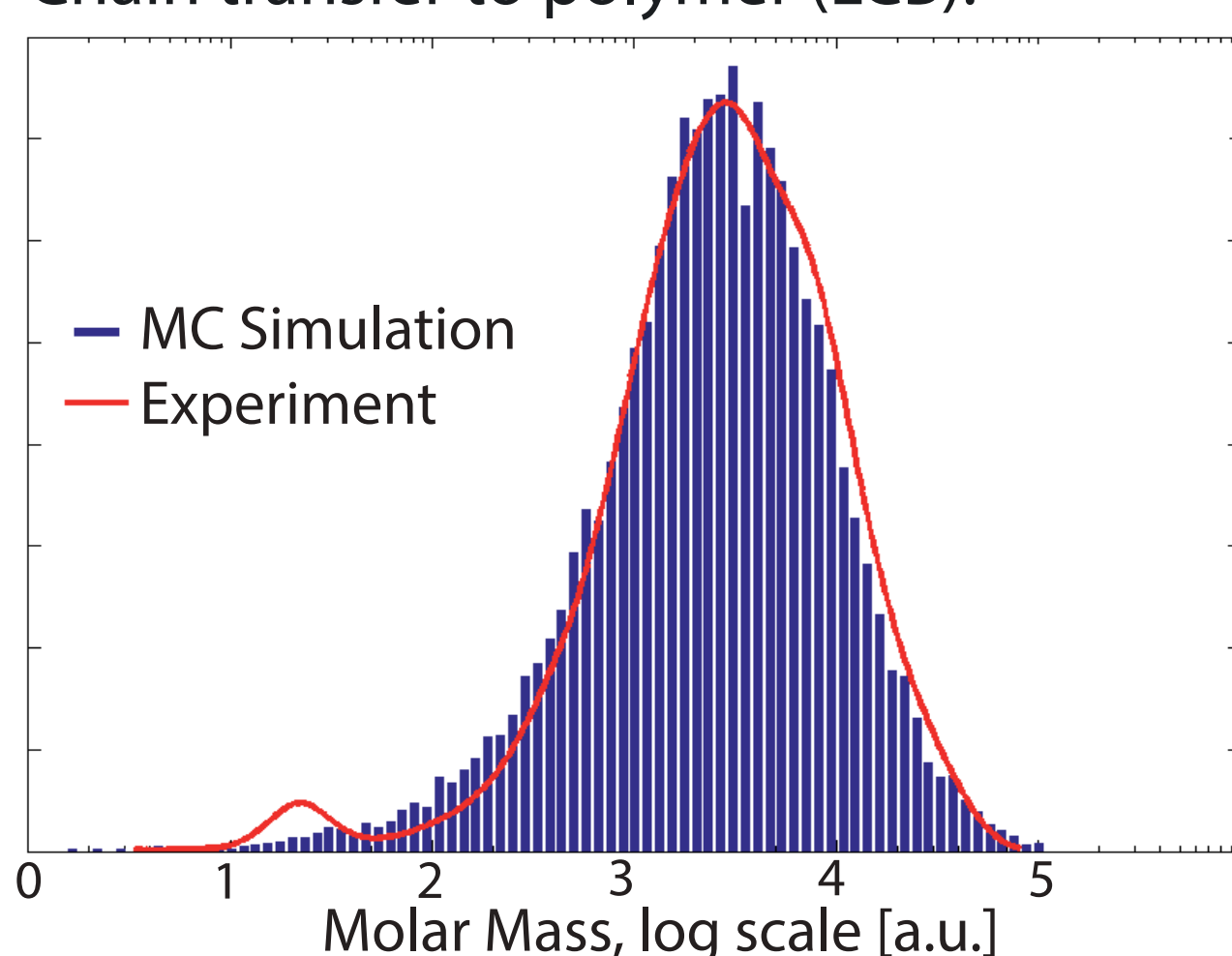


However, continuous approach considers polymer particles to be a continuous phase, enabling termination of radicals or transfer to polymer between separate particles. Thus, **molecular weight distribution might be incorrectly estimated.**

Monte Carlo Model

- ☆ Monte-Carlo model (M-C) is based on Tobita's „competition technique” [1,2], allowing for significant decrease in simulation time
- ☆ Kinetic scheme of copolymerization involves:

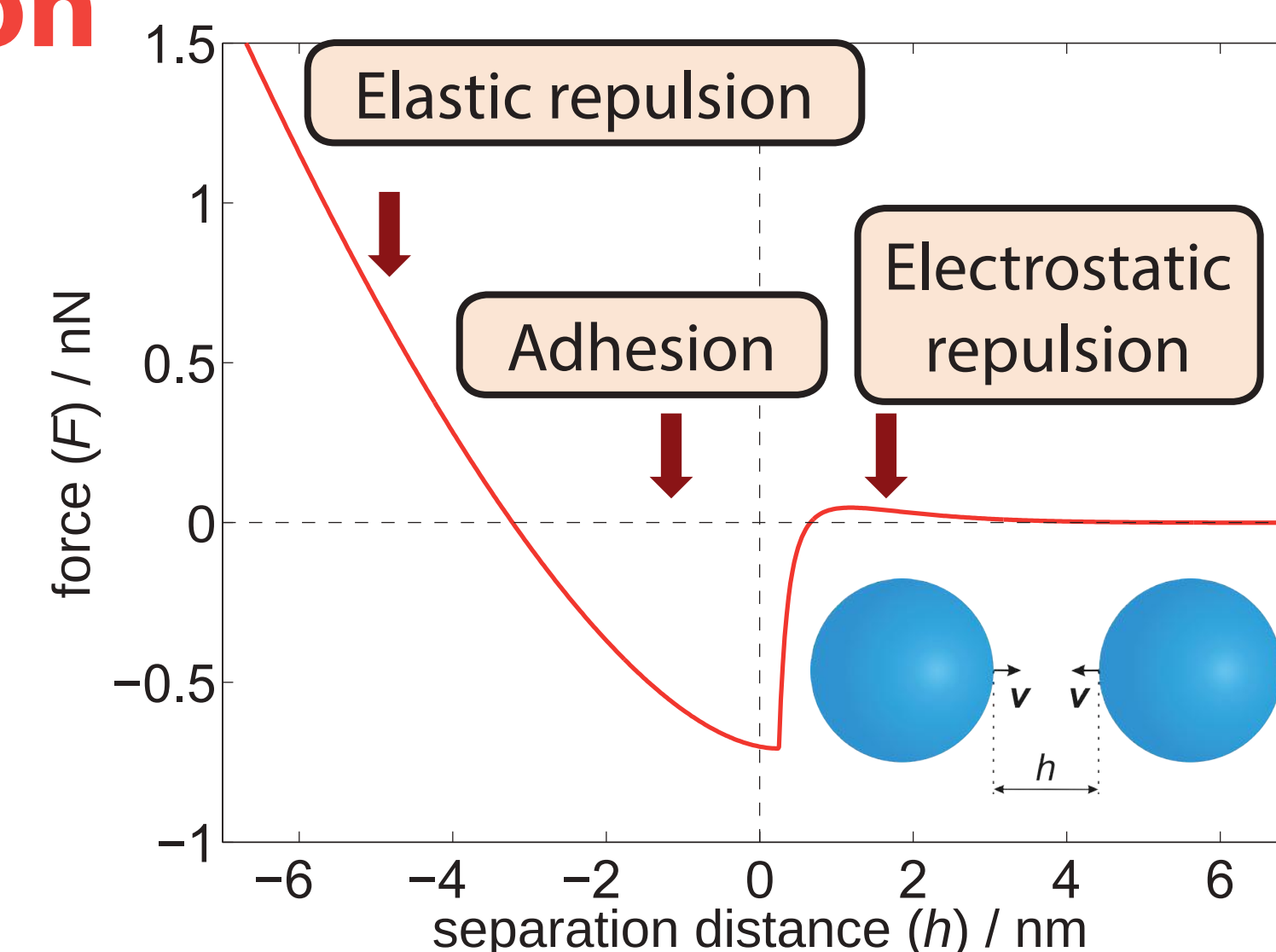
- ★ Initiation.
- ★ Propagation.
- ★ Termination (disproportionation/combination).
- ★ Chain transfer to monomer/mercaptan.
- ★ Chain transfer to polymer (LCB).



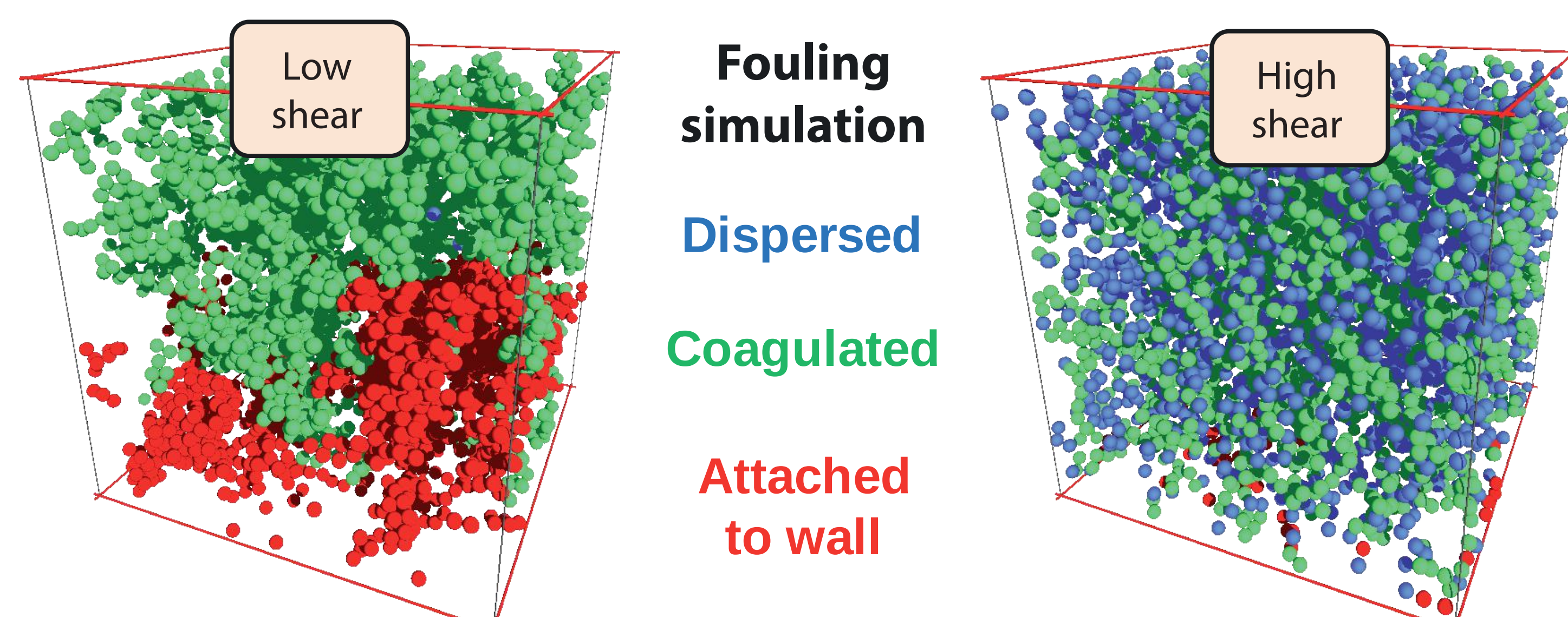
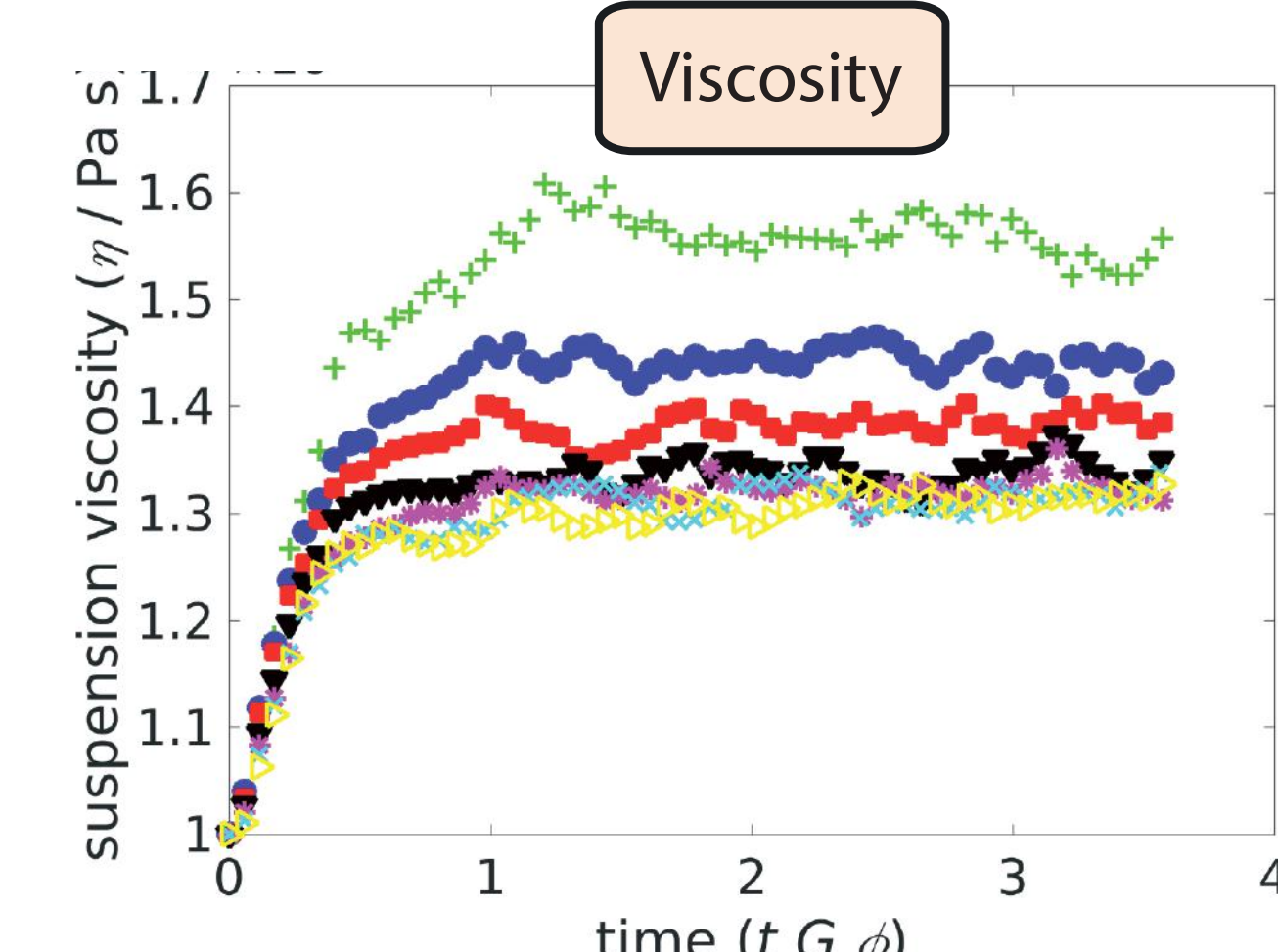
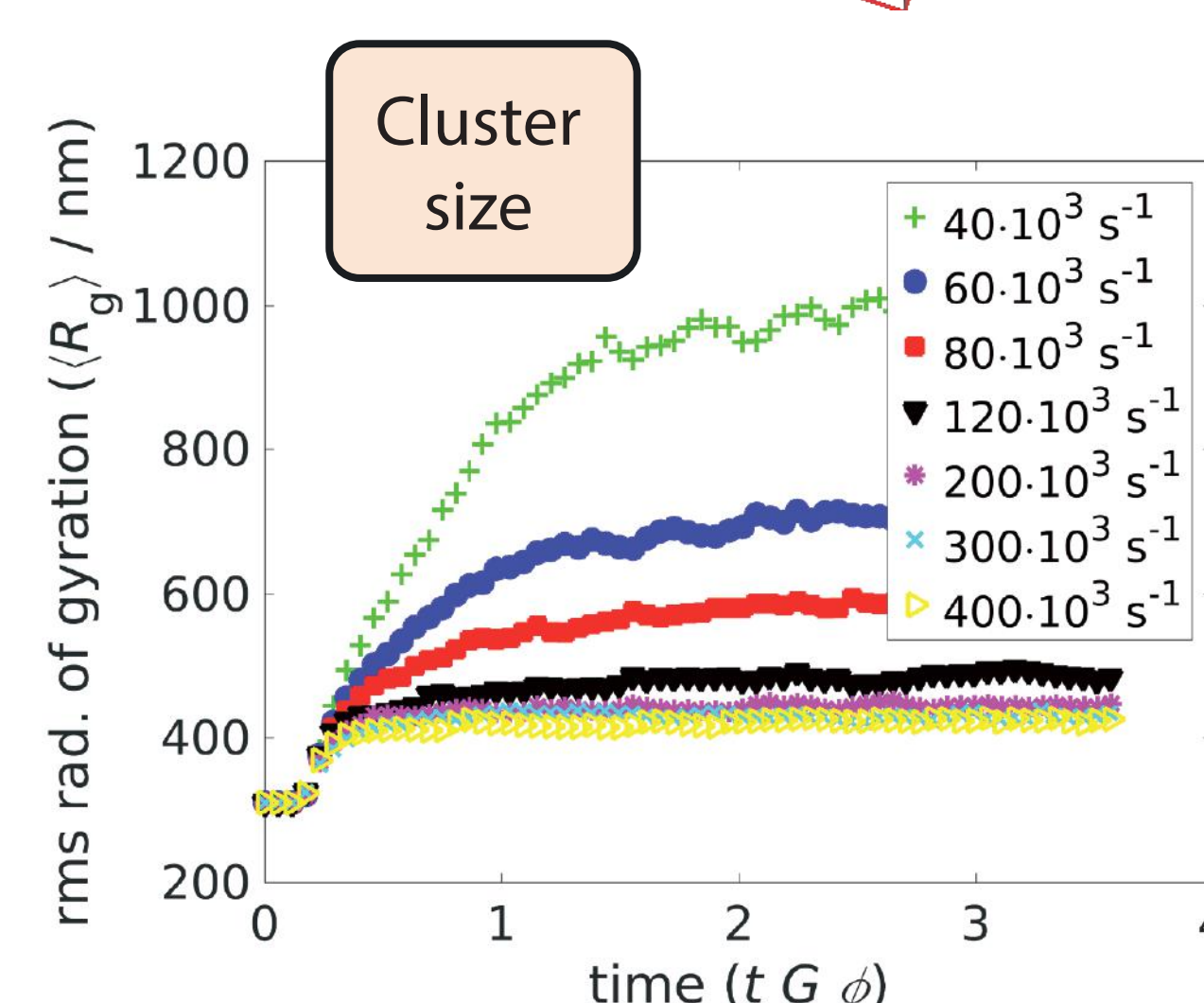
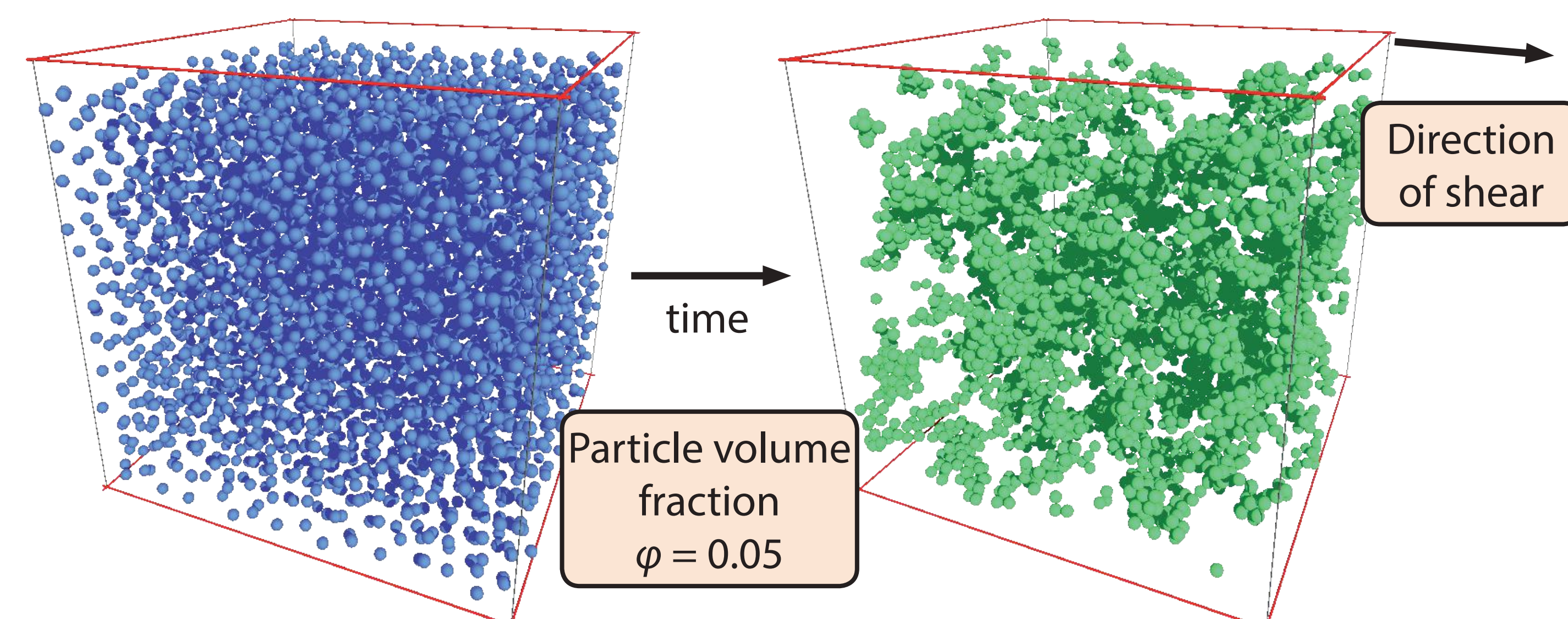
- ☆ Whole process is simulated in **several seconds** (on standard desktop PC in Matlab).
- ☆ Model predicts **full molecular weight** distribution (validated by 5 experiments) and **molecular architecture** with **branching density** (for now unsupported by any experiment)

Model of Coagulation and Fouling

Modeling particle dynamics using Discrete Element Method (DEM):
Inter-particle interactions described by:
- DLVO theory (non-contact interactions)
- JKR theory (solid body contact) and
- sliding, rolling & twisting resistance
Interactions with flow:
- two-way coupling between particles and flow



Coagulation simulation



References

- [1] H. Tobita, Monte Carlo Simulation of Emulsion Polymerization – Linear, Branched, and Crosslinked Polymers, *Acta Polym.*, 1995, **46**, 185-203
- [2] M. Slawinski: *Strategic Aspects of the Incorporation of Acrylic Acid in Emulsion Polymers*, PhD thesis, TU Eindhoven, 1999
- [3] A. Zubov, J. Pokorný, J. Kosek: Styrene-butadiene rubber (SBR) production by emulsion polymerization: Dynamic modeling and intensification of the process, *Chem. Eng. J.*, 2012, **207**, 414-420
- [4] M. Kroupa, M. Vonka, M. Soos, J. Kosek: Size and Structure of Clusters Formed by Shear Induced Coagulation: Modeling by Discrete Element Method; *Langmuir* 2015, **31**, 7727–7737
- [5] M. Kroupa, M. Vonka, M. Soos, J. Kosek: Utilizing the Discrete Element Method for the Modeling of Viscosity in Concentrated Suspensions; *Langmuir* 2016, **32**, 8451–8460

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