Modeling of emulsion copolymerization reactors: from kinetics and thermodynamics to the dispersion stability

Control and Real-time Optimisation of Intensive Polymerisation

FP7-NMP-2011-Small-5 Grant Agreement 280827

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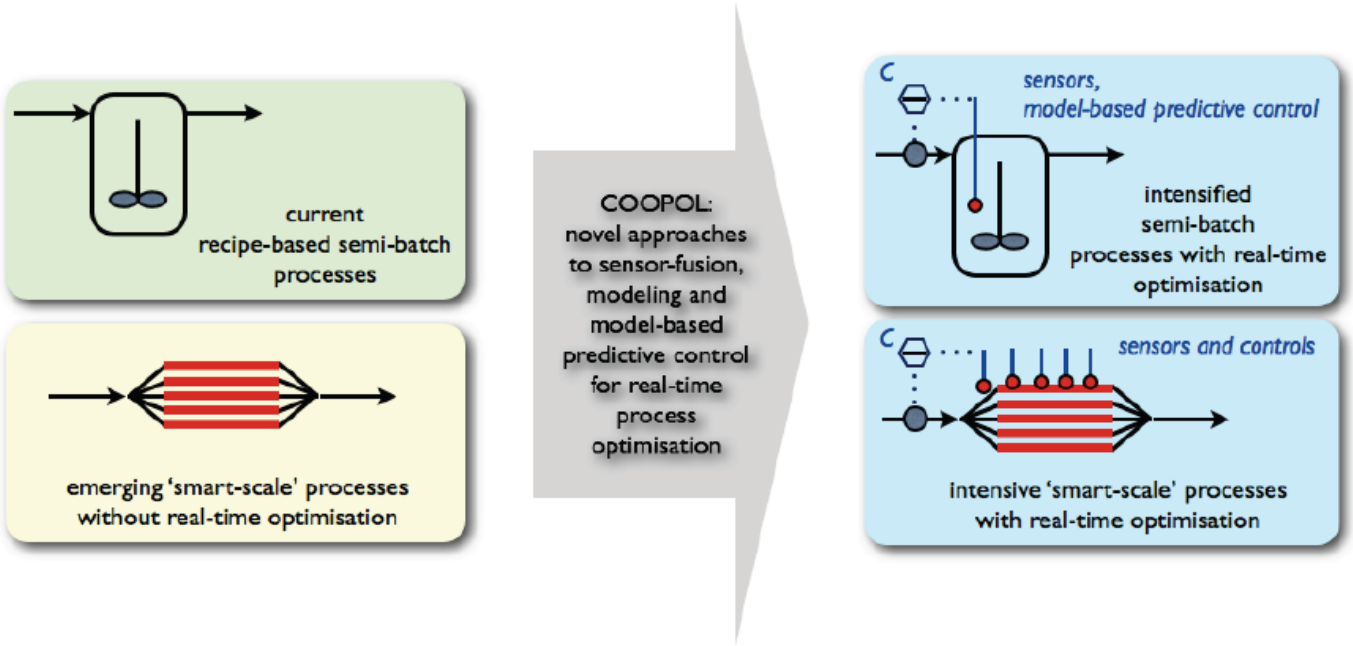
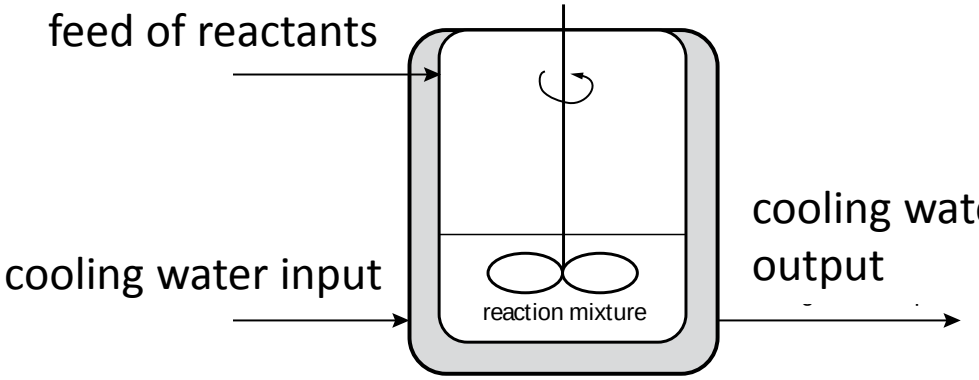
Motivation

- Concept of the COOPOL project:
  - develop robust real-time optimization-based control and sensing methodologies
- Our goals:
  - develop mathematical models for both existing semi-batch and emerging ‘smart-scale’ (e.g. continuous) processes



Strategy to achieve our goals

- Starting point:
  - Models of emulsion copolymerization previously developed (i) by our group[(A)], and (ii) by group of prof. Engell at TUD[(B)]
- Adaptation and improvement of models to our problem:
  - semi-batch: 4 monomers (two of them water soluble), seed
  - smart-scale: 2 monomers (insoluble in water), unseeded
- Model reduction – models suitable for on-line process control (robust and fast)



Smart-scale reactor
Courtesy of Fabian Lueth, University of Hamburg

A. Zubov, J. Pokorny, J. Kosek: Styrene-butadiene rubber (SBR) production by emulsion polymerization: Dynamic modeling and intensification of the process. *Chemical Engineering Journal* **207-208**, 414-420 (2012).

B. H. Brandt: *Online Anwendungen komplexer Modelle von Reaktionssystemen am Beispiel der Emulsions-Polymerisation*. Report, TU Dortmund (2009).

Presentation outline

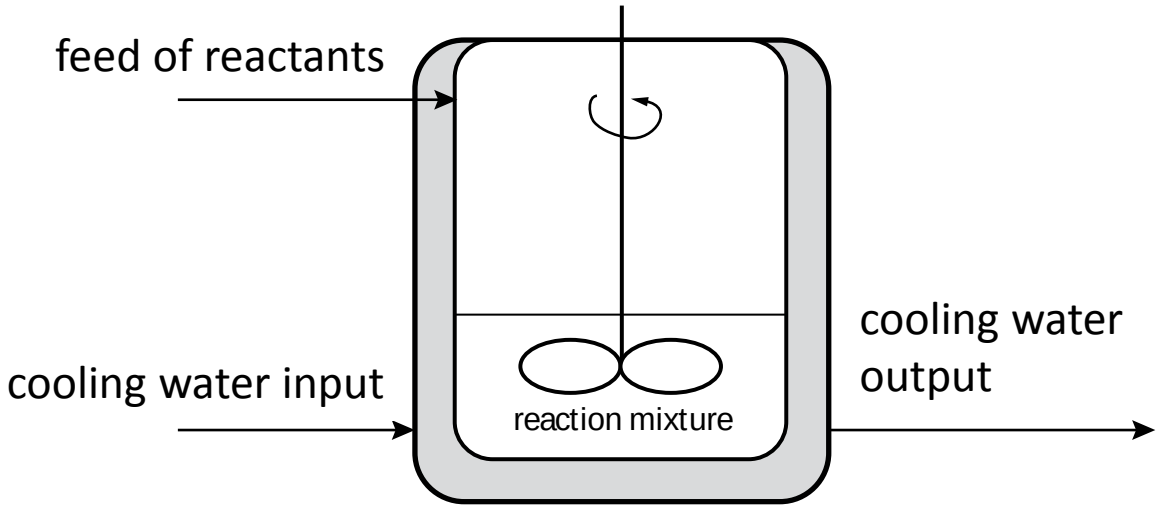
- 1) Process model for **semi-batch polymerization**
  - 4-monomer system: 2 hydrophobic + 2 water-soluble
  - Complex monomer partitioning
  - pH dependency of polymerization rate (dissociation)
- 2) Process model for polymerization in **smart-scale reactor**
  - Unseeded polymerization – nucleation of particles
  - Small particles: Monomer partitioning based on Morton equation
- 3) Innovative use of sensors
  - on-line **information about cross-linking**

SKIPPED

- 4) Modeling of **coagulation/fouling** dynamics
  - Predicting the boundaries for safe (coagulum free) operation

Semi-batch reactor modeling

- Monomer-starved conditions
- Hydrophobic (M1,M3) + hydrophilic (M2,M4) comonomers
- Need to **quickly** and **accurately** predict:
  - Conversion of monomers
  - Solid content
  - Polymer MWD



Semi-batch reactor modeling

- Separation of reaction medium into:
  - **Emulsion** copolymerization (M1+M3) in polymer phase.
  - **Solution** copolymerization (M2+M4) in water.

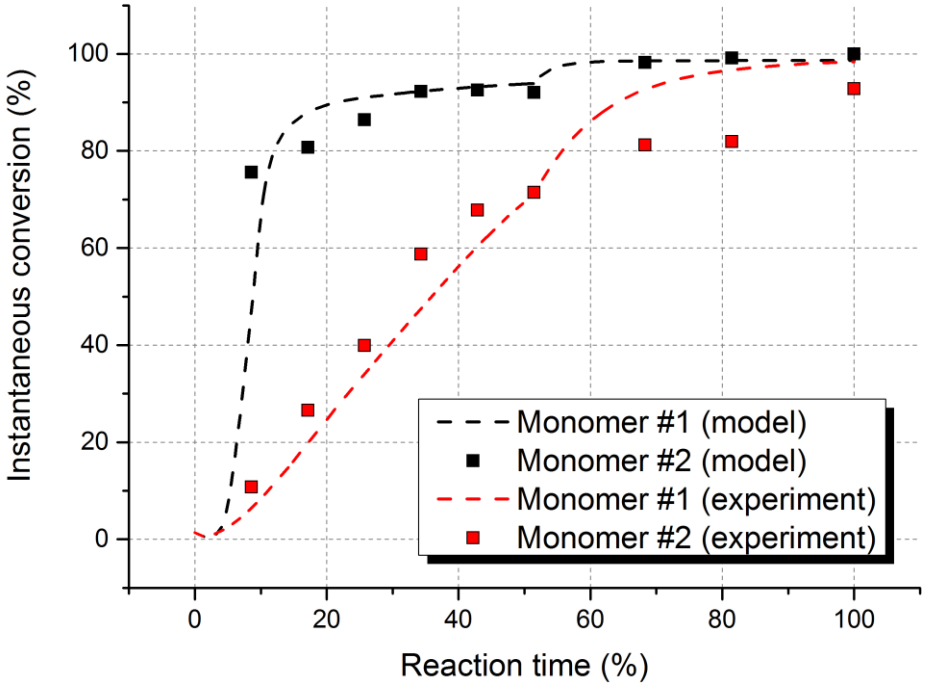
- Model formulated as system of ODE based on:
  - Material balance of non-polymeric species in all phases.
  - Material balance of radicals in polymer and aqueous phase.
  - Population balance of polymer moments (summed over polymer and aqueous phase).
  - Heat balance of reaction mixture and cooling jacket.

Semi-batch reactor modeling

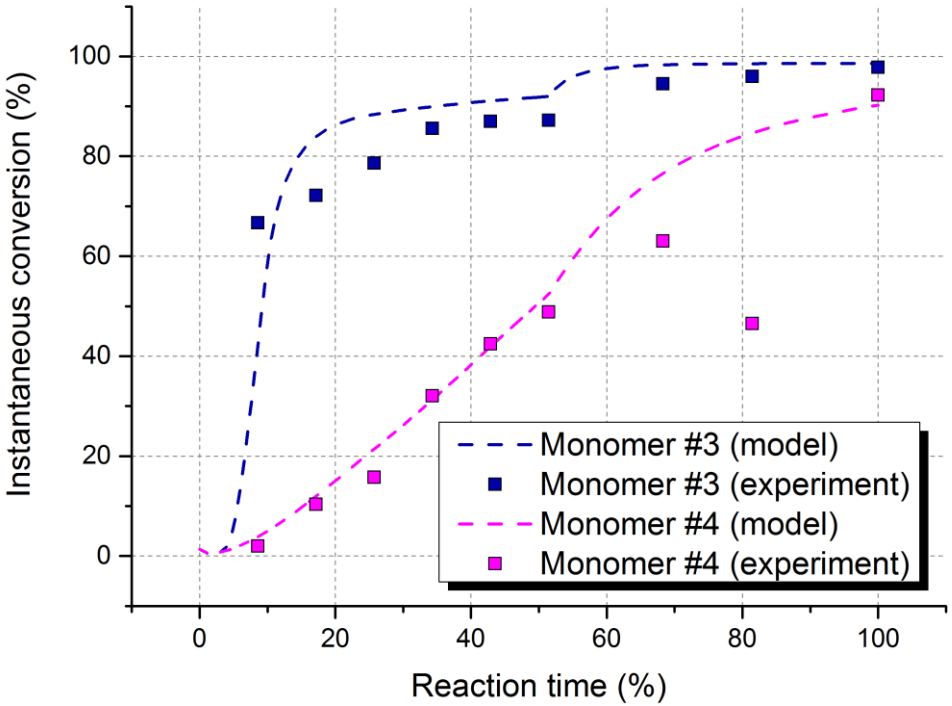
- Kinetic scheme involves:
  - Initiation + propagation.
  - Termination (combination/disproportionation).
  - Chain transfer to monomer and mercaptan.
  - Intramolecular chain transfer (backbiting) → SCB.

- Model validated by 15 laboratory experiments for:
  - Individual conversion of all monomers.
  - Solid content in the emulsion.
  - Average molecular weights of produced polymer.

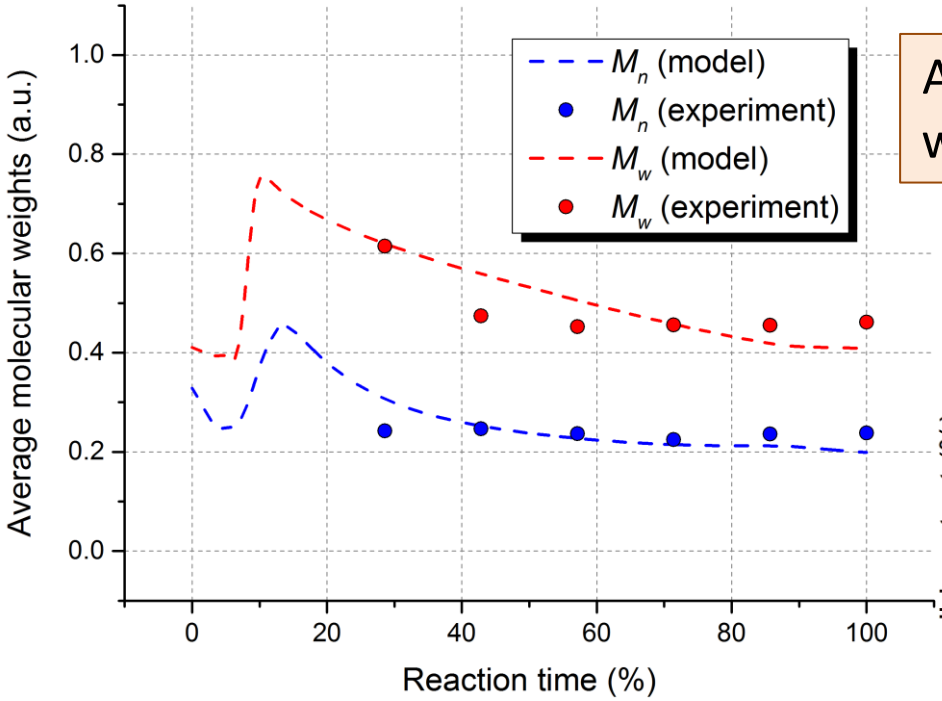
Semi-batch reactor modeling



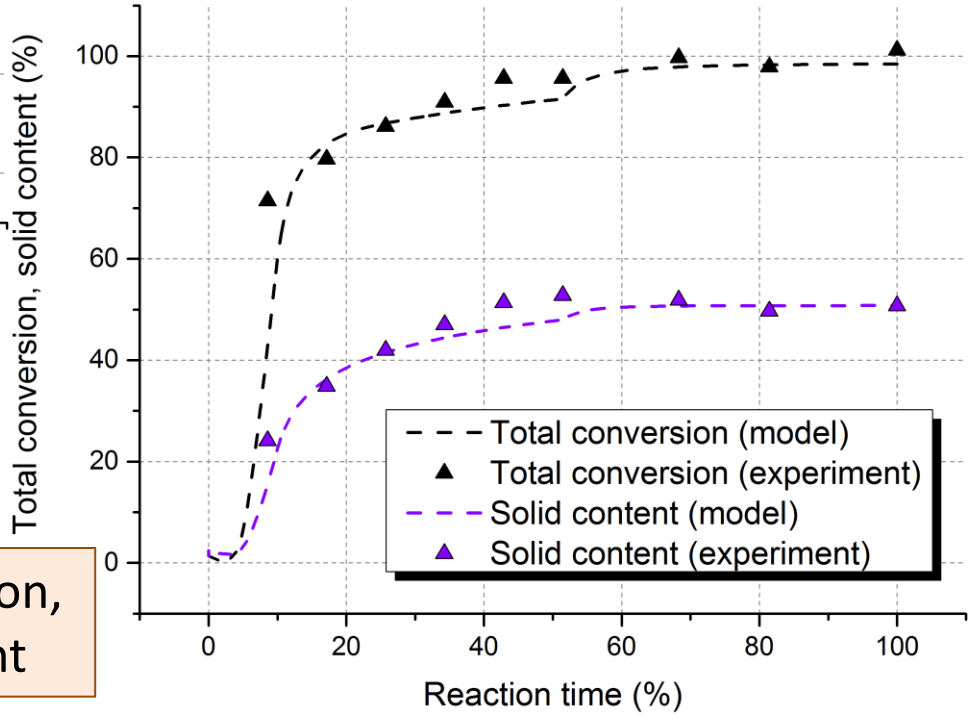
Instantaneous conversion of individual monomers



Semi-batch reactor modeling



Average molecular weights of polymer

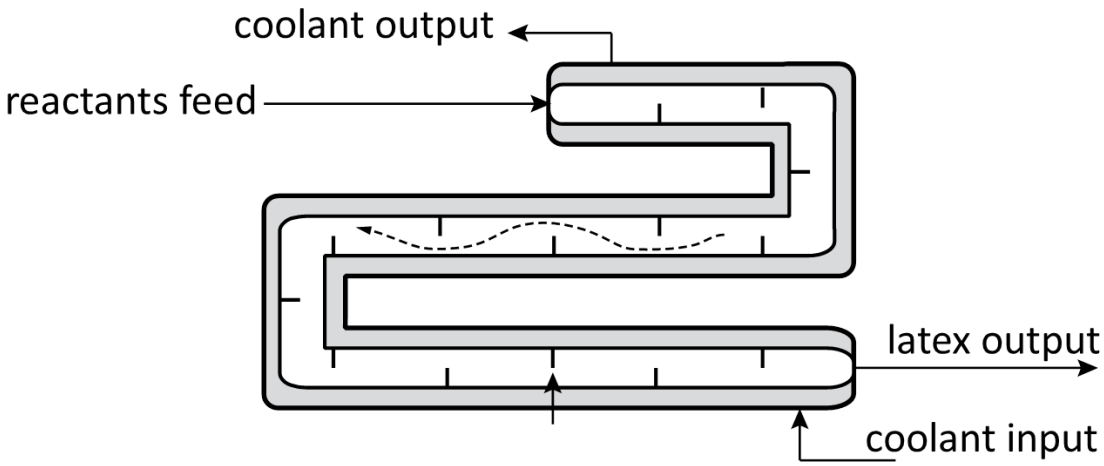


Total conversion, solid content

„Smart-scale“ reactor modeling

- Next to the model of semi-batch reactor, we also develop model for the emulsion polymerization in smart-scale reactor (basically **continuous tubular reactor**)
- Low investment costs – polymers for special applications

Courtesy of Fabian Lueth
University of Hamburg



„Smart-scale“ reactor modeling

- Modelled as axially dispersed plug-flow reactor using method of lines (MOL)
- Balance equations for state variables ψ
  - Monomers, polymer, water, initiator, emulsifier, average number of radicals per particle, number of particles ($\psi = c_{Mi}, c_P, \phi_w, c_I, c_E, n_{AVG}, N_T$)

state variable

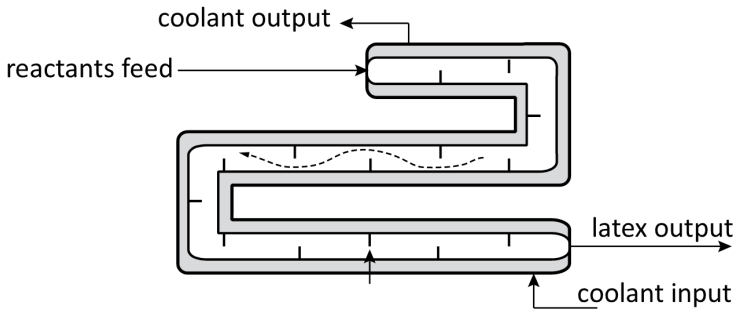
$$\frac{\partial \psi}{\partial t} + v\frac{\partial \psi}{\partial z} - D_e\frac{\partial^2 \psi}{\partial z^2} = \sigma$$

source term

- Danckwerts boundary conditions:

$$\frac{D_e}{v}\frac{\partial \psi}{\partial z} = \psi - \psi_e \qquad z = 0$$

$$\frac{\partial \psi}{\partial z} = 0 \qquad z = L$$

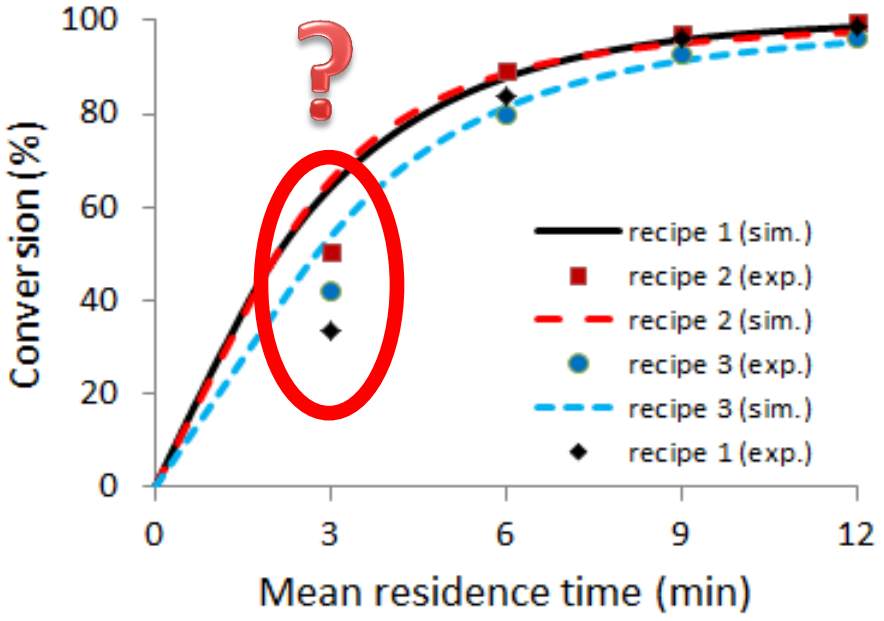


COOPOL

„Smart-scale“ reactor modeling

- Validation – conversion, comonomer content, Mw, Mn
- Using the same kinetic parameters as in semi-batch
- First simulations **revealed slower reaction rate** at the beginning of the reactor
  - nucleation implemented, but found to be almost instantaneous

- Possible cause – **thermodynamics of monomer partitioning**



Monomer partitioning

- Implementation of non-linear Morton-Kaizerman-Altier equation for the **monomer partitioning**
- Equilibrium of chemical potentials in all phases
- Lower monomer fractions in small particles – slower reaction

Partial molar Gibbs energy

Vol. frac. of polymer in particle

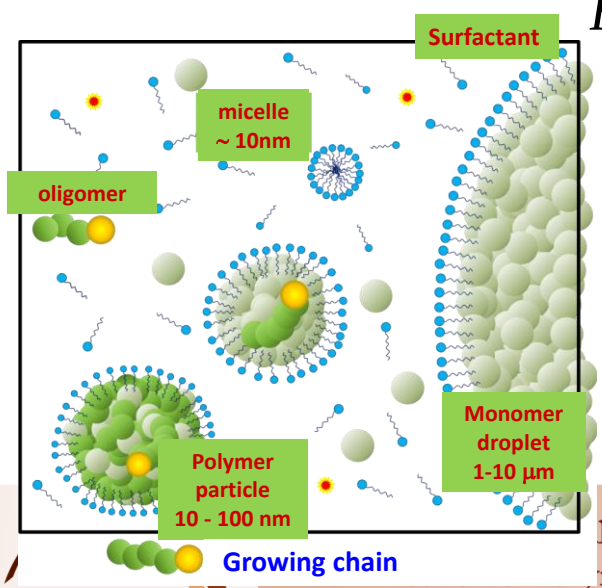
Flory-Huggins interaction param.

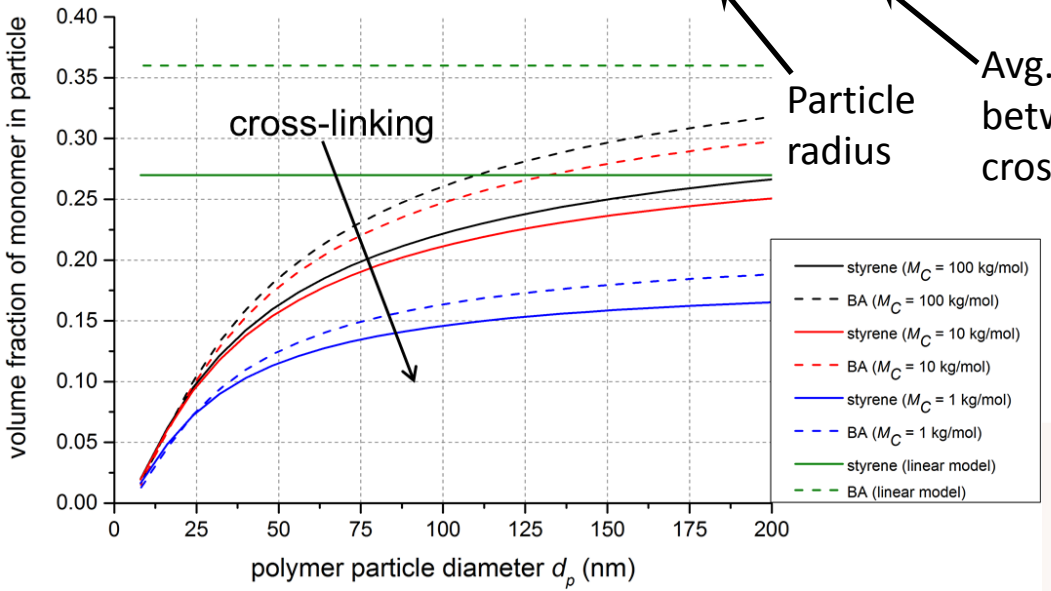
Interfacial tension

$$\frac{\Delta\overline{G}_{i,polymer}}{RT} = \ln(1-\phi_P) + \phi_P + \chi_{iP}\phi_P^2 + \frac{2\sigma V_{m,i}}{RTr_P} + \frac{V_m\rho_P}{M_C}\left(\phi_P^{1/3} + \frac{\phi_P}{2}\right)$$

Particle radius

Avg. MW between cross-links





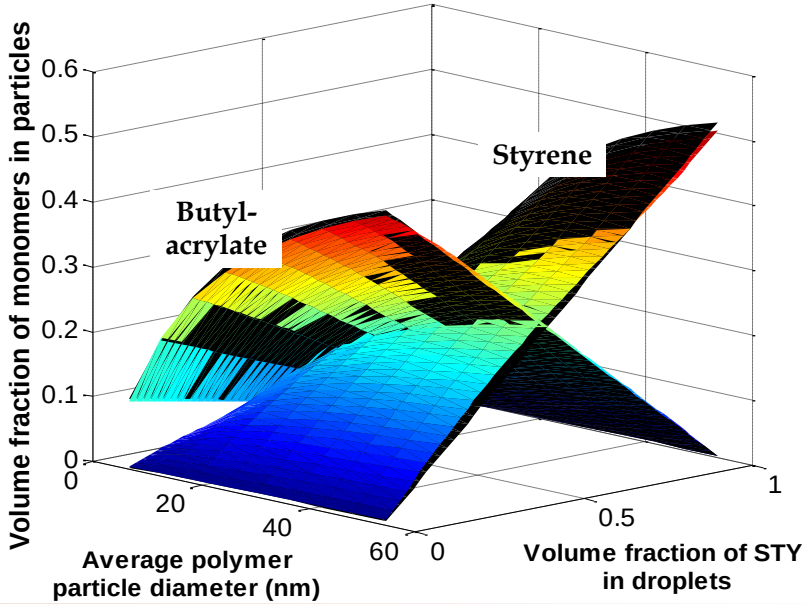
Monomer partitioning

- MKA equations are highly nonlinear, the integration needs a good initial guess and considerably slows down the calculations in the process model of tubular reactor
  - Empirical relationship used to predict volume fraction of monomers in polymer ϕ_i^P as a function of process conditions and parameters

$$\phi_i^P = a_{i,1}\left[a_{i,2}\sigma + \arctan\left(\frac{r_P}{a_{i,3}}\right)\right]\frac{k_i^P}{k_i^D}\phi_i^D$$

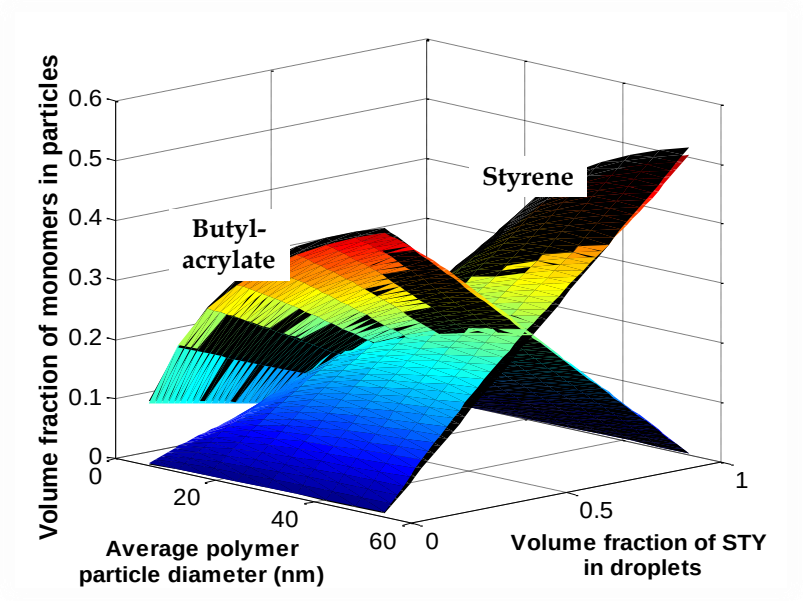
- Comparison of MKA solution (colored surface) with surrogate model (black surface)

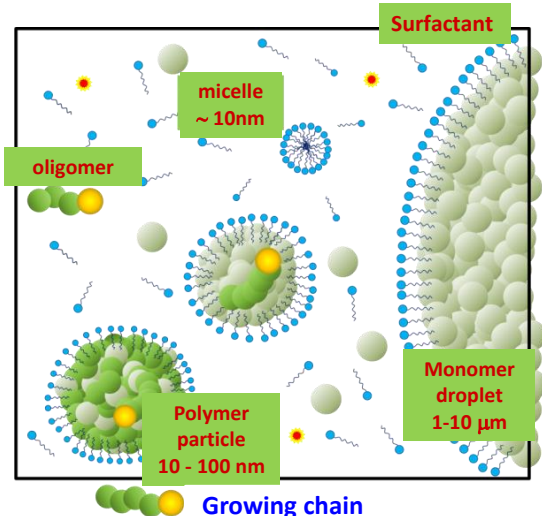
r_p	particle radius
σ	interfacial tension
T	temperature
Φ_i^D	volume fraction of monomer in droplets
k_i^P	partitioning coefficient between polymer and water
k_i^D	partitioning coefficient between polymer and droplet



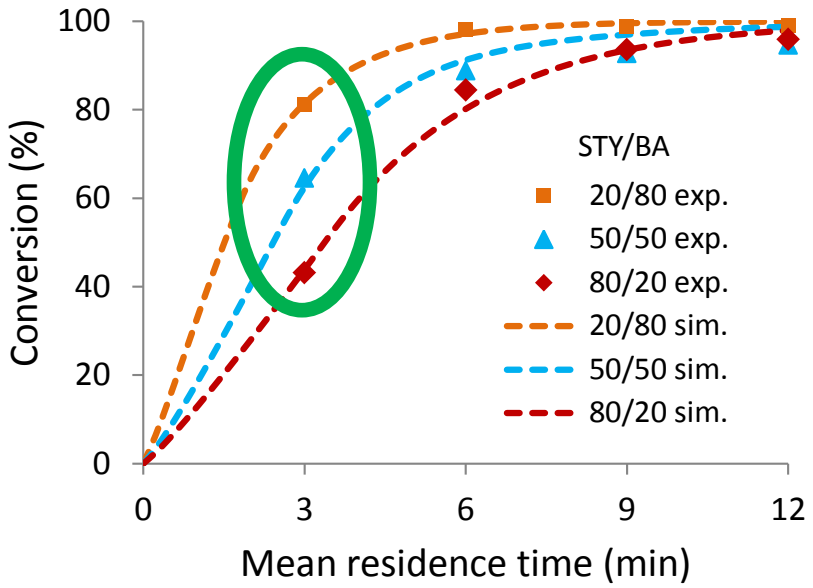
Monomer partitioning

- Implementation of non-linear Morton-Kaizerman-Altier equation for the monomer partitioning



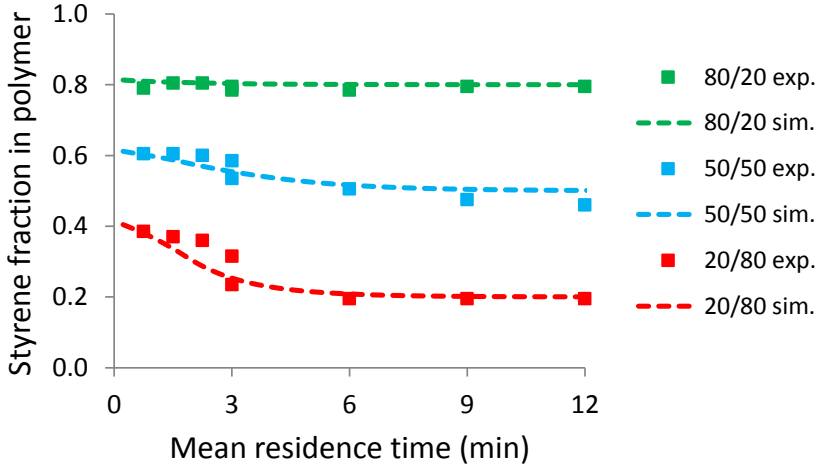


- Excellent agreement

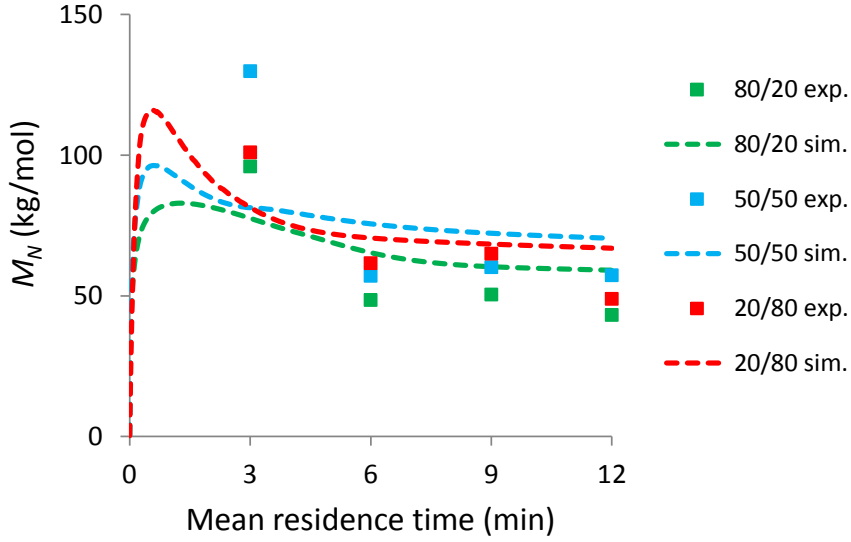


Monomer partitioning - results

- Comparison for different STY/BA ratios (30 wt.% monomer)



- Copolymer composition
  - Excellent agreement



- Molecular weight
  - reasonable agreement in number-average molecular weight

Motivation – Coagulation

- Stabilized dispersions are encountered in various applications
  - Food, cosmetics, etc.
  - Emulsion & suspension polymerization

http://en.wikipedia.org/wiki/Emulsion_polymerization

Motivation – Coagulation

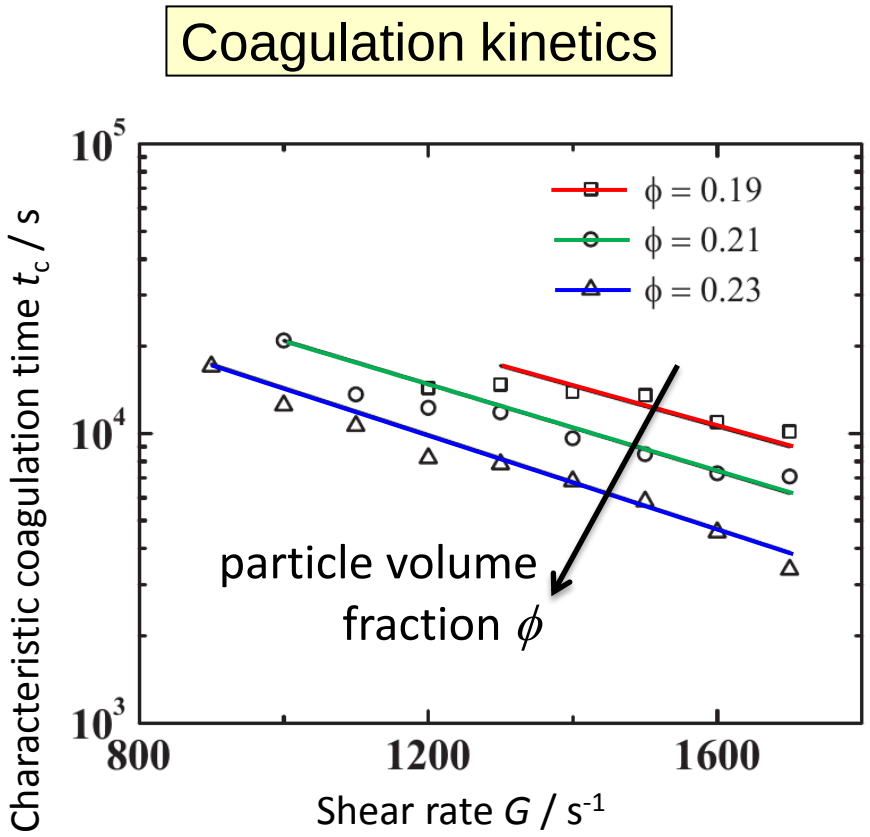
- Stabilized dispersions are encountered in various applications
  - Food, cosmetics, etc.
  - Emulsion & suspension polymerization
- Coagulation may cause serious financial losses

Coagulum in an industrial reactor

TubeTech International, Ltd.

Motivation – Coagulation

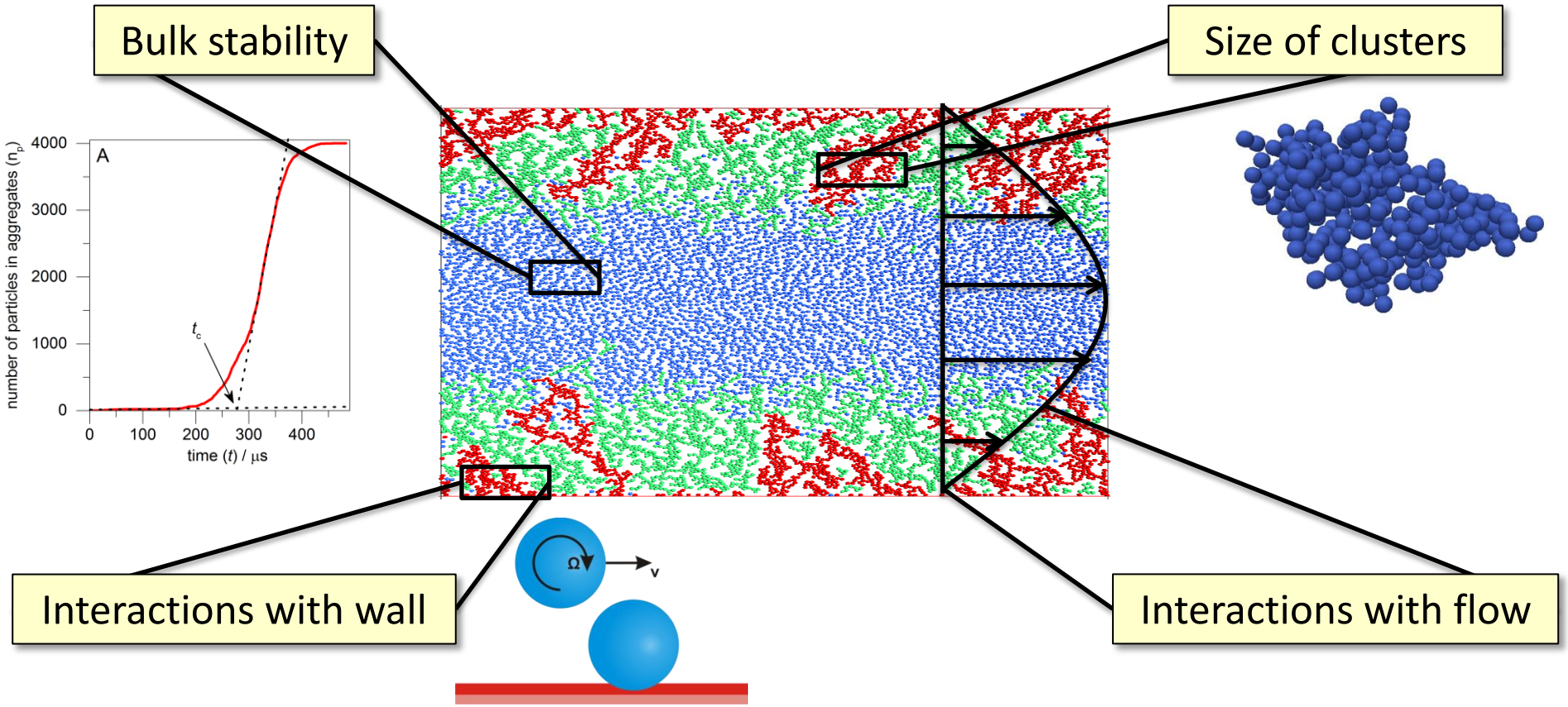
- Stabilized dispersions are encountered in various applications
  - Food, cosmetics, etc.
  - Emulsion & suspension polymerization
- Coagulation may cause serious financial losses
- Proper understanding of the coagulation mechanism is crucial for the operation of industrial units.



A. Zaccone, et al., *J. Chem. Phys.* 2010

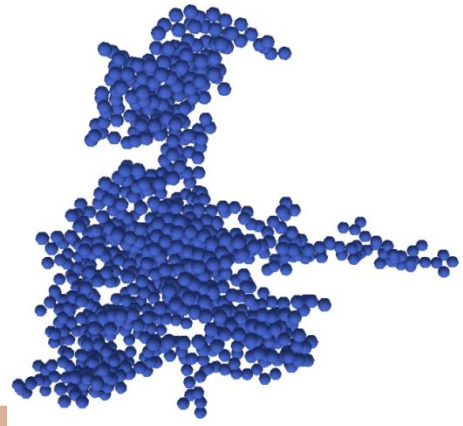
Development of a predictive model of coagulation

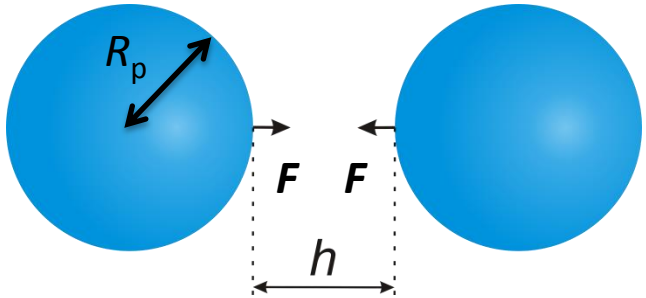
- Coagulation & fouling – complex phenomena
- **Model accounting for all effects is needed**



Advantages of the DEM model

- Large number of particles (currently 5000)
  - Enables modeling of **crowded systems**
  - Captures interactions between **many clusters** instead of simulations with a single cluster
- Direct incorporation of inter-particle forces
  - Our model describes interaction of particles that are **elastic**, **adhesive** and **stabilized**
  - Particle-fluid interaction is modeled by two-way coupling

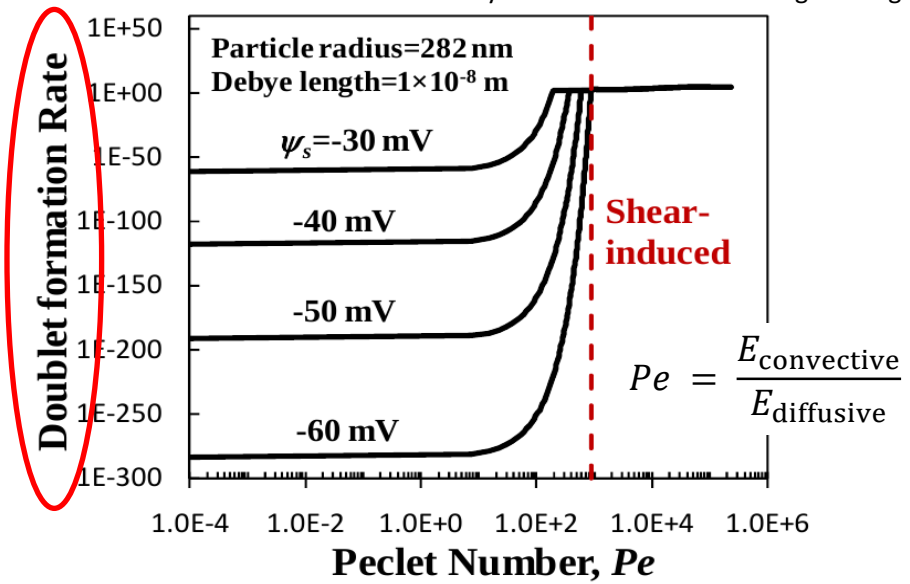


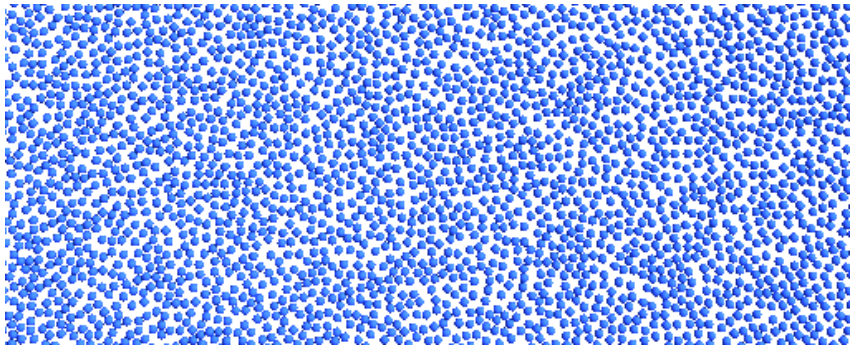


Stability of dispersions

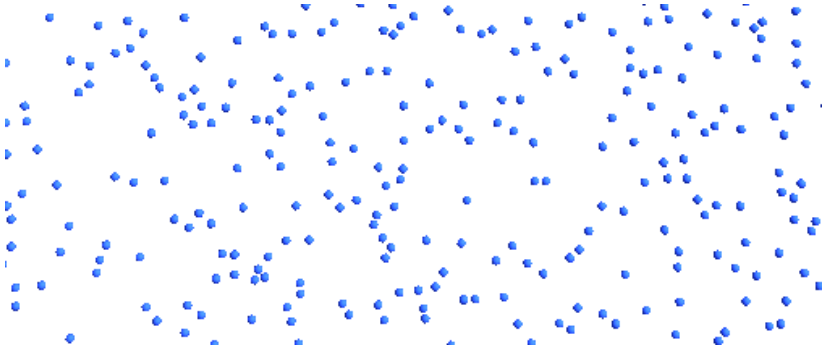
- In concentrated dispersions, individual collisions are no longer independent.
- How is then the coagulation kinetics computed?

M. Morbidelli: Lecture Notes on Polymer Reaction & Colloid Engineering





$\varphi \approx 0.50$



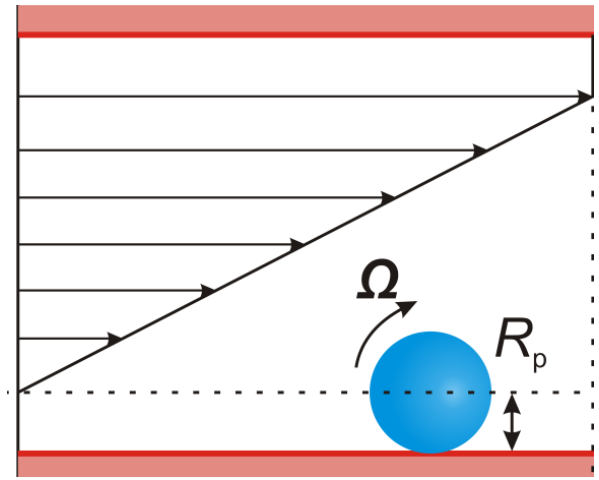
$\varphi \approx 0.05$

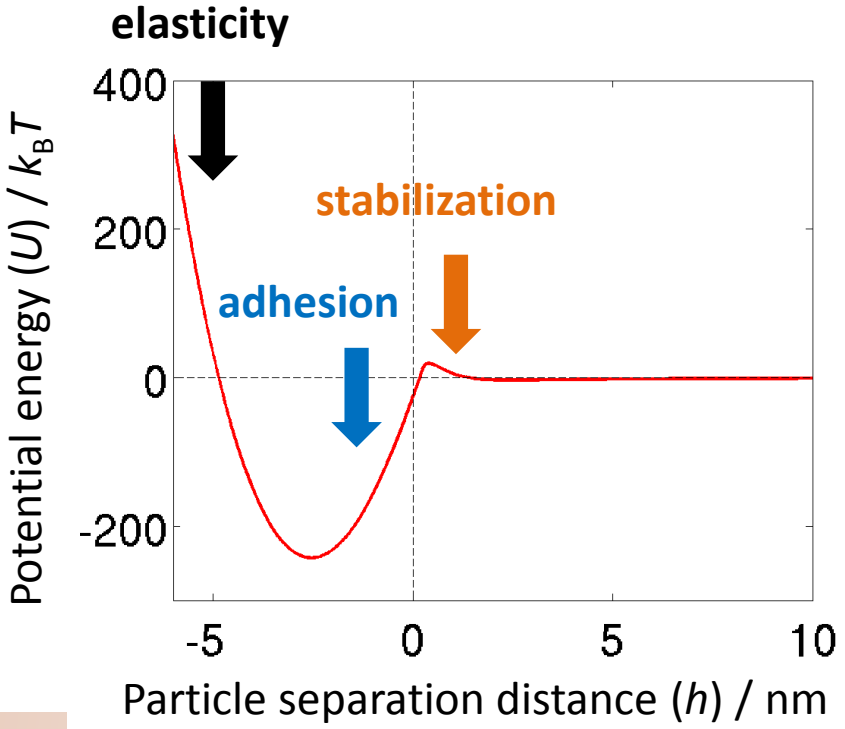
Discrete Element Method (DEM)

- Particles described as discrete elements

Newton's second law → $\frac{d^2\boldsymbol{x}}{dt^2} = \frac{\boldsymbol{F}}{m}$ $\qquad$ $\frac{d\boldsymbol{\Omega}}{dt} = \frac{\boldsymbol{M}}{I}$ ← Angular momentum balance

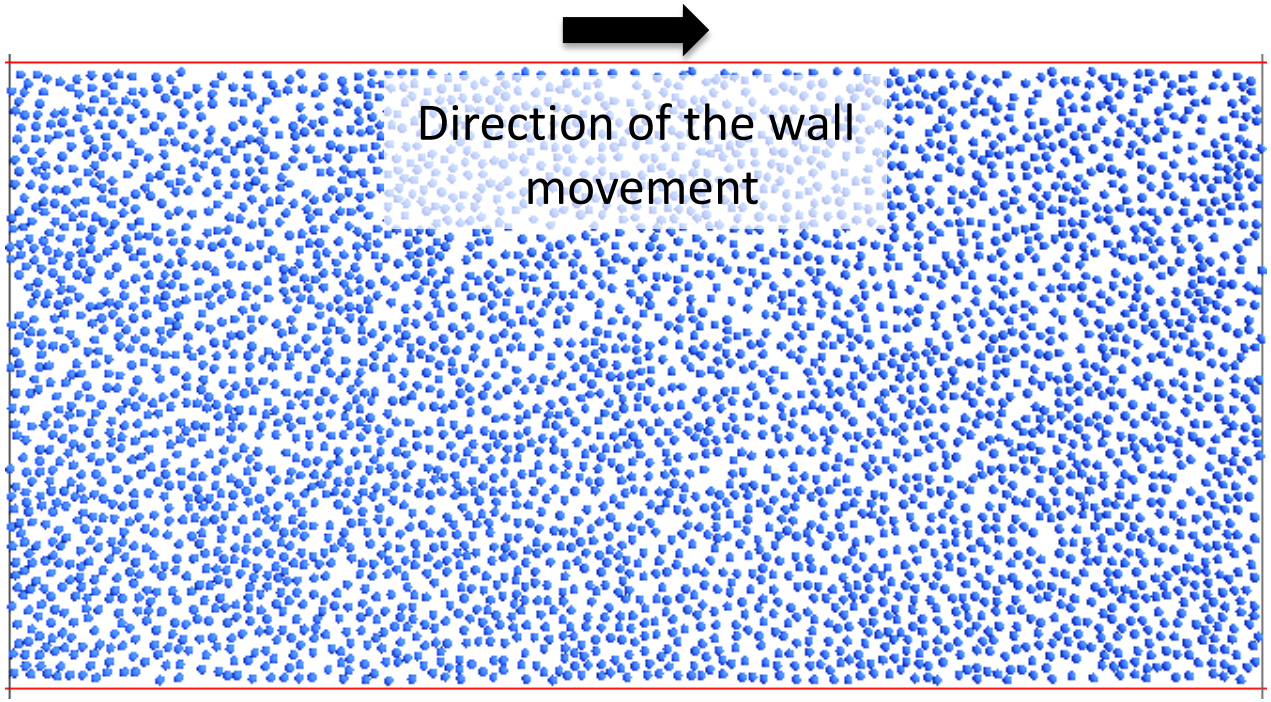
- Normal interactions – connection of DLVO & JKR theory
- Tangential interactions
  - Sliding, rolling, twisting
- Model of simple shear





Initial setup

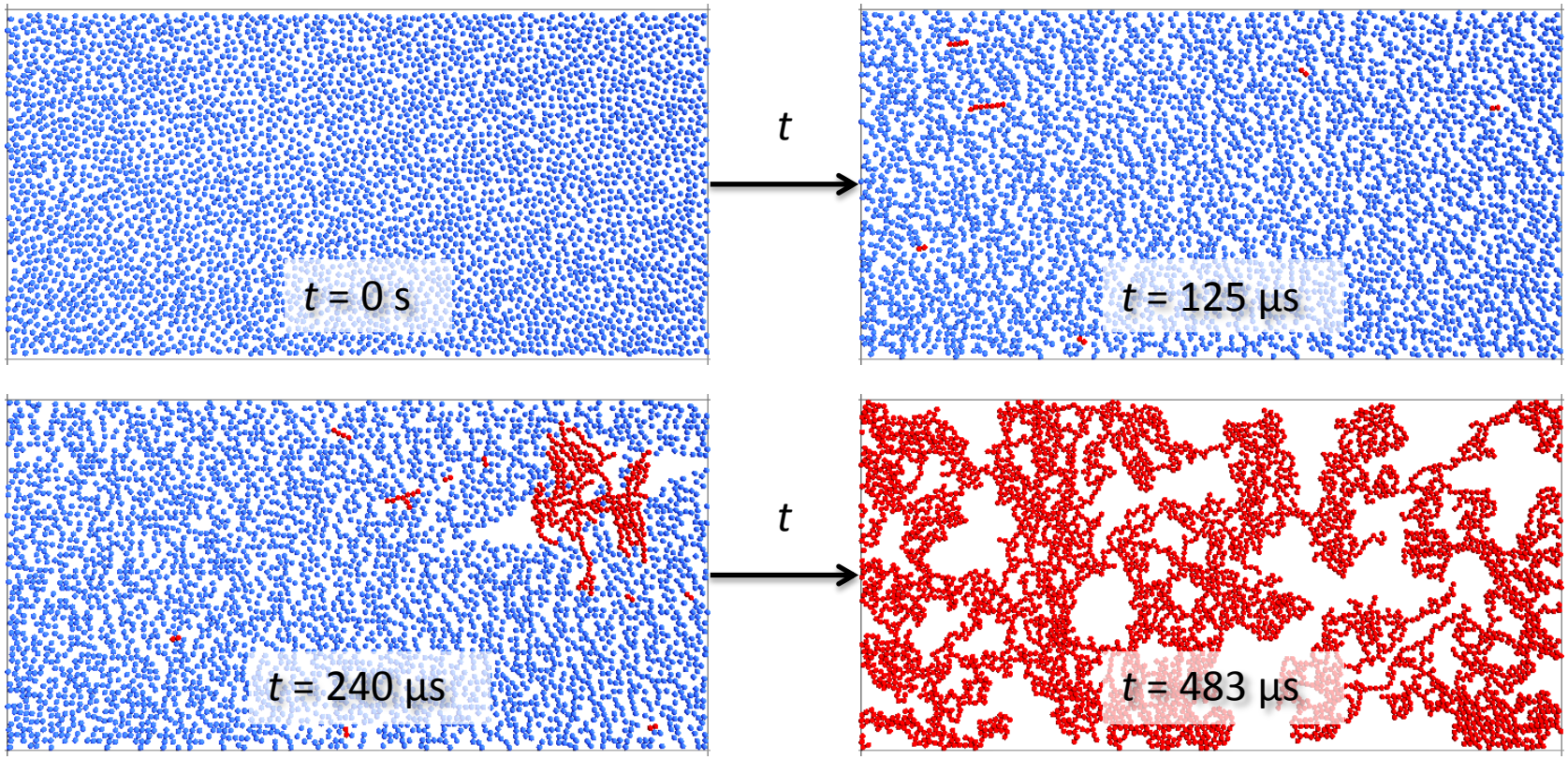
- A concentrated system
- Initially, particles are placed in a “safe” distance, such that no interaction occurs.



Parameters of the system	
R_p	50 nm
ρ_p	1000 kg·m^{-3}
A_H	1.3·10^{-20} J
κ^{-1}	1 nm
ψ_0	-30 mV
E_Y	40 MPa
γ	3 mJ·m^{-2}

Results – coagulation dynamics

- Coagulation in stabilized systems – activated process
- Fast aggregate growth occurs after initial lag-phase.



Kroupa M., Vonka I., Kosek J.; *Langmuir,* 2014

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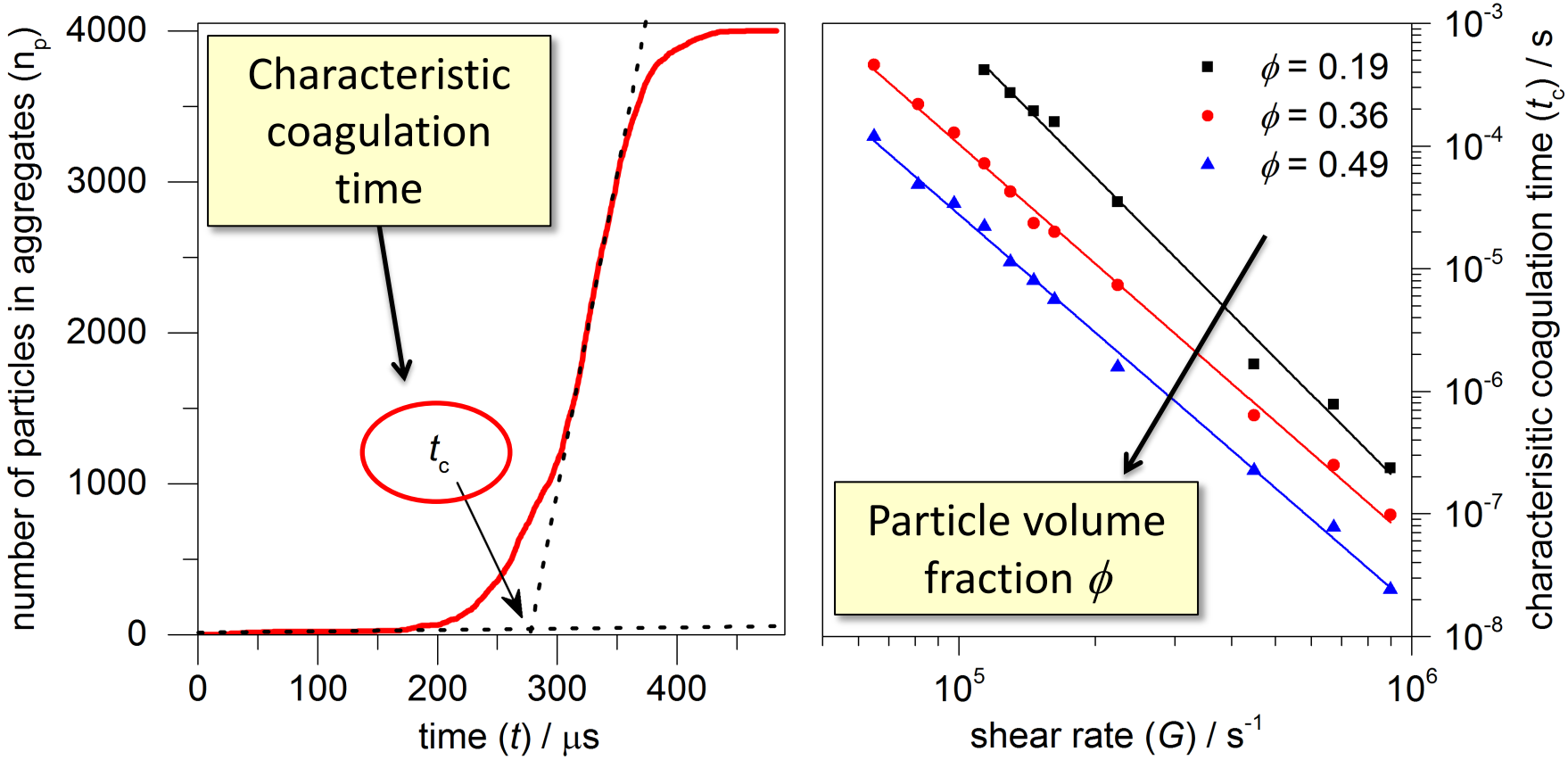
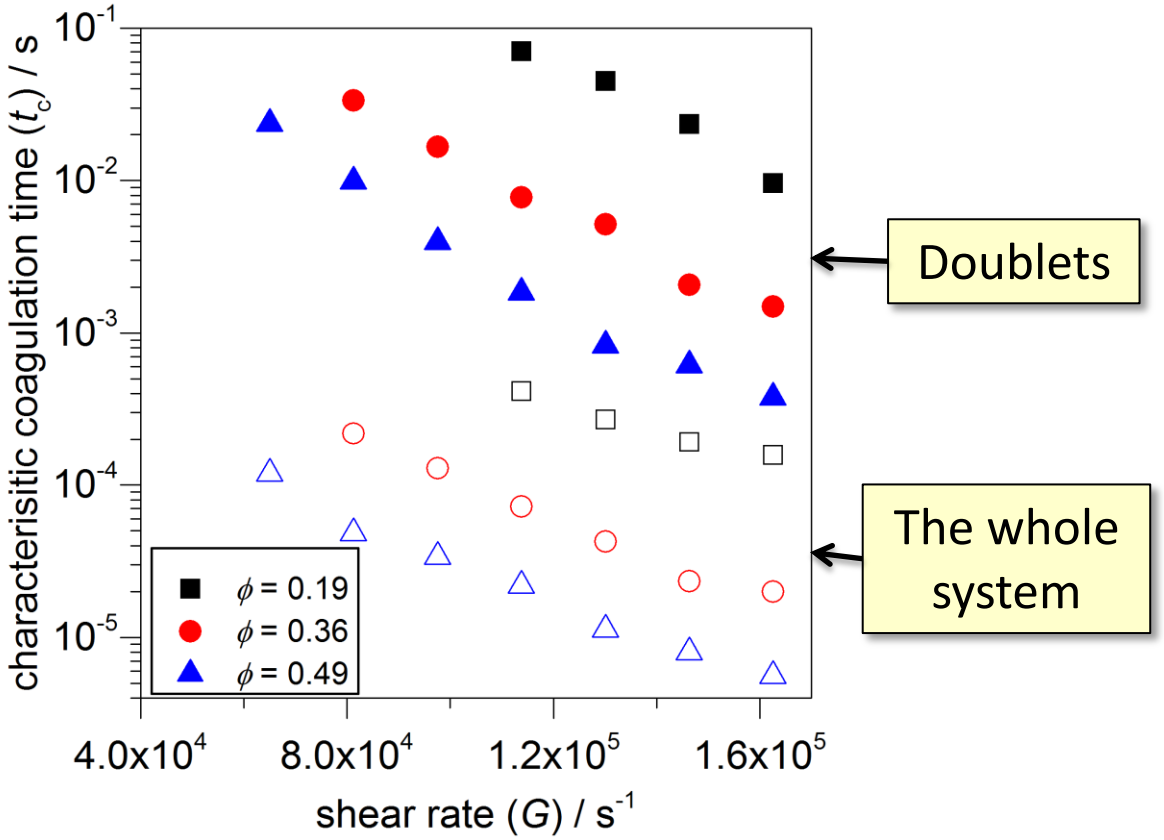


Kroupa M., Vonka I., Kosek J.; *Langmuir,* 2014

Coagulation dynamics - doublet formation

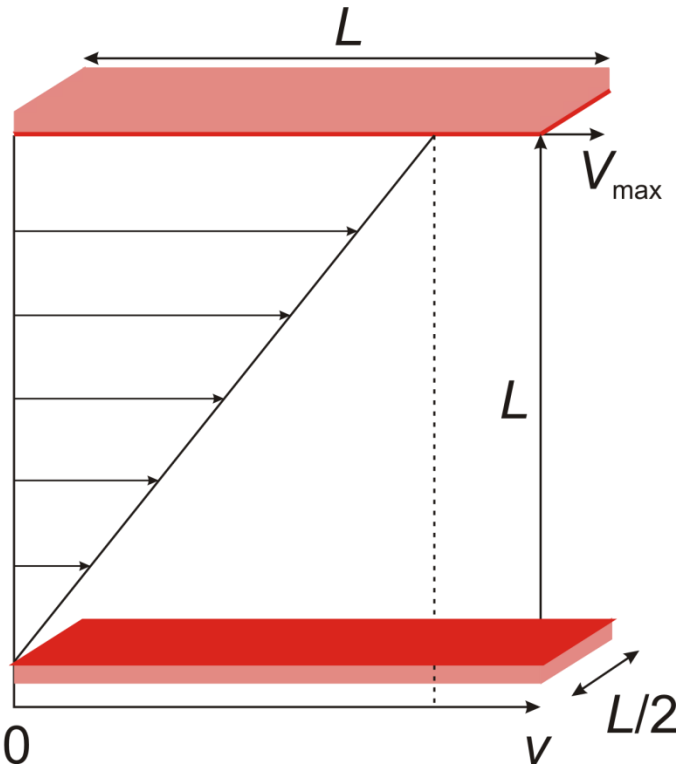
- Doublet formation – approx. two orders of magnitude slower than the coagulum formation

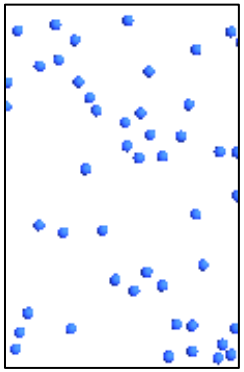


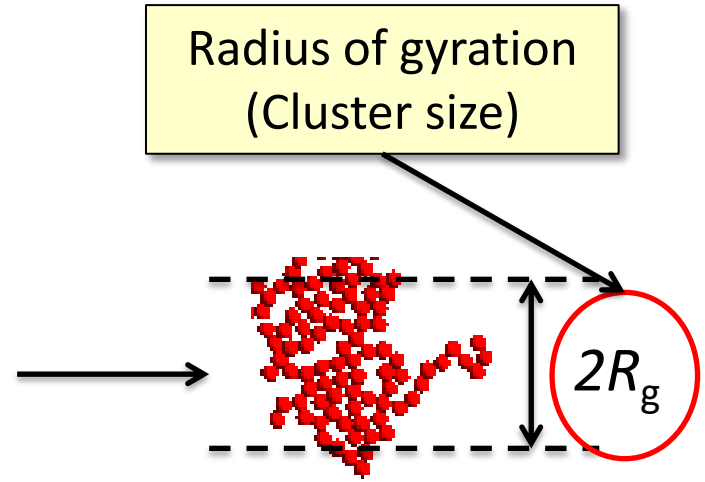
Kroupa M., Vonka I., Kosek J.; *Langmuir,* 2014

Size of the resulting clusters

- 3D model needed to fully capture structure of clusters
- Particle volume fraction $\varphi = 0.05$
- Initial setup: non-agglomerated system





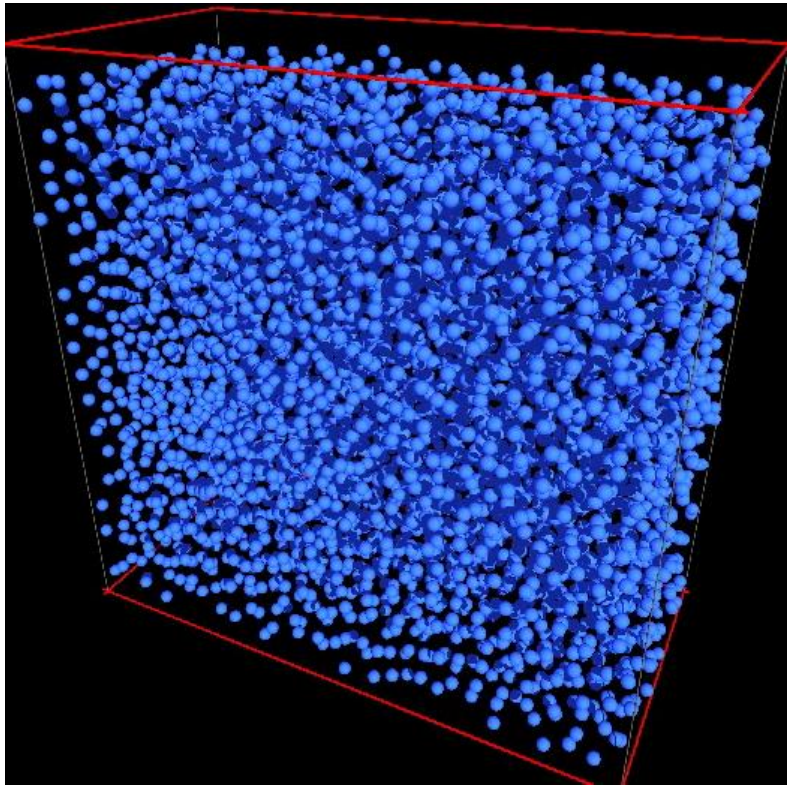


Size of the resulting clusters

- 3D model needed to fully capture structure of clusters
- Particle volume fraction $\varphi = 0.05$
- Initial setup: non-agglomerated system

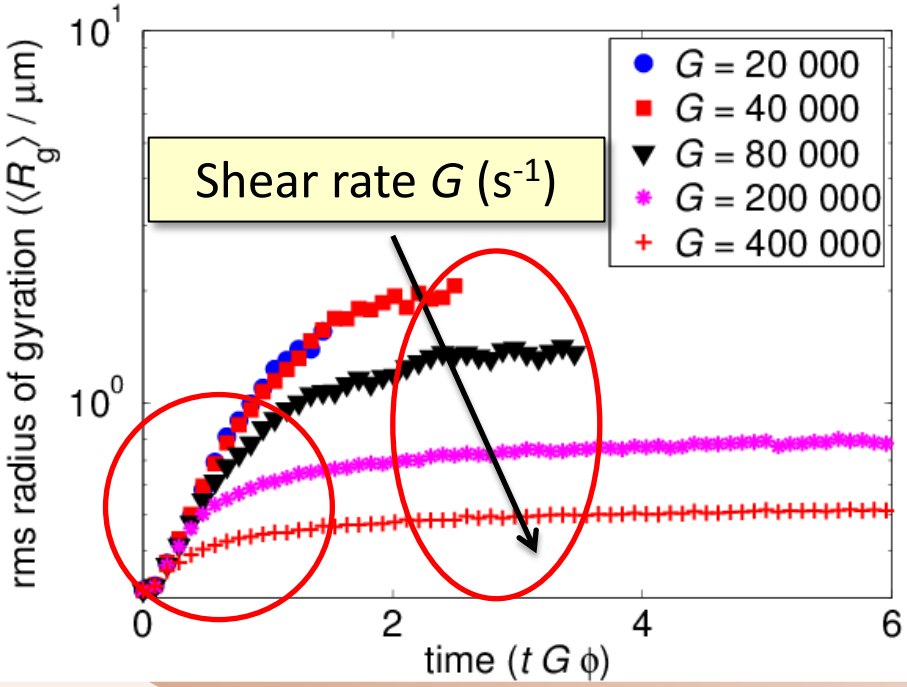
Non-stabilized system

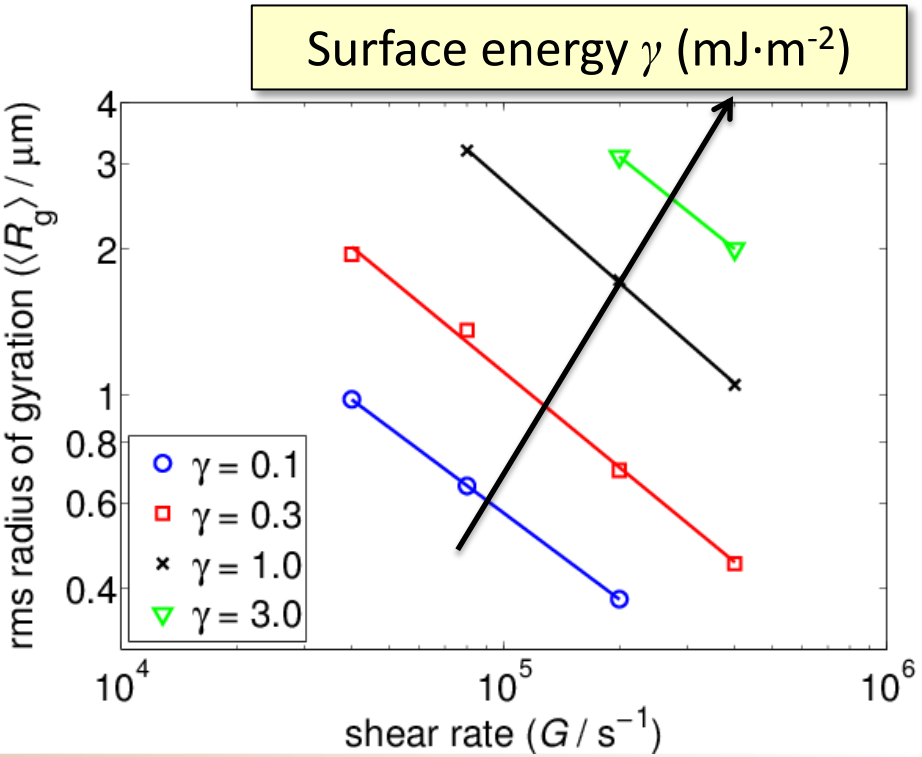
Parameters of the system	
R_p	405 nm
ρ_p	1000 kg·m^{-3}
A_H	1.3·10^{-20} J
ψ_0	0 mV
E_Y	1000 MPa
γ	0.3 mJ·m^{-2}



Size of clusters – non-stabilized

- Coagulation in non-stabilized system (no energy barrier)
- At the beginning controlled solely by coagulation
- The final size of aggregates is the result of interplay between coagulation and breakage





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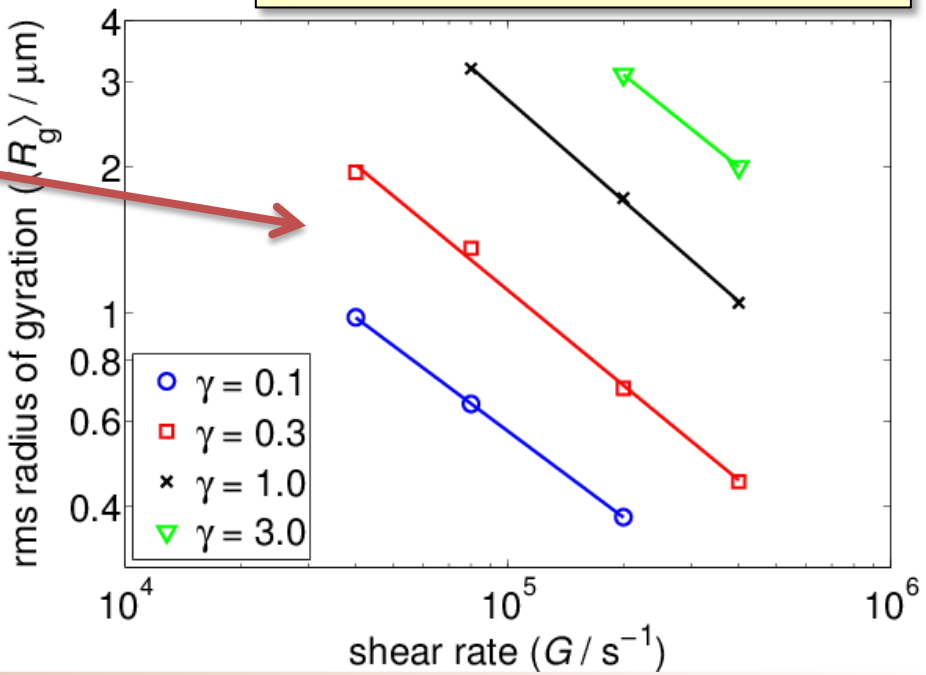
Surface energy γ (mJ·m^{-2})

Slope of the fitted lines:
$p = 0.64 \pm 0.03$

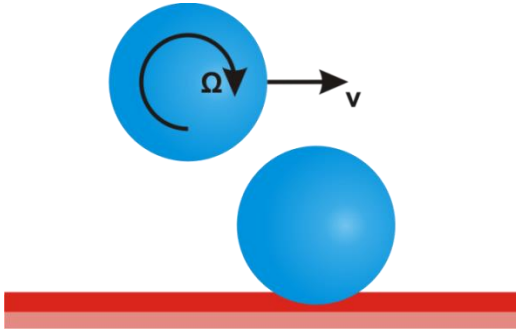
Theoretical scaling:
$p = 0.66$

For fractal dimension $d_f = 2.7$
Zaccone A., et al.; *Phys. Rev. E,* 2009

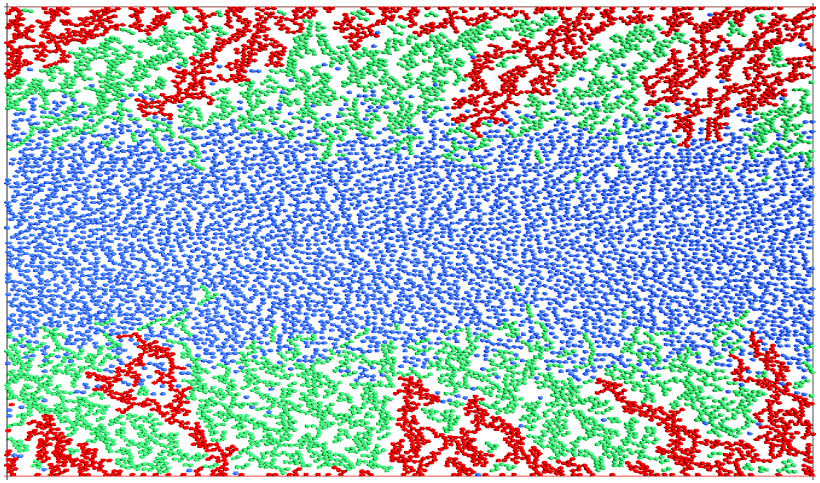


Future work

- Detailed study of the **particle-wall** interactions

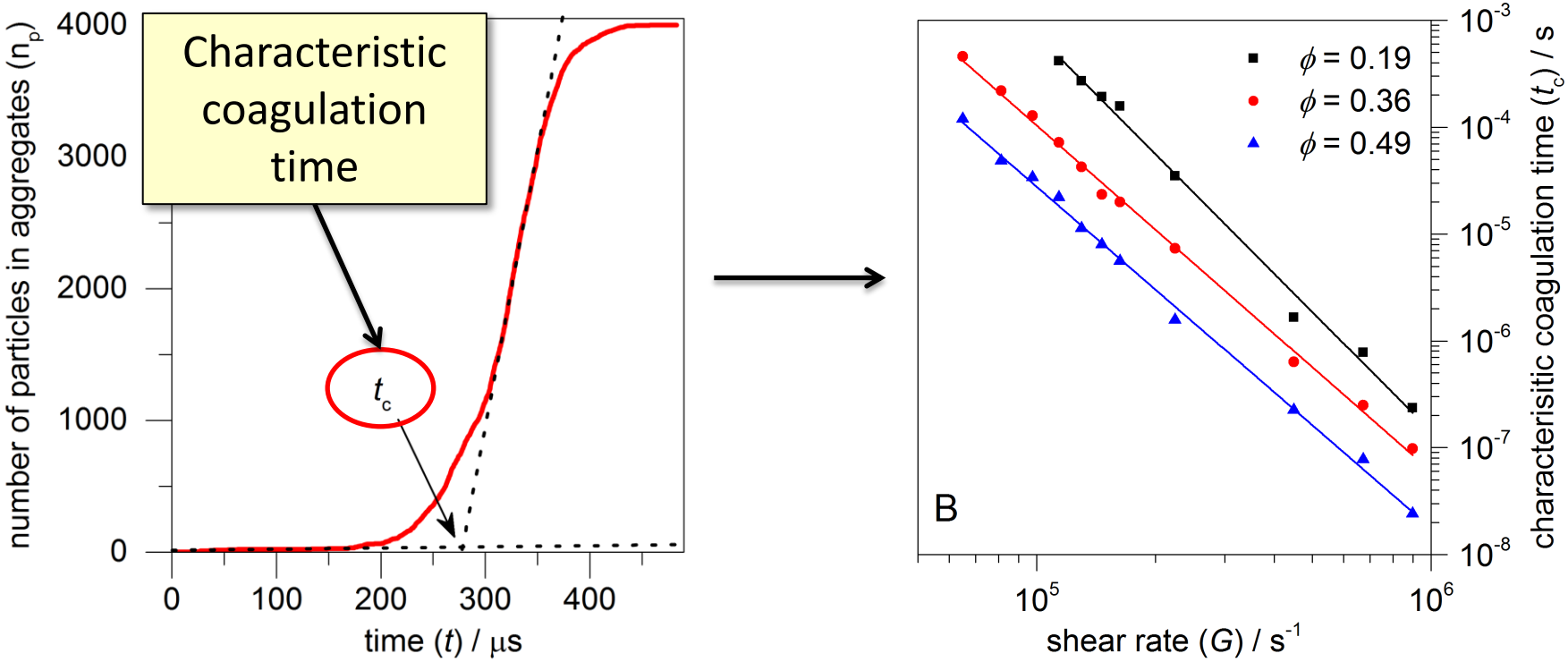


- Simulations of **fouling** in a micro-channel



Summary

- Coagulation of stabilized dispersions was modeled using the Discrete Element Method (DEM)
- Simulations showed strong dependence of **coagulation time** on volume fraction and shear rate.



Kroupa M., Vonka I., Kosek J.; *Langmuir,* 2014

Summary

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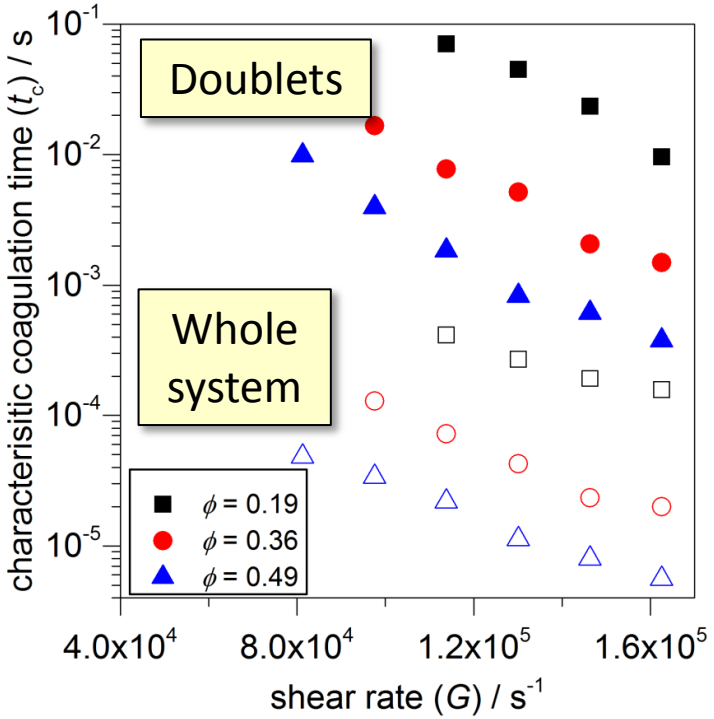

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- Simulations showed strong dependence of coagulation time on volume fraction and shear rate.
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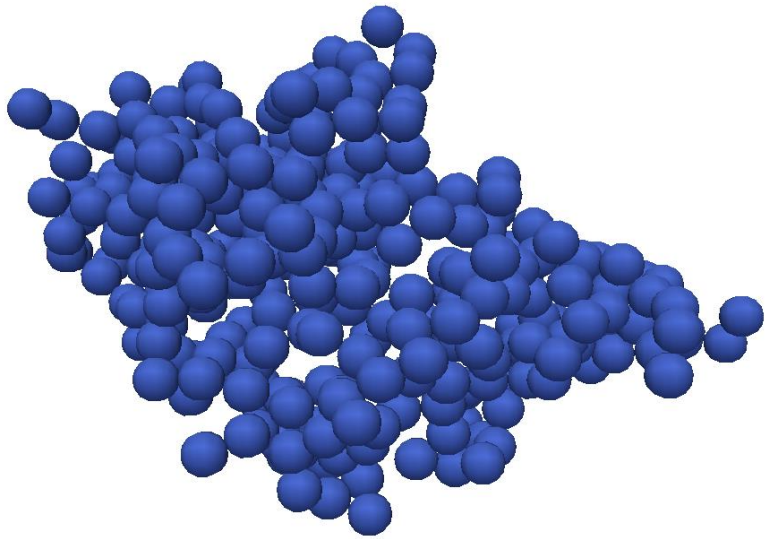
- **Size** of the resulting clusters is determined by coagulation and breakage and depends on surface energy



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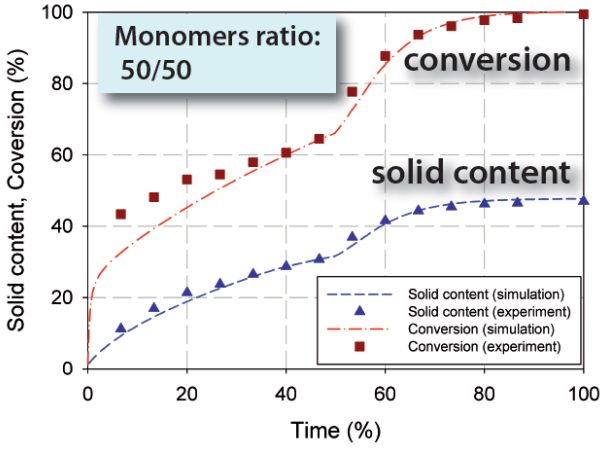
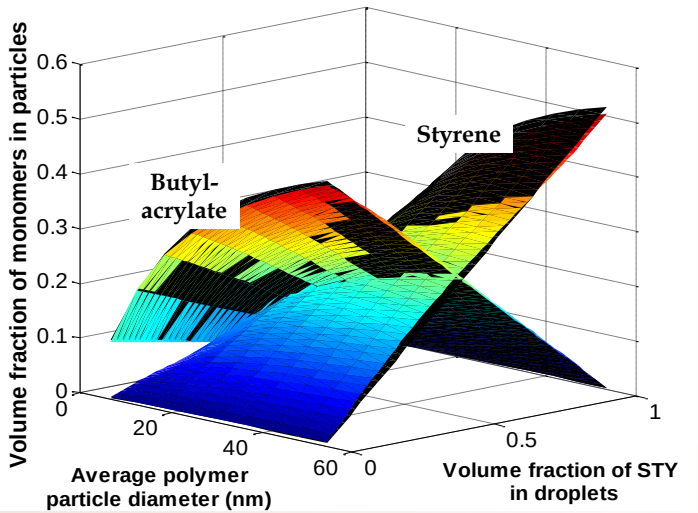
Conclusions – model development

- **Models for both semi-batch and smart-scale** reactors were developed and validated by laboratory data
- Models are currently implemented for **on-line control of real pilot-plant reactors**
- First-principle **mathematical model of coagulation** developed to predict characteristic coagulation time
  - now being adapted for use in real systems





Control and Real-time Optimisation of Intensive Polymerisation

FP7-NMP-2011-Small-5 Grant Agreement 280827