

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

LAMMPS Workshop, August 10-13, 2021

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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



- Verbund sites
- Selected research and development sites



Introduction (the Why)





Introduction (the Why)





Home & Personal CarGoverned by Packaging Solubility and Interfacial Effects













We create chemistry

Coarse-Graining: Scaling of Length and Time

Coexistence for Dissipative Particle Dynamics (DPD)





monomer monomer



monomer polymer



polymer

polymer



Coexistence Model



Interphase transition

Second virial coefficient

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

$$B_{2}(a_{ij}) = \frac{2\pi(6 + a_{ij} - 3e^{-a_{ij}/2})}{3a_{ij}}$$
$$-\frac{\sqrt{2}(1 + a_{ij})\pi^{3/2} \operatorname{erf}\left(\sqrt{a_{ij}/2}\right)}{a_{ij}^{3/2}}$$
$$\varphi_{i}^{c} = \left[1 + \left(\frac{B_{2}(a_{ii})}{B_{2}(a_{jj})}\right)^{c_{11}} \left(\frac{N_{i}}{N_{j}}\right)^{c_{12}}\right]^{-1}$$

Critical point

Coexistence

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

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

Data Gathering

	Fitting			Validation				Δ 11
	Ι	II	III	IV	V	VI	VII	
$\overline{a_{ii}}$	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



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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

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

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- If you would like to follow along: Download a fresh version of EMC from <u>https://montecarlo.sourceforge.net/</u> 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 <u>https://www.ks.uiuc.edu/Research/vmd/</u>
- 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

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Danny van der Haven Stephan Köhler Eduard Schreiner

BASE 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

