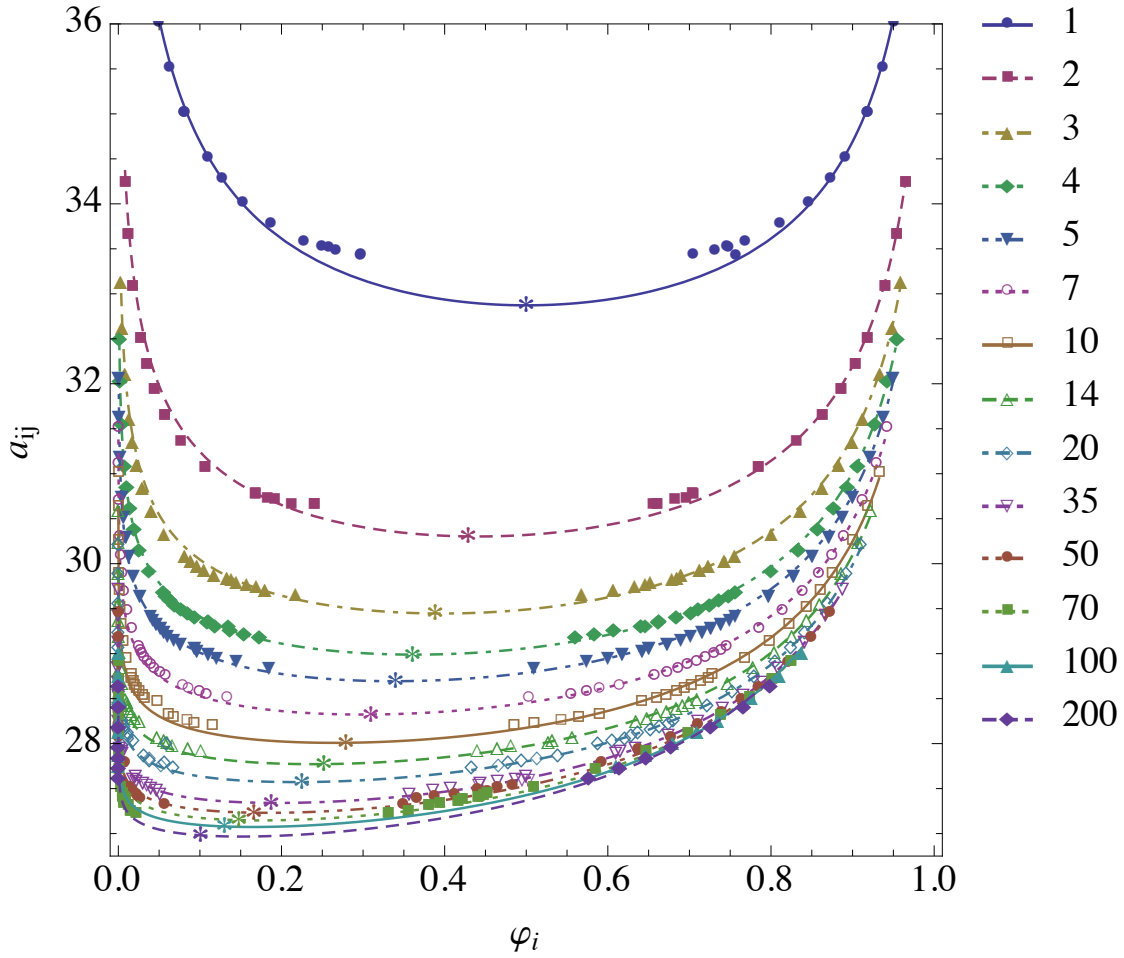
BASF
We create chemistry

Closed-Form Coexistence Equation for Phase Separation of Polymeric Mixtures in Dissipative Particle Dynamics

LAMMPS Workshop,
August 10-13, 2021

Pieter J. in ’t Veld



BASF Then and Now

1865: Modest beginnings –

- A dye factory
- Sited in Ludwigshafen
- With 30 workers

2020: World-leading chemical company –

- The world's largest integrated chemicals plant at Ludwigshafen
- More than 115,000 employees and
- Six Verbund sites as well as 338 additional production sites worldwide

BASF Worldwide: Sites

- Regional centers
- Selected sites
- Verbund sites
- Selected research and development sites

Introduction (the Why)


Home & Personal Care


Coatings

Packaging


Automotive


Construction


Water


Wind

BASF
We create chemistry

Introduction (the Why)

Home & Personal Care

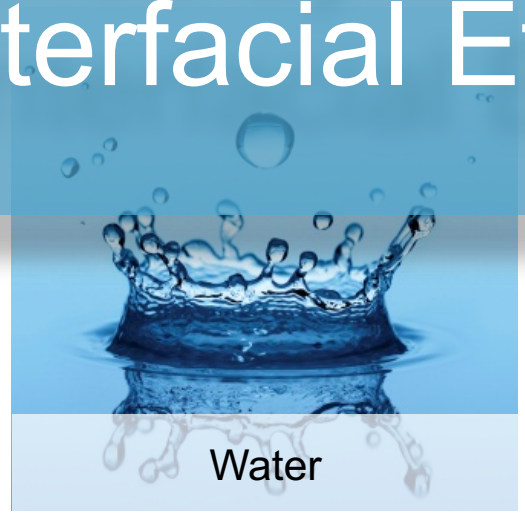
Coatings

Packaging

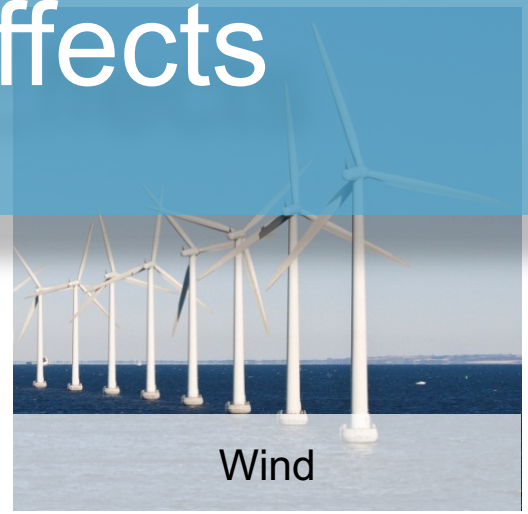
Governed by
Solubility and Interfacial Effects

Automotive

Construction



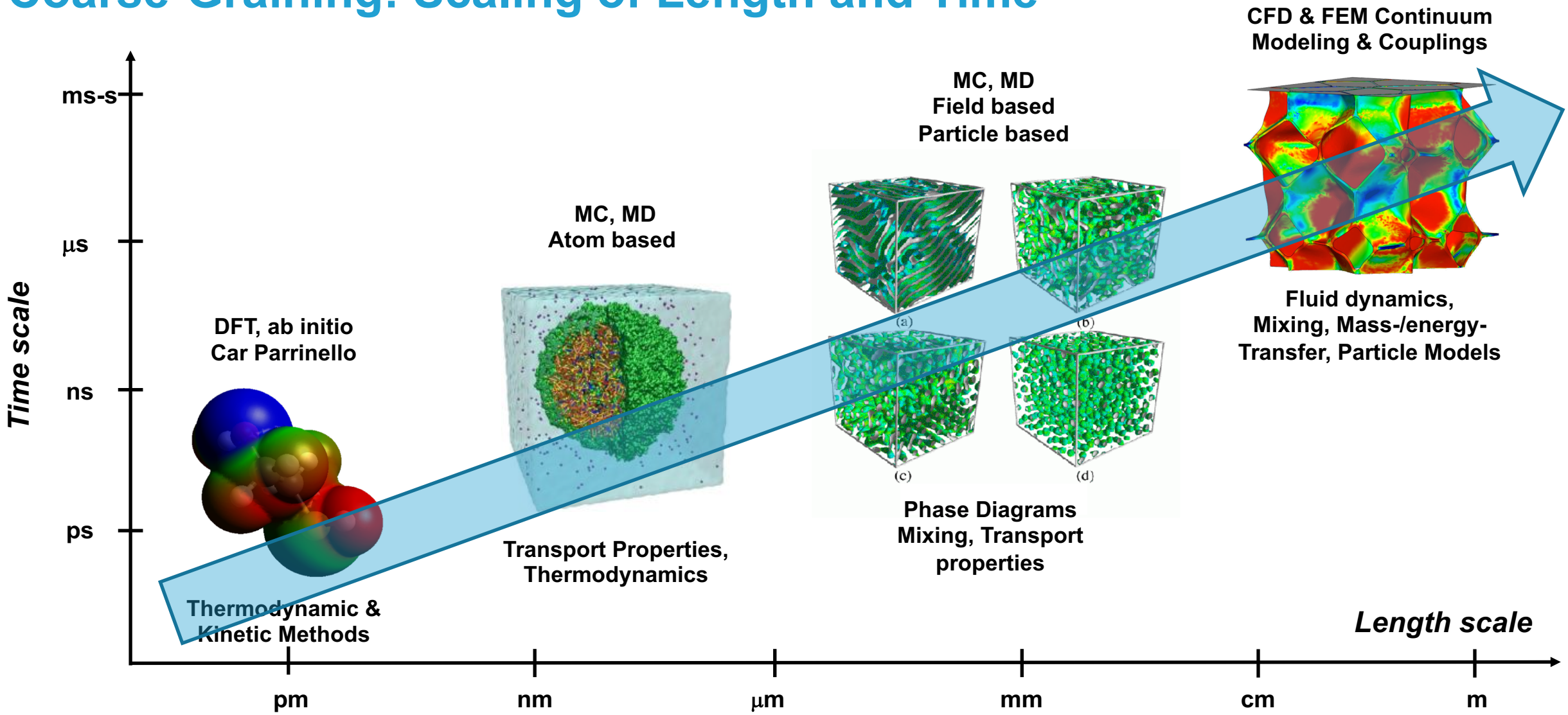
Water



Wind

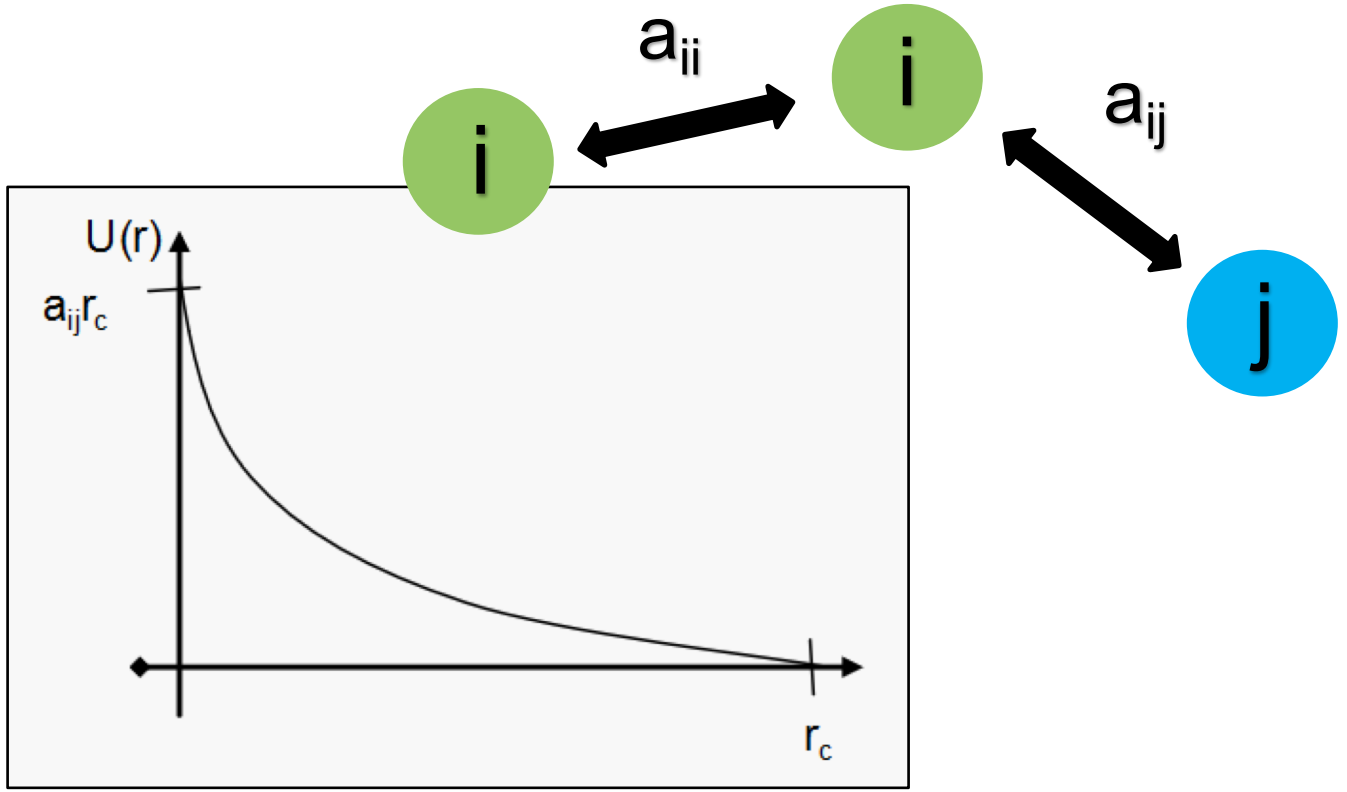
BASF
We create chemistry

Coarse-Graining: Scaling of Length and Time

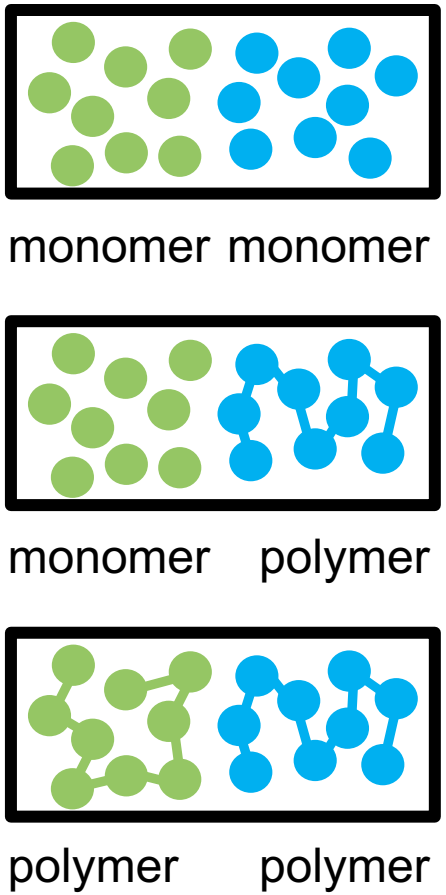


BASF
We create chemistry

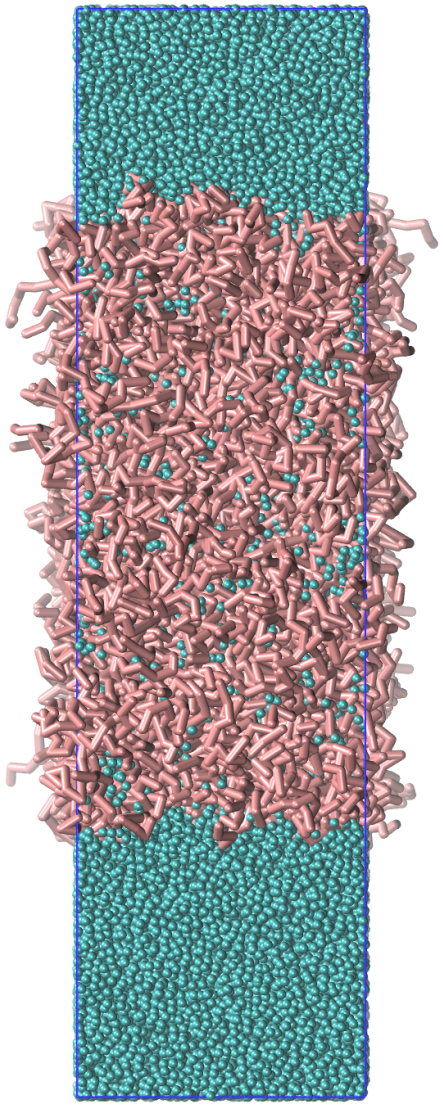
Coexistence for Dissipative Particle Dynamics (DPD)



$$\vec{f}^{C}(\vec{r}_{ij}) = \begin{cases} \frac{a_{ij}}{r_c}\left(1 - \frac{r_{ij}}{r_c}\right)\hat{r}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$



Coexistence Model



- Interphase transition

$$\varphi_i(z) = \varphi_i^{\ominus} + \frac{\varphi_i^{\oplus} - \varphi_i^{\ominus}}{2} \times \left[\tanh\left(\frac{z - z_0 + c}{\zeta} \right) - \tanh\left(\frac{z - z_0 - c}{\zeta} \right) \right]$$

- Second virial coefficient

$$B_2(a_{ij}) = \frac{2\pi(6 + a_{ij} - 3e^{-a_{ij}/2})}{3a_{ij}} - \frac{\sqrt{2}(1 + a_{ij})\pi^{3/2}\mathrm{erf}\left(\sqrt{a_{ij}/2}\right)}{a_{ij}^{3/2}}$$

- Critical point

$$\varphi_i^c = \left[1 + \left(\frac{B_2(a_{ii})}{B_2(a_{jj})} \right)^{c_{11}} \left(\frac{N_i}{N_j} \right)^{c_{12}} \right]^{-1}$$

- Coexistence

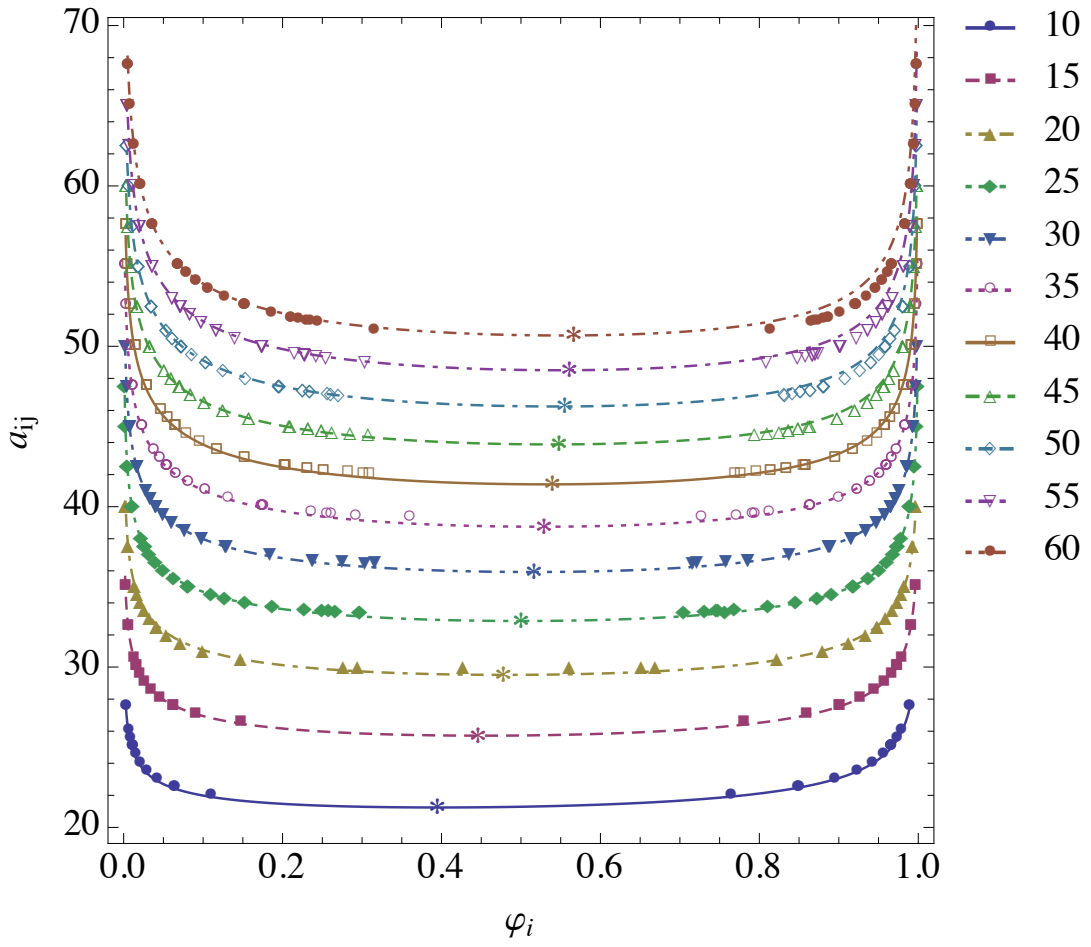
$$a_{ij}(\varphi_i) = \kappa_{ij} \left[\ln\left(\frac{1}{\varphi_i} \right) \right]^{\lambda_{ij}} + \kappa_{ji} \left[\ln\left(\frac{1}{1 - \varphi_i} \right) \right]^{\lambda_{ji}} + \delta_{ij}$$

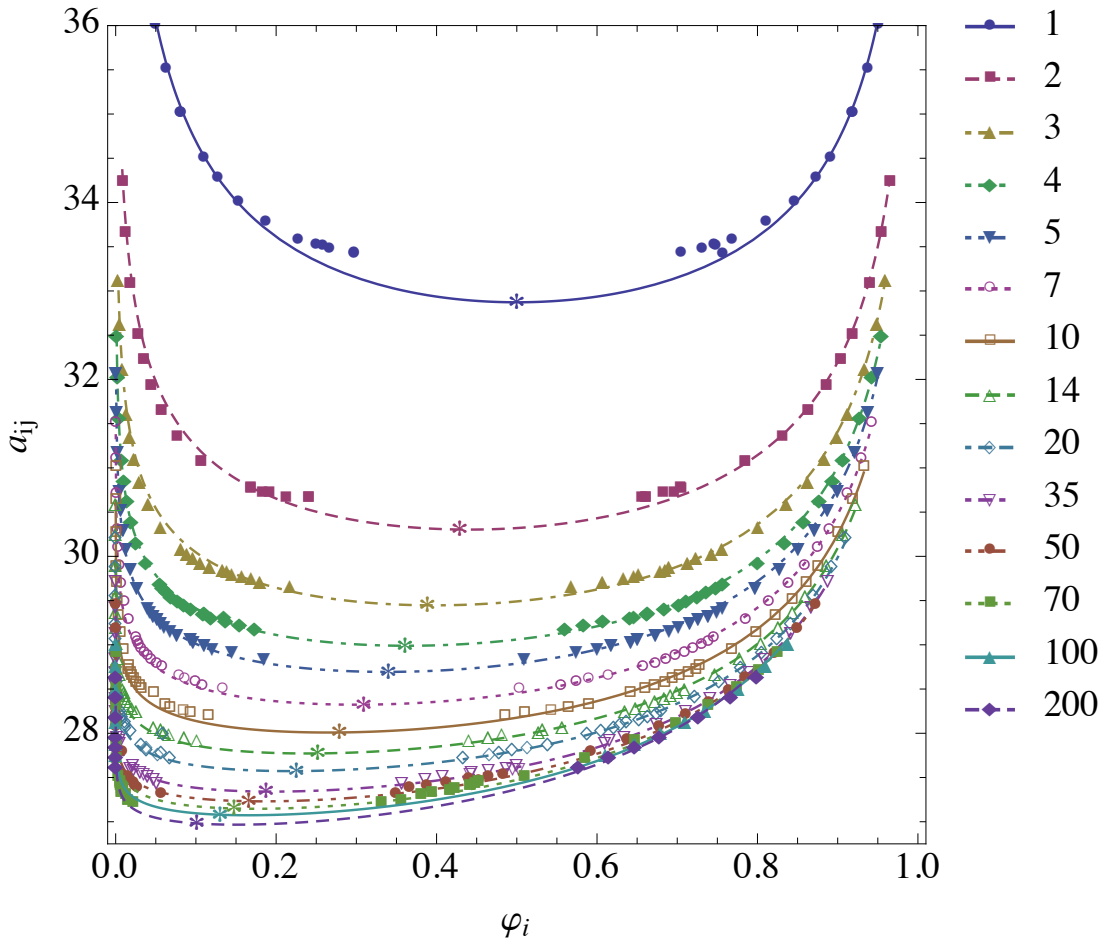
v.d. Haven et al., *J. Chem. Phys. B* **2021**, *125*, 7485

Data Gathering

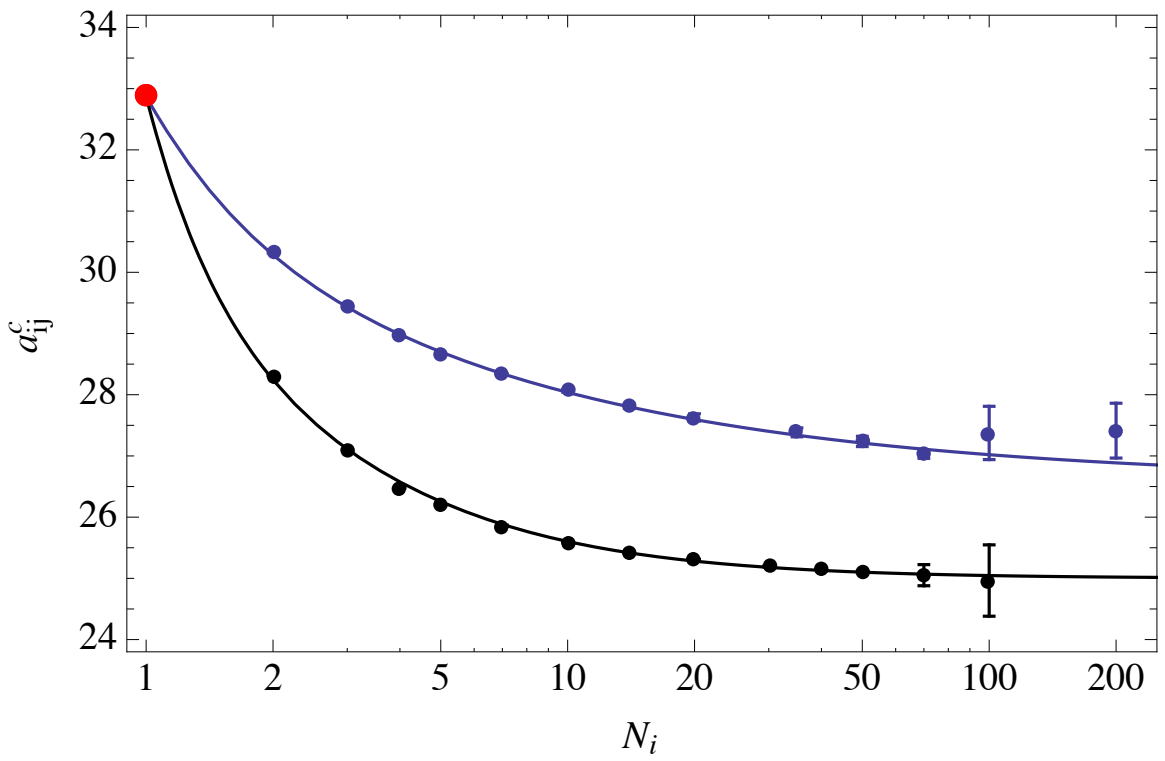
	Fitting			Validation				All
	I	II	III	IV	V	VI	VII	
a_{ii}	25	25	25	15	40	25	25	10 – 60
a_{jj}	10 – 60	25	25	40	15	25	15	10 – 60
N_i	1	1 – 200	1 – 100	1 – 200	1 – 100	10 – 40	10 – 40	1 – 200
N_j	1	1	N_i	1	N_i	40	40	1 – 100
n_{data}	750	976	326	344	372	88	118	5664
FH-GW	–	4.78	1.21	–	–	0.27	–	5.42*
FH-rGW	9.07	6.67	2.25	14.6	2.03	0.27	0.31	7.07
VDH	0.77	0.28	0.15	3.20	0.97	0.06	0.32	1.02

Fitted Data



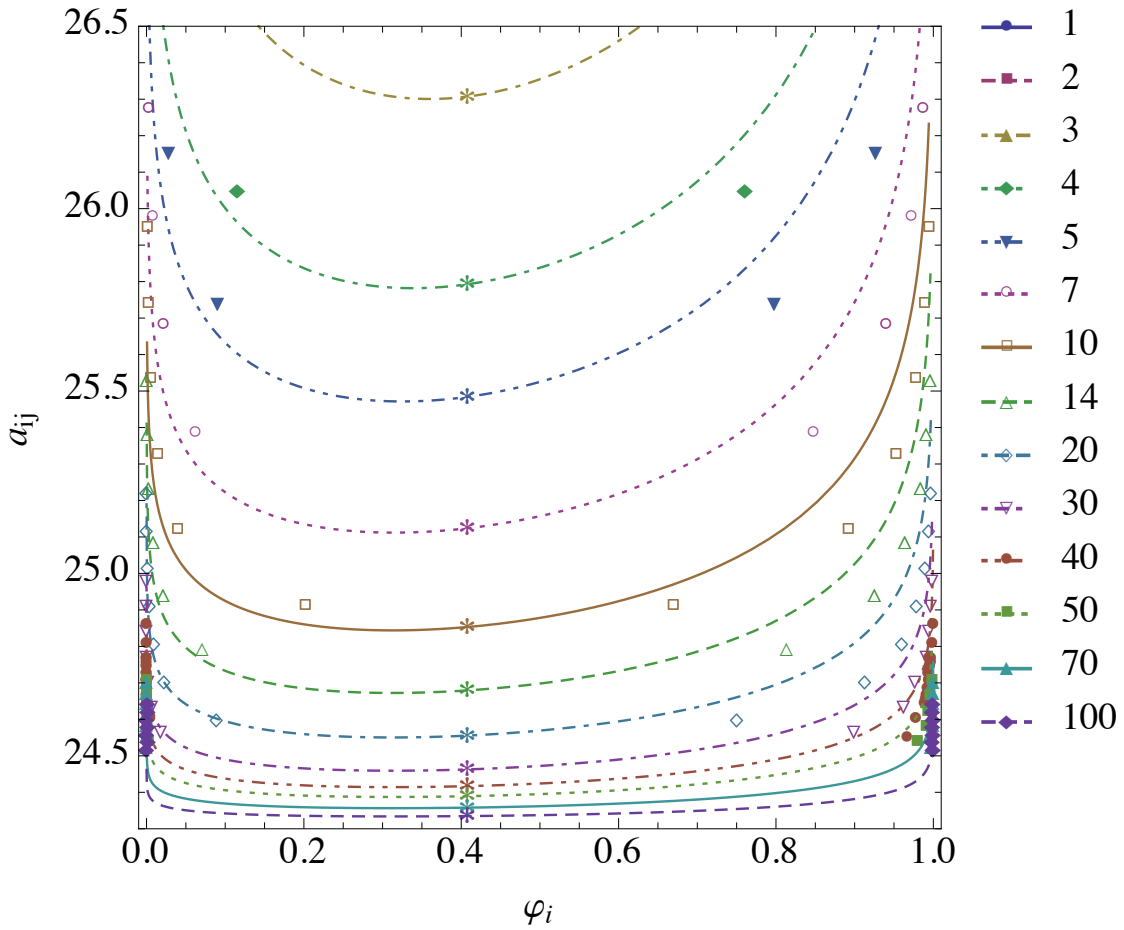


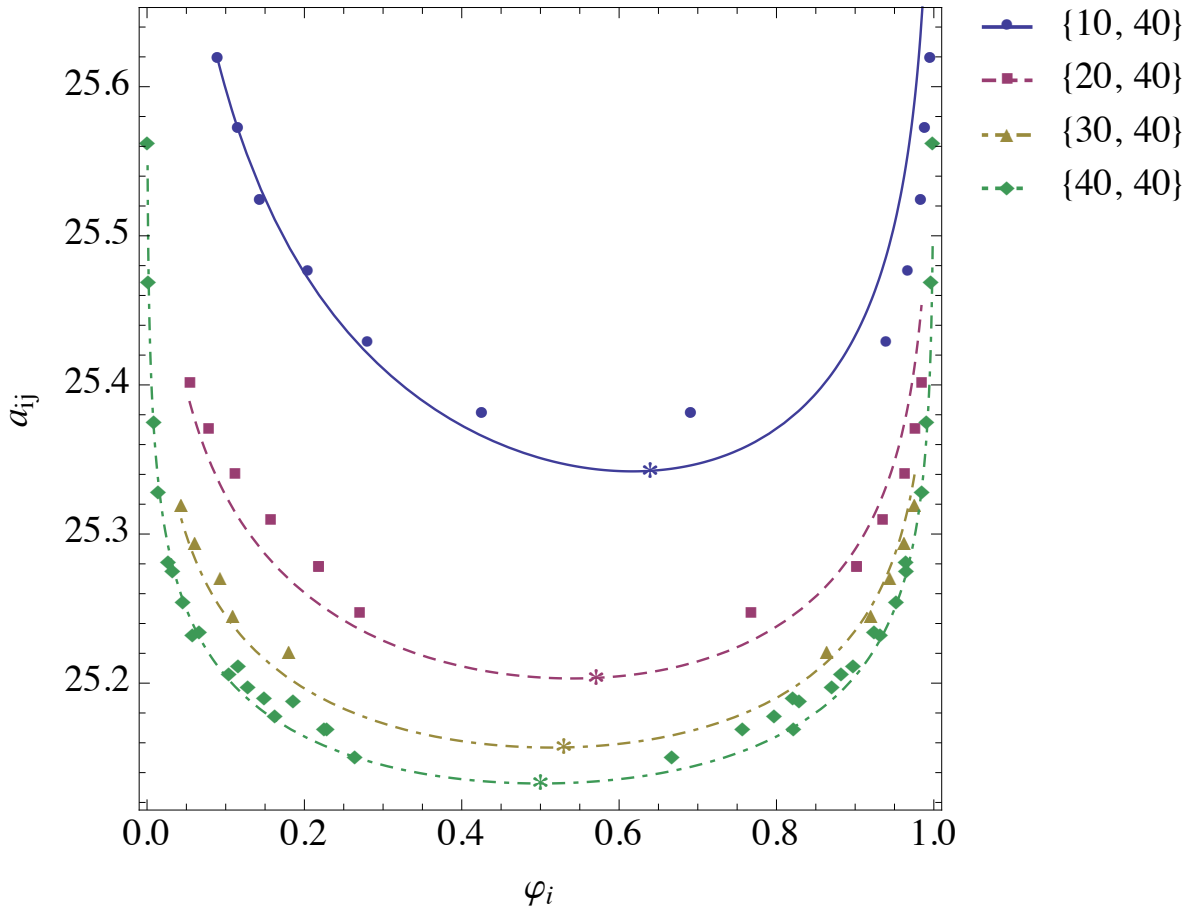
Critical Point



- Critical point as function of chain length for
  - Polymer-monomer systems (blue)
  - Polymer-polymer systems (black)
- Position of the monomer-monomer critical point has to be part of both lines
- This only is guaranteed when the bonded neighbor interaction displays the same compressibility as the nonbonded neighbors
  - Non-bonded 1-2 interaction is off
  - Bonded potential identical to interchain nonbonded interaction

Predicted Polymer-Polymer Data

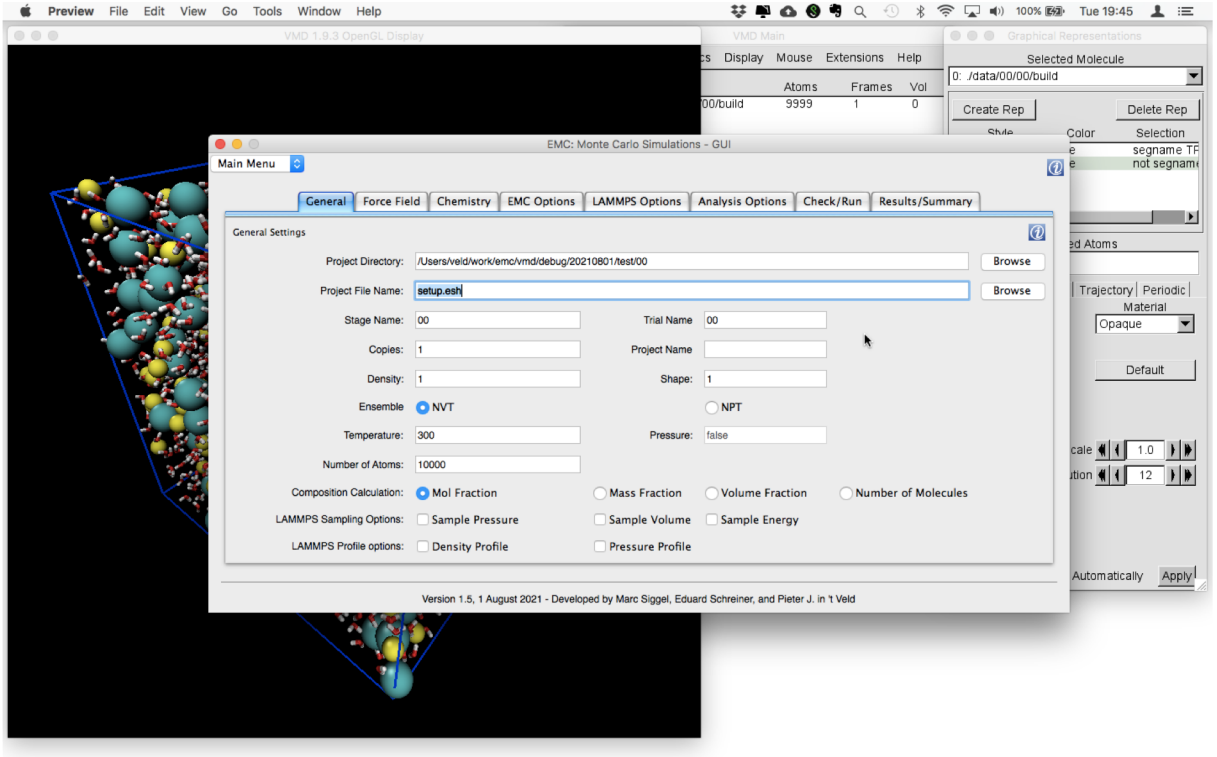




Summary

- The coexistence equation was successfully fit to the simulated data
- The mean absolute percentage error of the equation when compared to all data is 1.02%
- In total, 5664 simulations were run to create the necessary data
- The data was generated by using EMC Setup as a work flow of EMC in combination with LAMMPS
- The EMC Setup script provides a concise solution for producing large amounts of data, which can be used for many applications, one of which would be the generation of descriptors for machine learning approaches
- A full scientific expose can be found in Van der Haven et al., *J. Phys. Chem. B* **2021**, *125,* 7485

EMC Break-Out Session: Friday, August 13, 12:50pm



- If you would like to follow along:
  Download a fresh version of EMC from https://montecarlo.sourceforge.net/ by using the browser in the Virtual Machine as used for LAMMPS
- Introduction of a VMD plug-in (./v9.4.4/vmd)
  - Download VMD from https://www.ks.uiuc.edu/Research/vmd/
- Explanation of EMC Setup for dealing with large sets of simulations
- You can post your questions and suggestions for Friday in the #emc channel on Slack

Acknowledgements

This work was performed in corporation with

Danny van der Haven

Stephan Köhler

Eduard Schreiner

We create chemistry

EMC Setup Script

- EMC Setup scripts consists of
  - One environment section
  - One or more template section
- The environment section defines
  - Project name
  - Run queue (can be local)
  - Run time
  - Analysis windows
- A template contains
  - Option section
    - System settings and sizing
    - Analysis tools
  - Groups section
    - SMILES for molecule or monomer
  - Cluster section
    - Fractions
  - Polymer section
    - Definition of polymer chains