Martin Thomas Horsch
Scientific Computing Department
STFC Daresbury Laboratory
UK Research and Innovation

SkaSim

Massively parallel MD simulation and multiscale modelling of cavitation

In collaboration with:

Hans Hasse, TU Kaiserslautern
Manfred Heilig, BASF SE
Max Kohns, TU Kaiserslautern
Kai Langenbach, TU Kaiserslautern
Stephan Werth, TU Kaiserslautern

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN
LEHRSTUHL FÜR THERMODYNAMIK

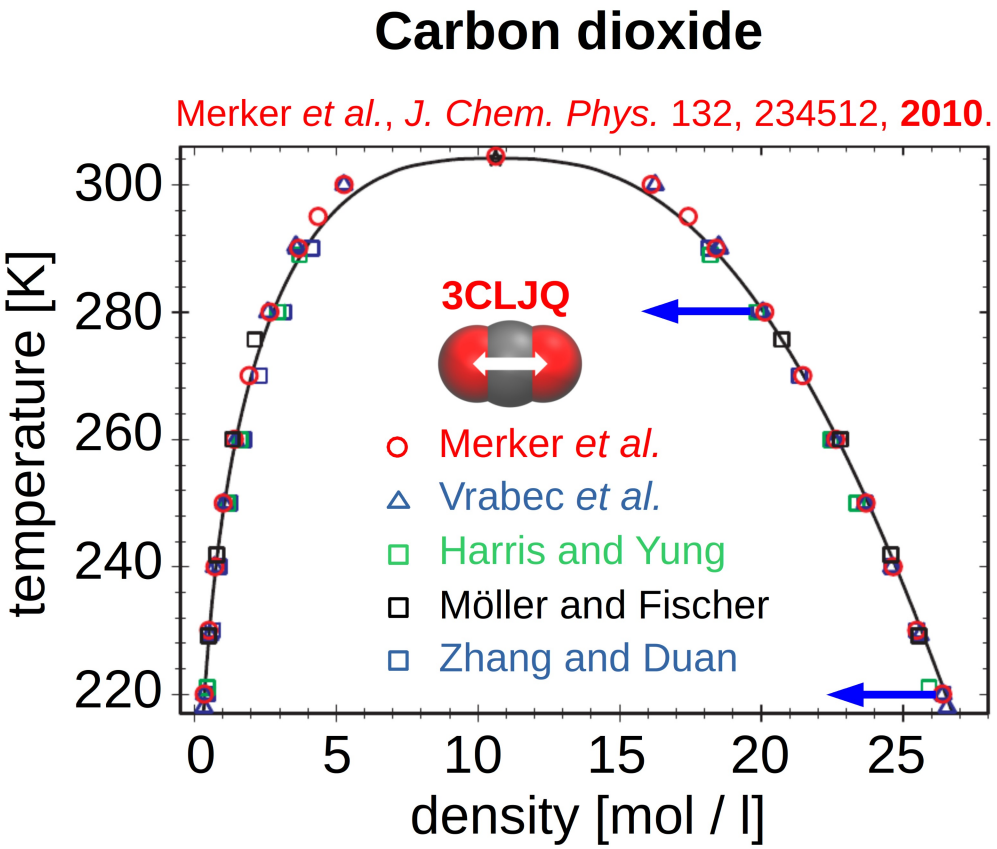
BASF
We create chemistry

CECAM Workshop

“Statistical Mechanics of Interfaces: Dynamic Phenomena”

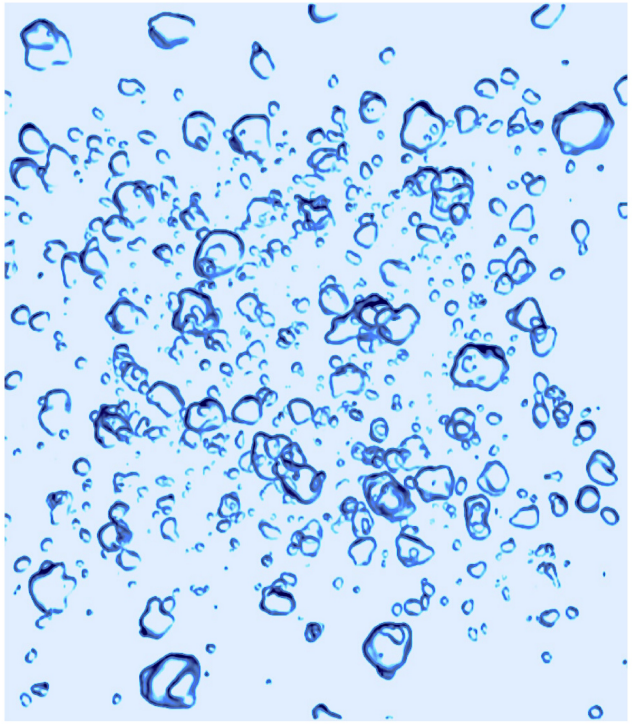
Berlin, 5th October 2018

Homogeneous liquid-to-vapour nucleation



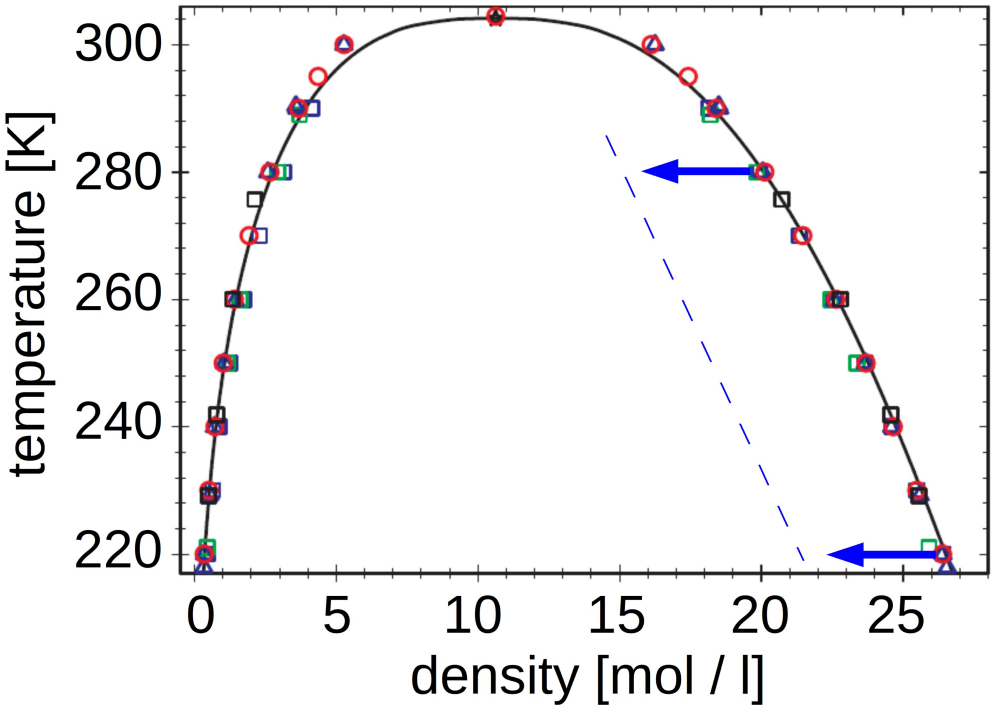
Homogeneous liquid-to-vapour nucleation

Bubble formation



Carbon dioxide

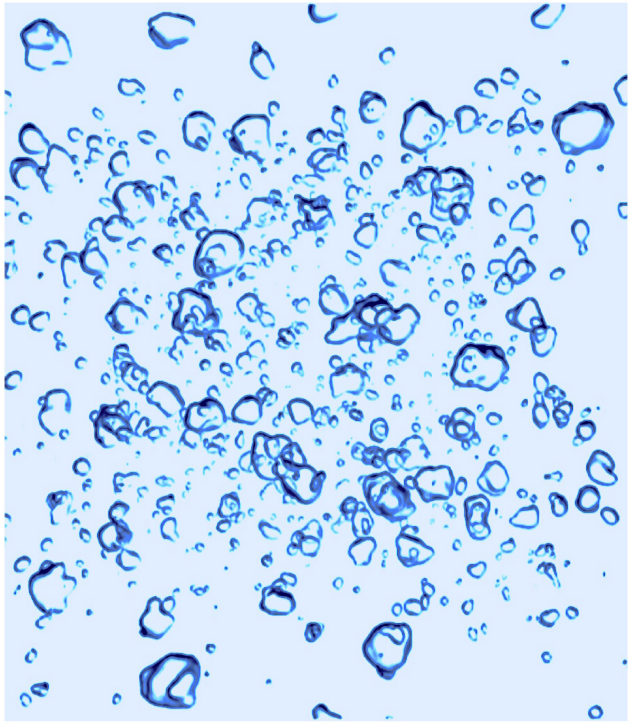
cavitation close to spinodal line



MD simulation of nucleation requires large systems and performant codes.

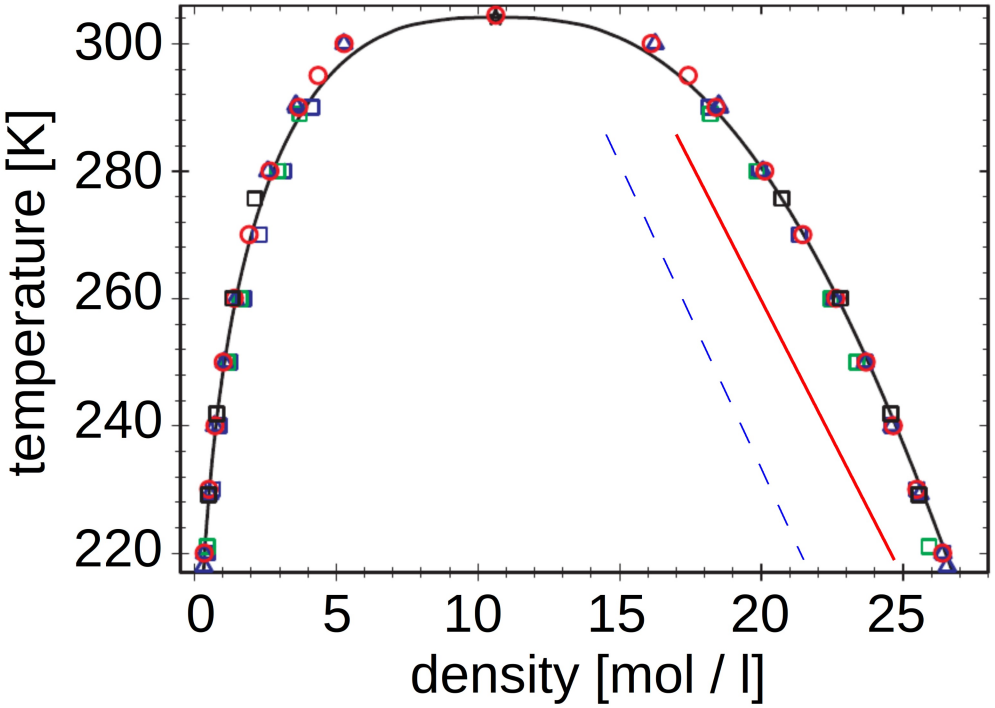
Homogeneous liquid-to-vapour nucleation

Bubble formation



Carbon dioxide

cavitation far from spinodal line



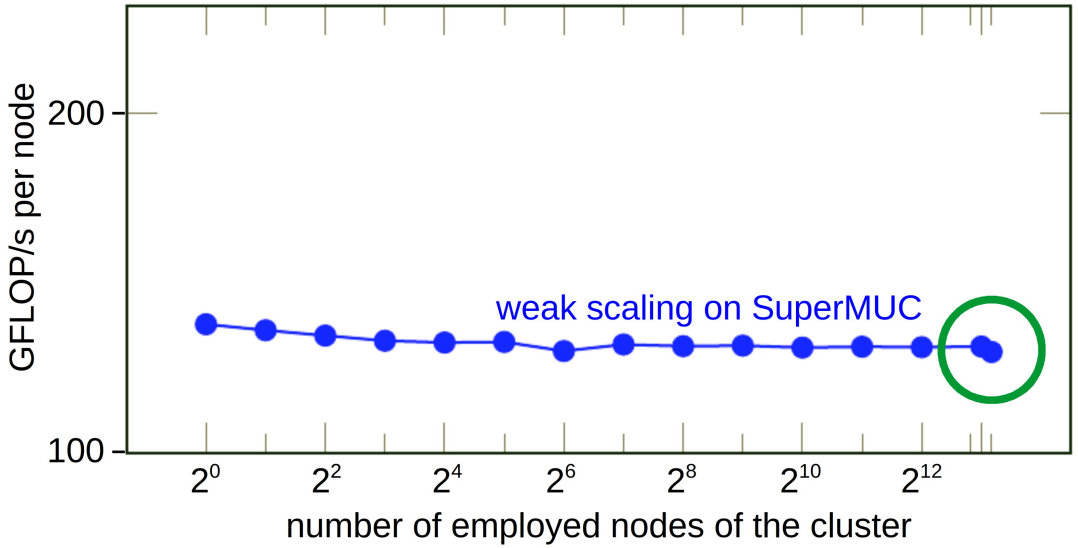
Nucleation theory and/or multiscale modelling needed for technical regime.

Scalable MD simulation of large systems

SuperMUC (Garching):
SandyBridge architecture

http://www.ls1-mardyn.de/

(large systems 1: molecular dynamics)[1, 2]



N = 4 125 000 000 000
2013 molecular dynamics world record[2]

SuperMUC
weak scaling

[1]C. Niethammer *et al.*, *J. Chem. Theory Comput.* 10(10), 4455 – 4464, **2014**;
[2]W. Eckhardt *et al.*, *Proc. ISC 2013*, LNCS 7905, 1 – 12, **2013**.

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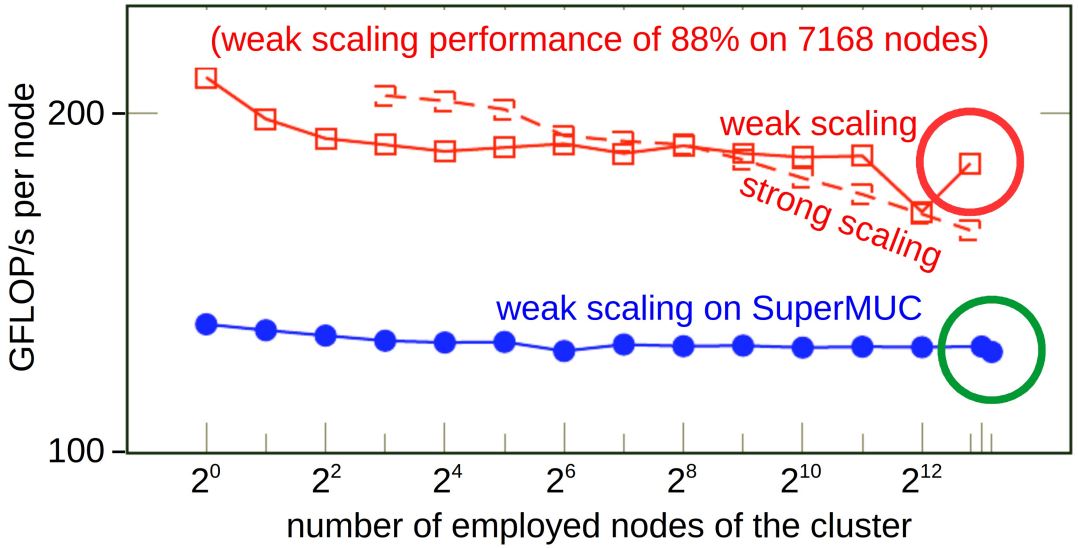
Computational Molecular Engineering

Scalable MD simulation of large systems

Hazel Hen (Stuttgart):
Haswell architecture

http://www.ls1-mardyn.de/

(large systems 1: molecular dynamics)[1, 2]



(cores per node: 24 for Hazel Hen, 16 for SuperMUC)

N = 21 000 000 000 000
2018 molecular dynamics world record[2]

Hazel Hen
weak scaling

[1]C. Niethammer *et al.*, *J. Chem. Theory Comput.* 10(10), 4455 – 4464, **2014**;
[2]P. Neumann, S. Seckler, N. Tchipev, *et al.*, private communication, **2018**.

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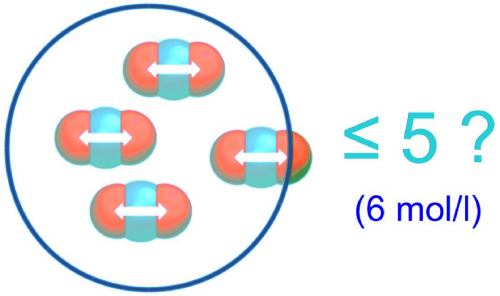
Computational Molecular Engineering

Bubble formation in metastable liquid carbon dioxide

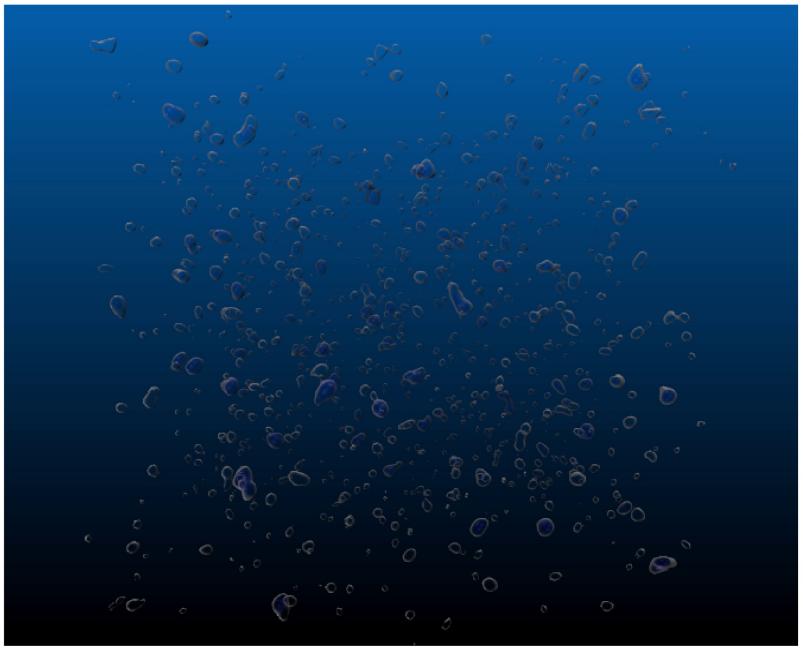
Canonical MD simulation of cavitation in carbon dioxide.

Evaluation of local density at 180 x 180 x 180 grid points:



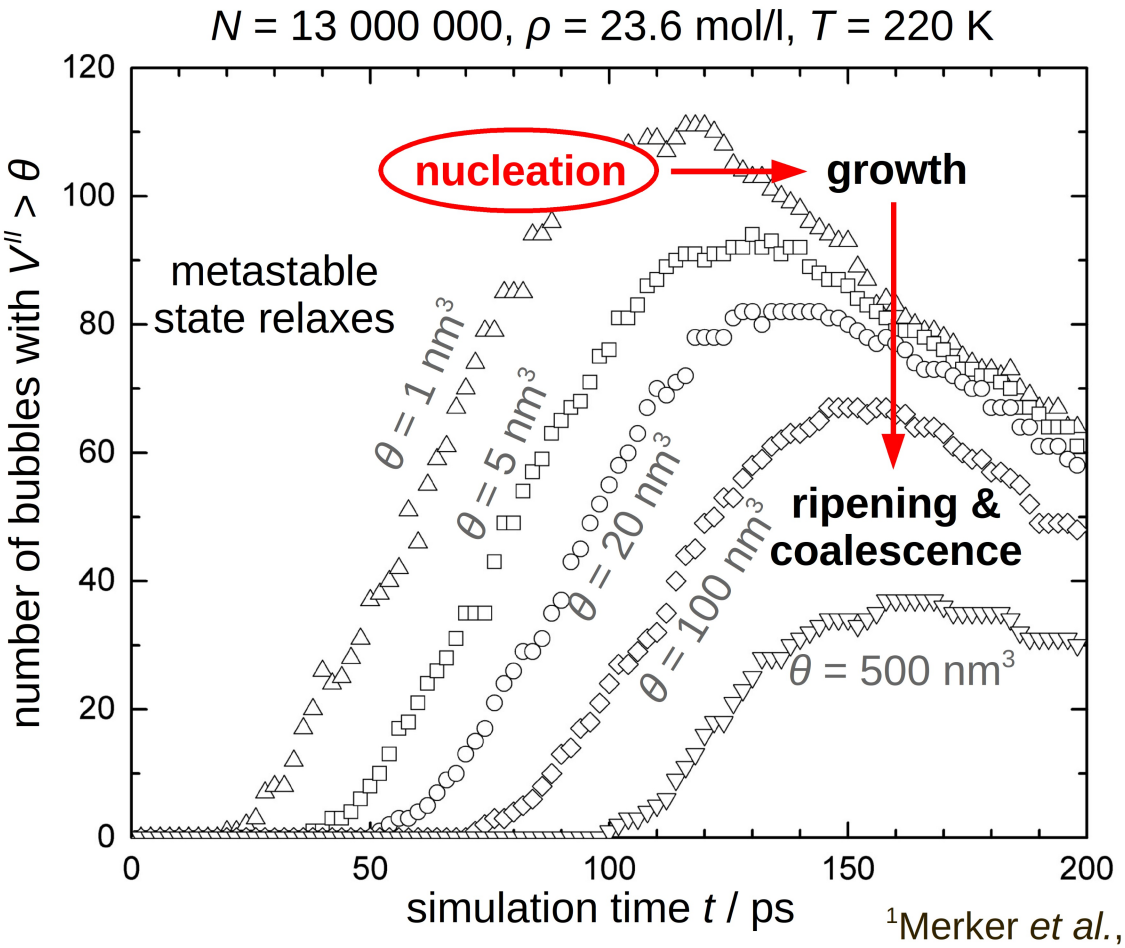
Liquid phase: More than five neighbours present within a radius of 6.9 Å around the grid point.

metastable liquid carbon dioxide



up to 100 million interaction sites

Nucleation rate from population statistics[2]



Observation of

- metastable relaxation,
- **nucleation**,
- growth of supercritical bubbles,
- ripening / coalescence

θ = 1, 2, 5, 10, 20, 50, 100, 200, and 500 nm^3

3CLJQ model by Merker *et al.*[1] for carbon dioxide

[1]Merker *et al.*, *J. Chem. Phys.* 132, 234512, **2010**;

[2]Yasuoka and Matsumoto, *J. Chem. Phys.* 109, 8451, **1998**.

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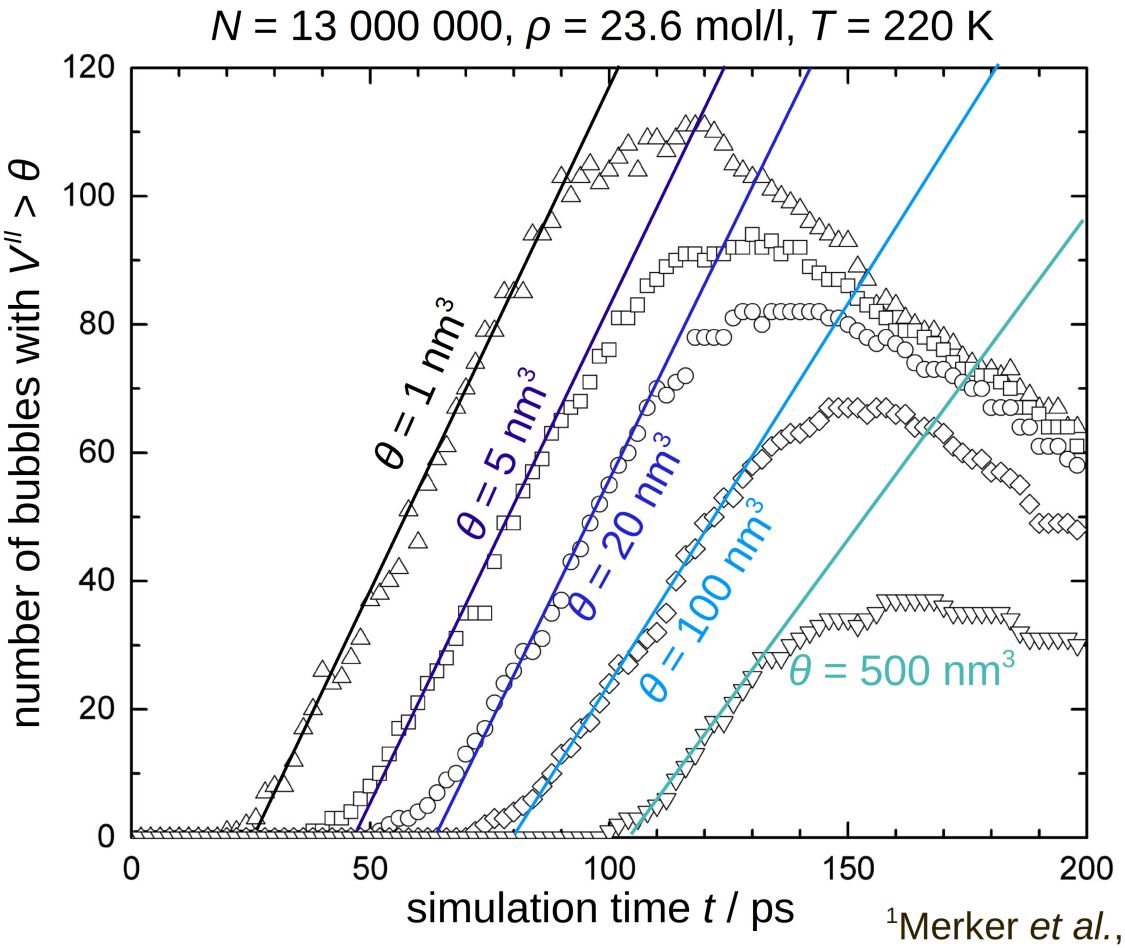

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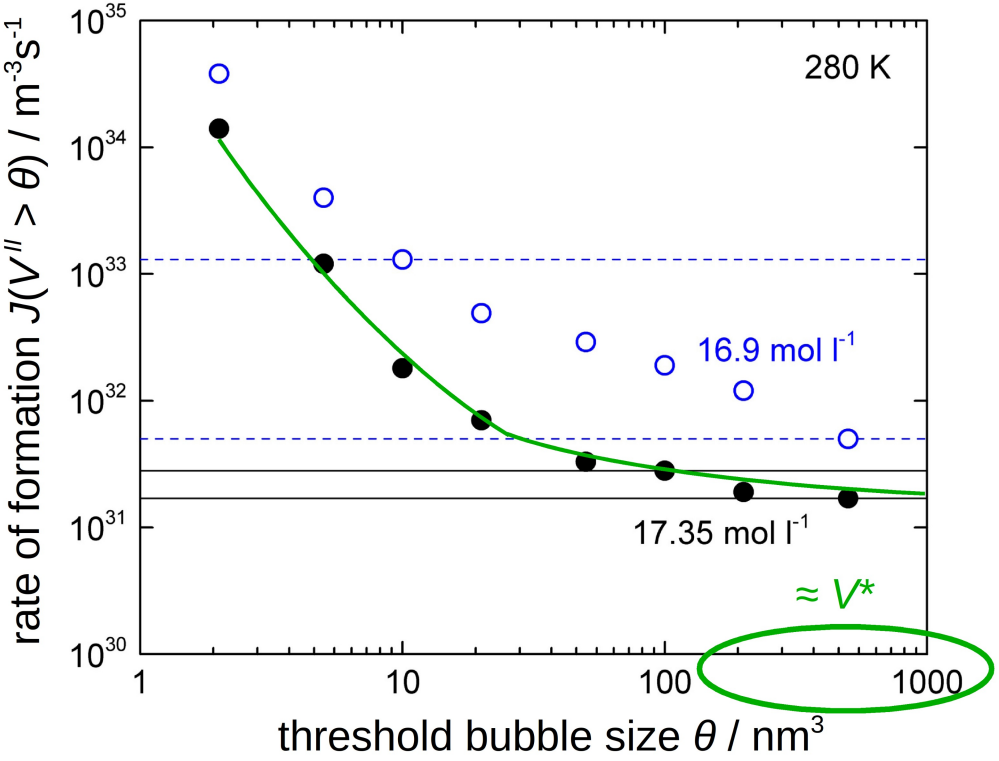
Nucleation rate from population statistics

Subcritical bubbles are formed at a higher rate.

Objective: Determine the macroscopic nucleation rate *J*.

The rate of formation $J(V^{II} > \theta)$ from the method of Yasuoka and Matsumoto depends on the threshold size θ.

Two types of finite-size effects are present, due to bubble size and due to system size.



(K. Langenbach *et al.*, *J. Chem. Phys.* 148, 124702, **2018**.)

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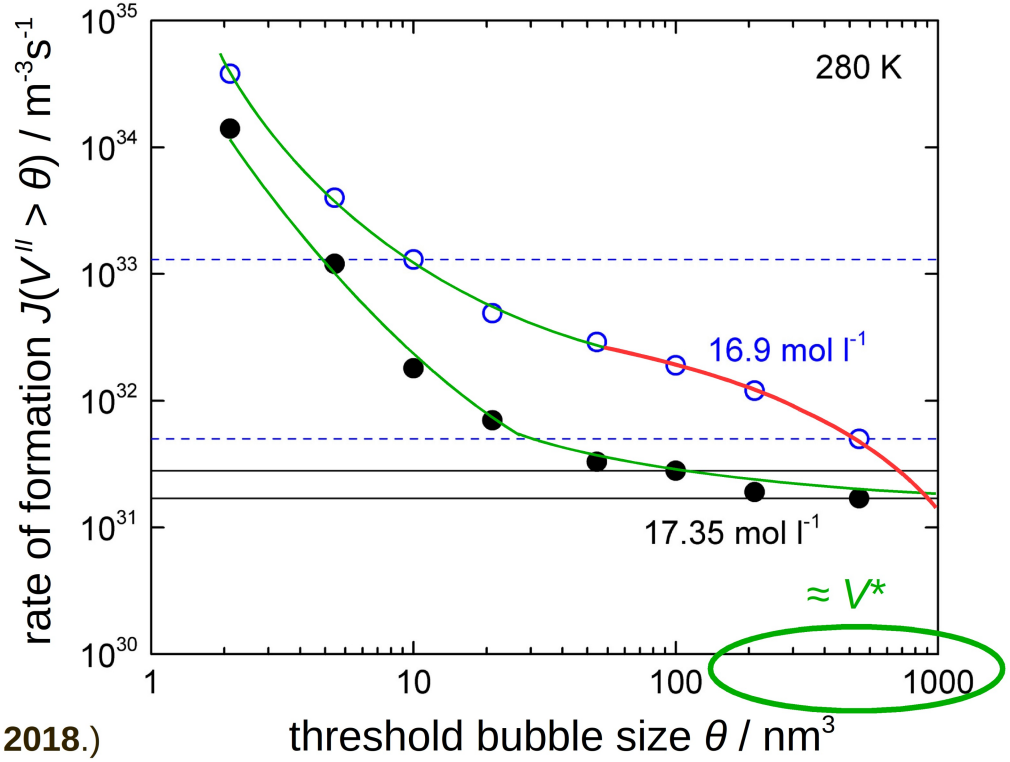
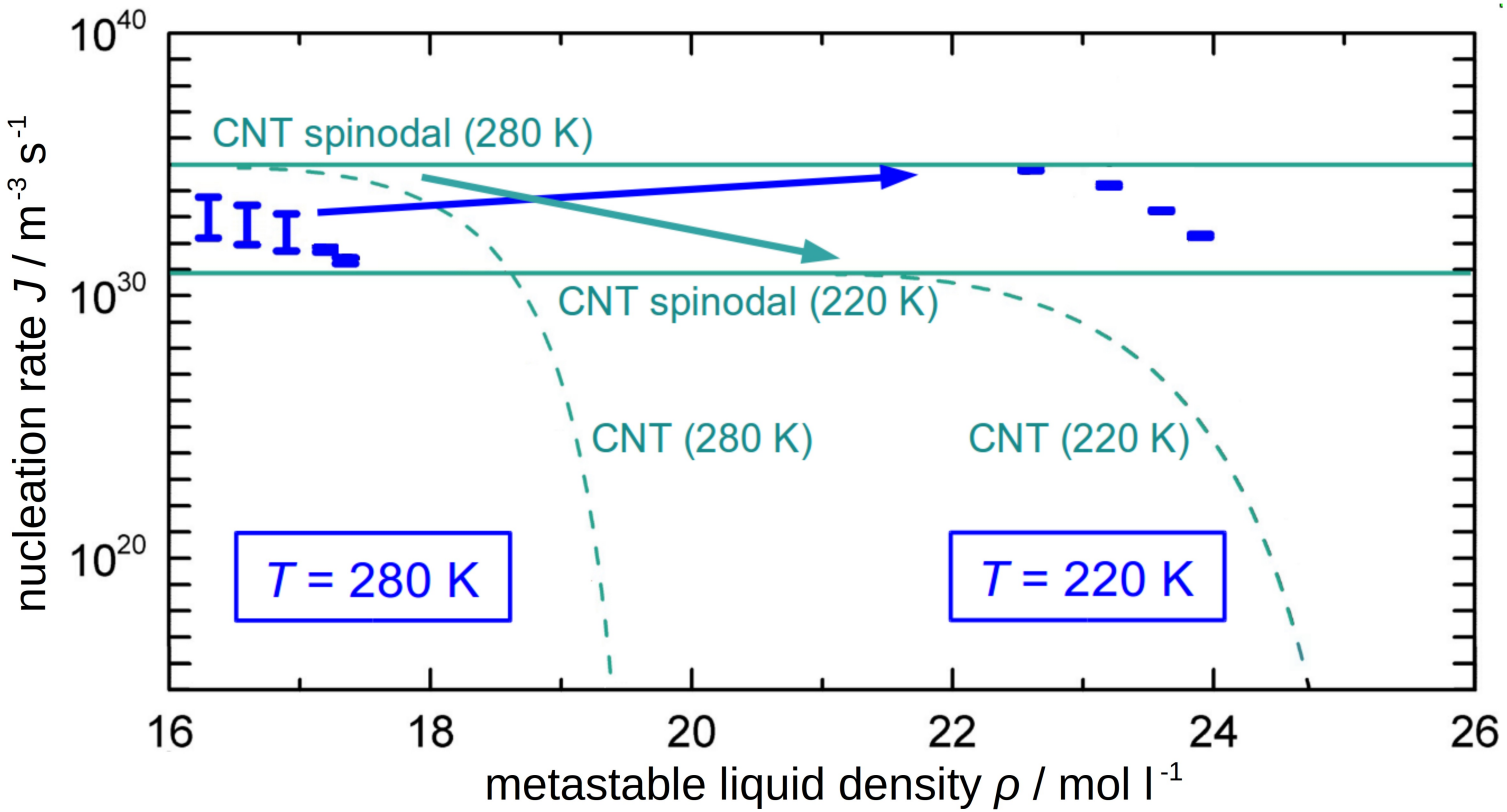


(K. Langenbach *et al.*, *J. Chem. Phys.* 148, 124702, **2018**.)

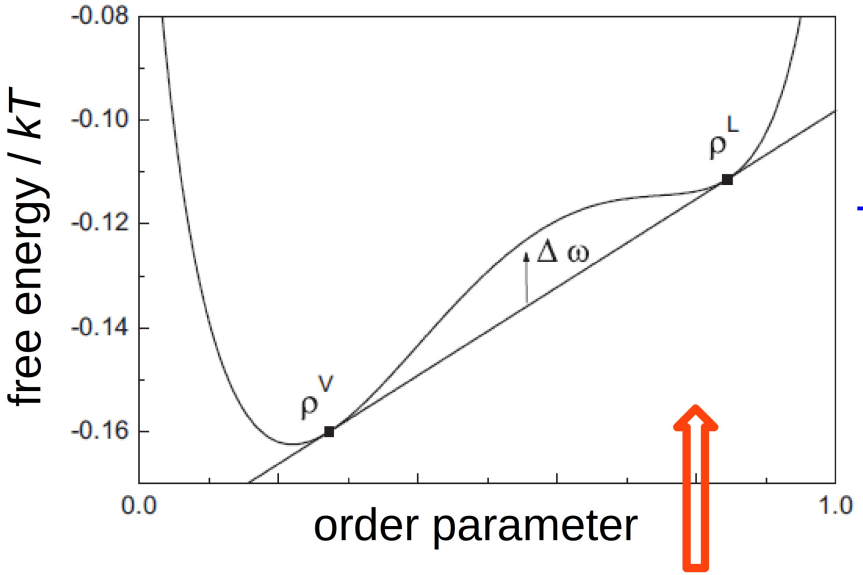
For large bubbles, the rate of formation is limited by the system volume.

Comparison to the classical nucleation theory

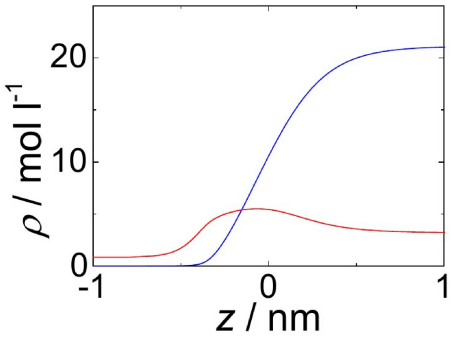
$$\text{nucleation rate } J = J_0 \exp\left(-\frac{\Delta A^*}{kT}\right)$$



Density gradient theory with PC-SAFT equation of state



$+\kappa(\nabla\rho)^2$

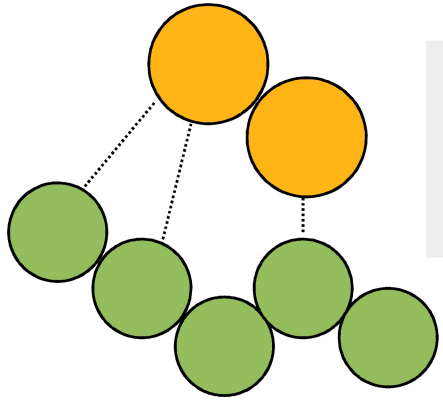


γ

[1] L. D. Landau, E. M. Lifshitz, *Phys. Z. Sowjet.* 8, 153, **1935**;
[2] J. W. Cahn, J. E. Hilliard, *J. Chem. Phys.* 28, 258, **1958**;
[3] C. I. Poser, I. C. Sanchez, *Macromol.* 14, 361, **1981**;
[4] M. P. A. Fisher, M. Wortis, *Phys. Rev. B* 29, 6252, **1984**;
[5] H. Kahl, S. Enders, *Phys. Chem. Chem. Phys.* 4, 931, **2002**.

Perturbed-Chain Statistical Associating Fluid Theory

$$A = A^{\text{ideal}} + A^{\text{hard chain}} + A^{\text{dispersion}} + A^{\text{association}}$$

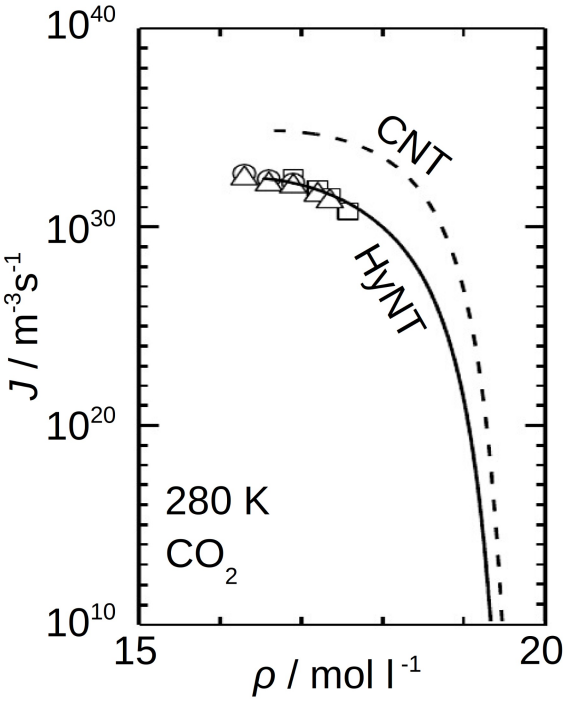


adjusted to model properties

[6] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 40, 1244, **2001**;
[7] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 41, 5510, **2002**.

Hybrid nucleation theory using MD, DGT, and PC-SAFT

$$J = J_0 \exp\left(-\frac{\Delta A^*}{kT}\right)$$



thermodynamic factor from density gradient theory with the PC-SAFT EOS

kinetic factor from molecular dynamics

(K. Langenbach *et al.*, *J. Chem. Phys.* 148, 124702, **2018**.)

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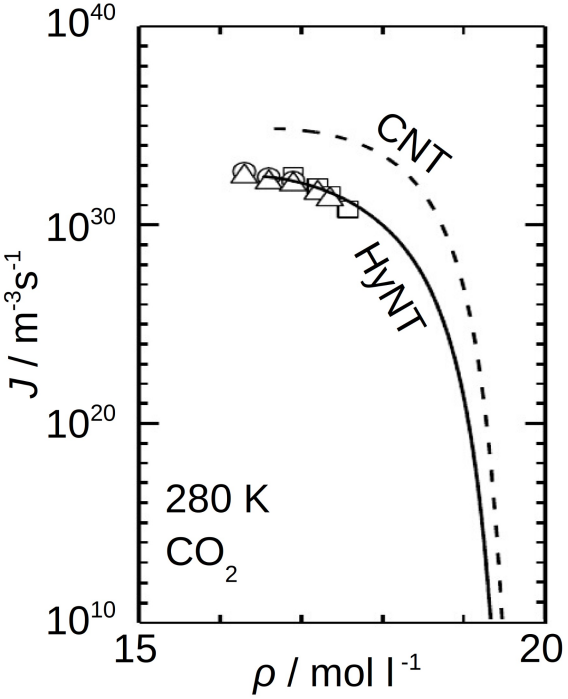
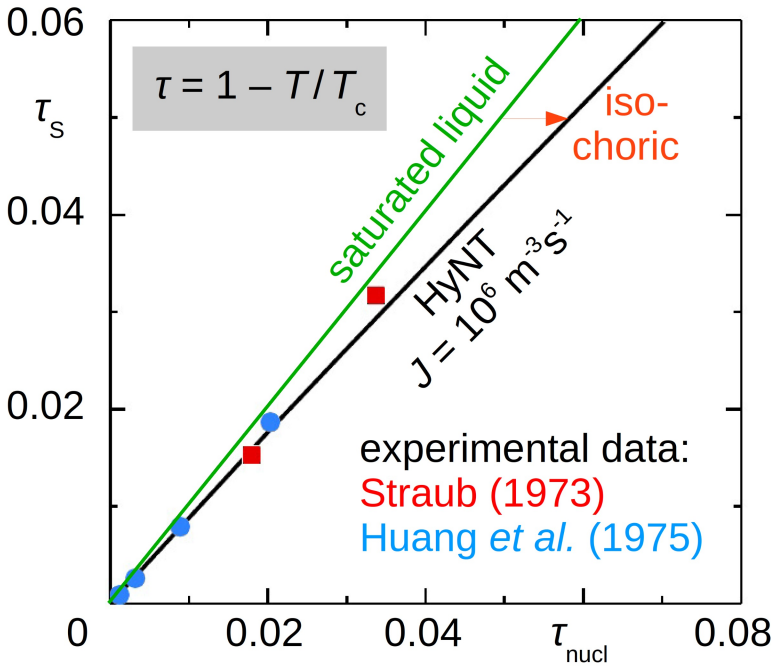


extrapolation by the hybrid nucleation theory

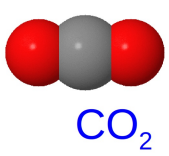


(K. Langenbach *et al.*, *J. Chem. Phys.* 148, 124702, **2018**.)

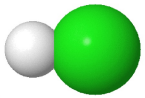
Interfacial enrichment in fluid mixtures

Multiscale modelling and simulation of vapour-liquid interfaces of fluid mixtures

Modelling approach



CO_2

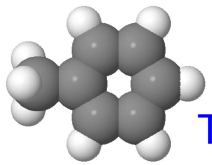


HCl

Molecular dynamics

+

Density gradient theory



Toluene

pure fluid models and two binary subsystems from previous work

One binary system, i.e., toluene + CO2, from present work

Homogeneous fluid properties: PC-SAFT equation of state, parameters from previous work

DGT influence parameter: Adjusted to surface tension data

Computational Molecular Engineering

LABORATORY OF ENGINEERING THERMODYNAMICS

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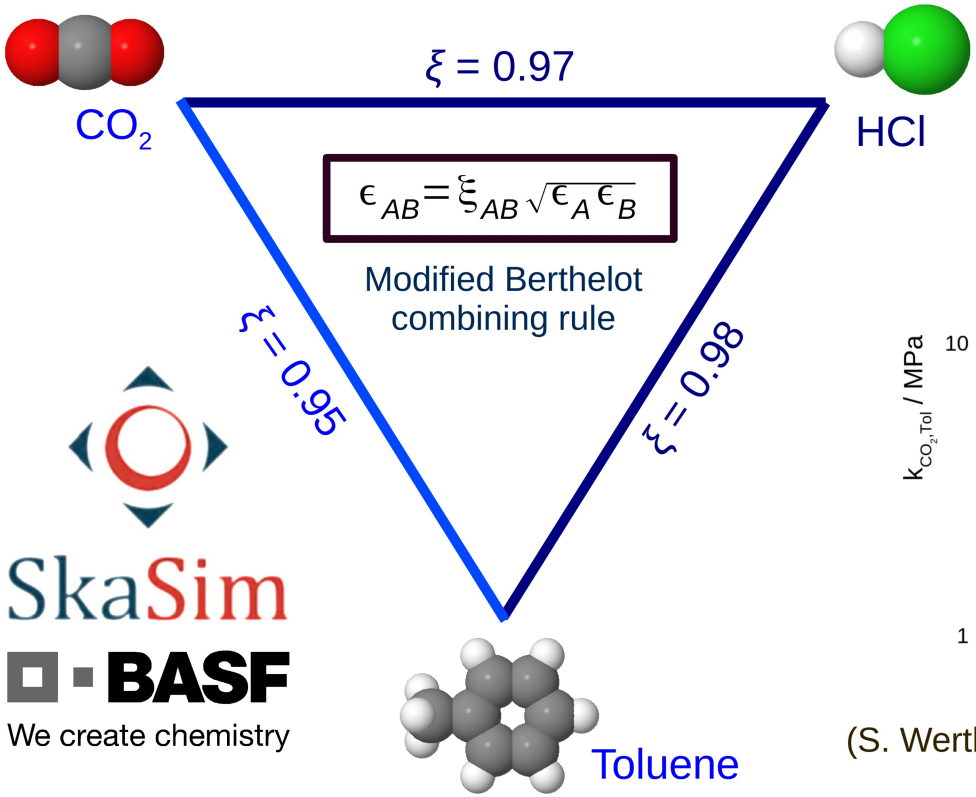
We create chemistry

Interfacial enrichment in fluid mixtures

Multiscale <u>modelling and simulation</u> of vapour-liquid interfaces of fluid mixtures

Model parameterization – molecular force field, for MD simulation



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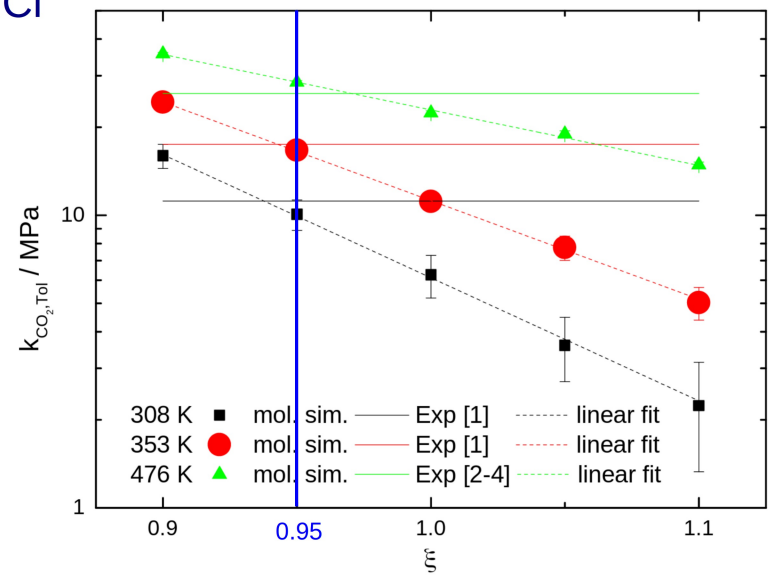
Henry coefficient (i.e., VLE)

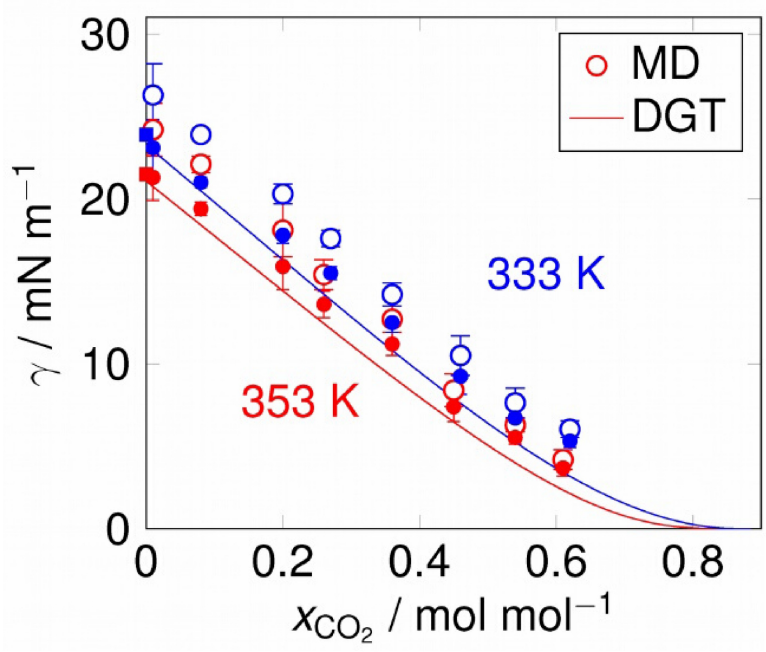


(S. Werth *et al.*, *Fluid Phase Equilib.* 427, 219 – 230, **2016**.)

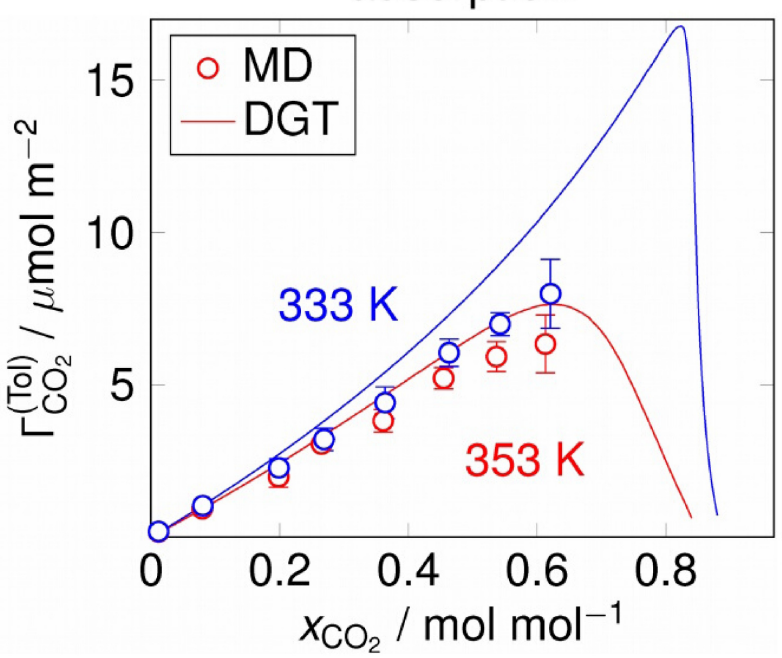
Interfacial enrichment in fluid mixtures

Simulation and comparison between modelling and simulation approaches

surface tension



adsorption



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Interfacial enrichment in fluid mixtures

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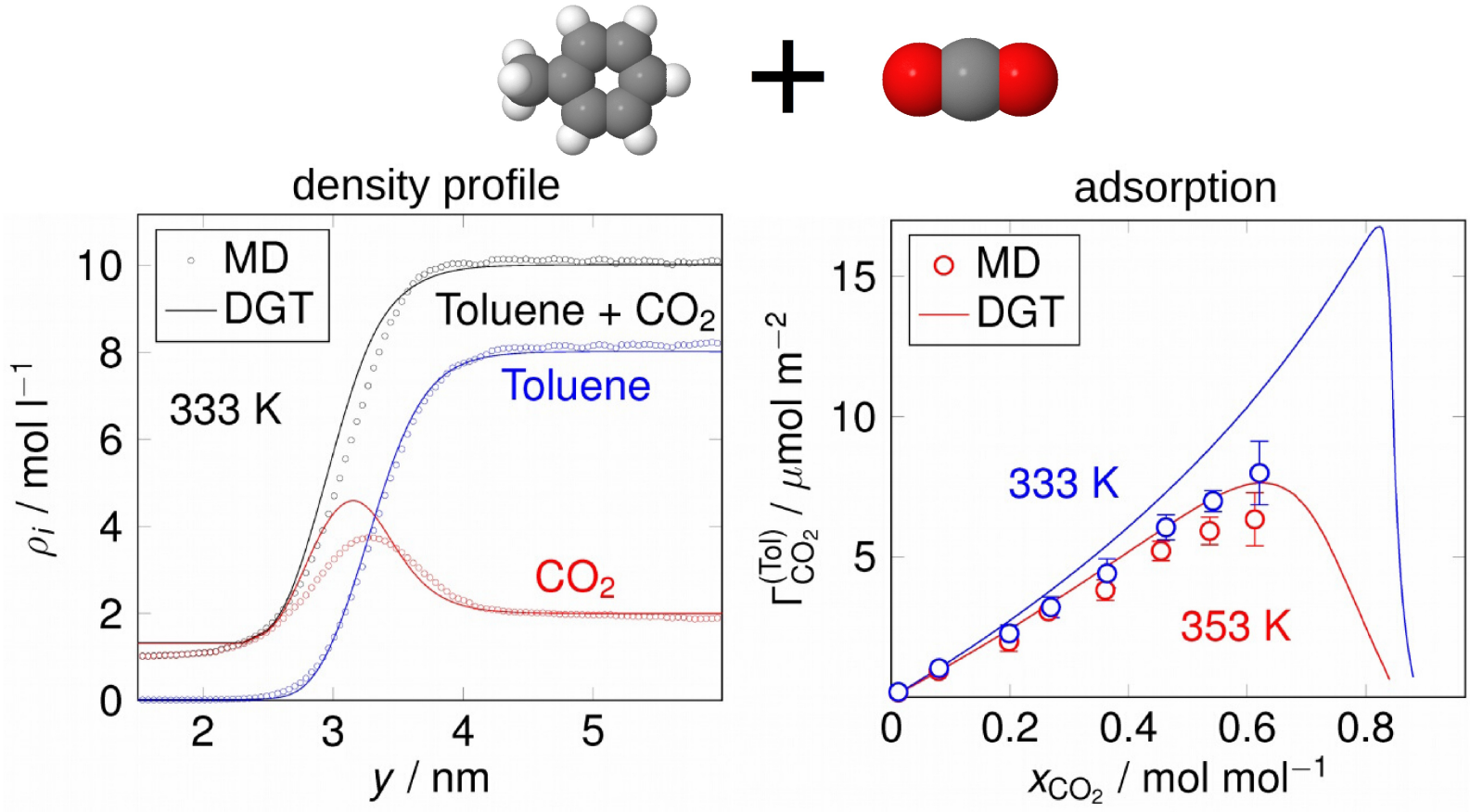

(S. Werth *et al.*, *Fluid Phase Equilib.* 427, 219 – 230, **2016**.)

Conclusion

Molecular modelling and simulation of **bubble formation by homogeneous nucleation** requires the efficient use of HPC resources by scalable MD simulation.

Here, *ls1 mardyn* was employed on over 100 000 cores to simulate **metastable liquid carbon dioxide** in systems containing up to 100 000 000 interaction sites.

The **classical nucleation theory** does not capture the decay of the free energy barrier at the spinodal, and it predicts the temperature dependence of the nucleation rate in the spinodal limit inaccurately.

A **hybrid nucleation theory** was developed by combining density gradient theory and the PC-SAFT equation of state with MD simulation results.

MD and DGT + PC-SAFT agree well on **interfacial enrichment** at vapour-liquid interfaces of mixtures; perspective: Investigation of bubble formation in mixtures.