Molecular simulation and theory of homogeneous cavitation

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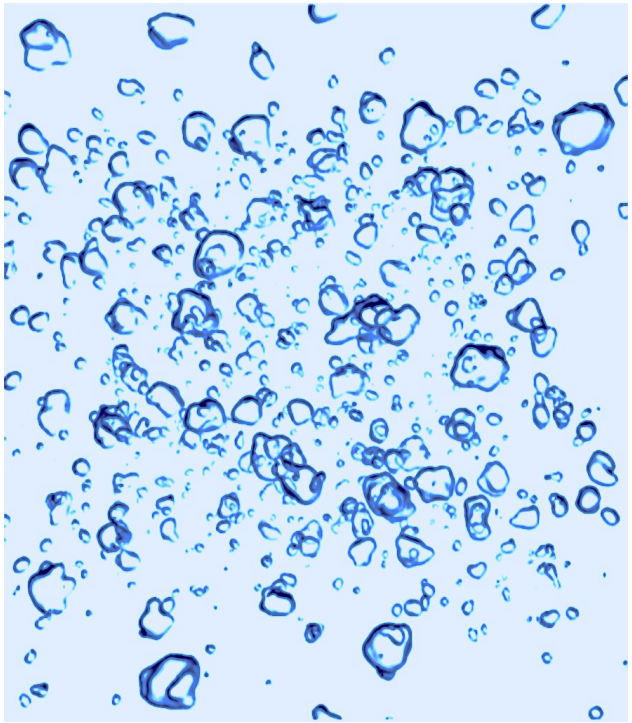
Computational Molecular Engineering

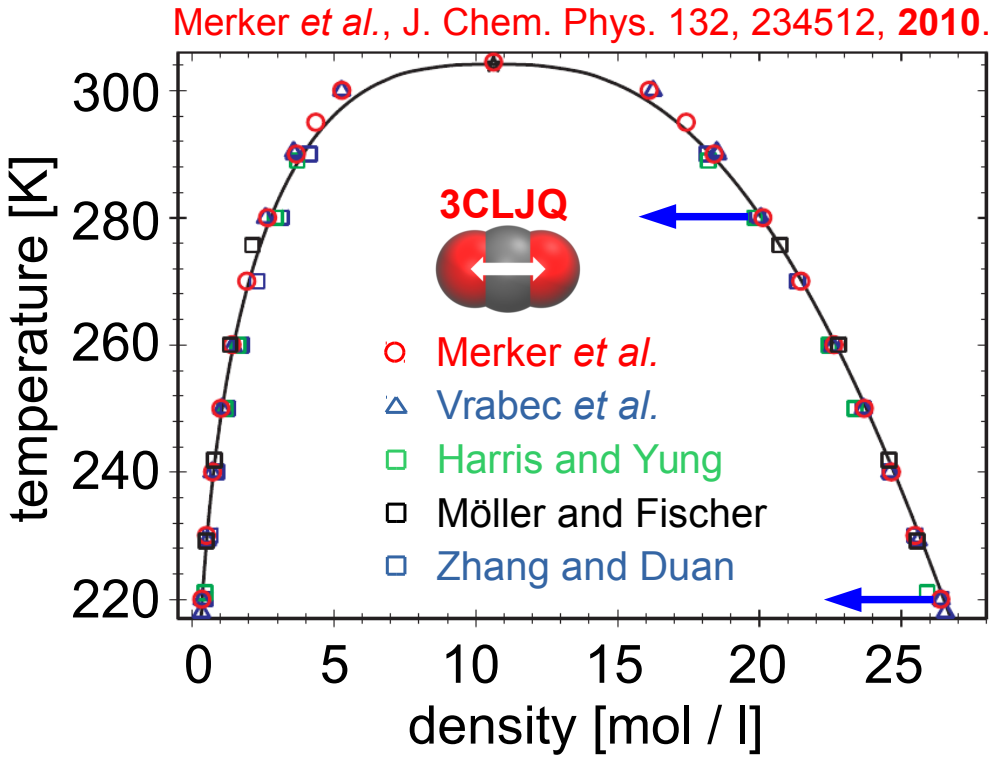
ProcessNet MolMod Conference
Frankfurt am Main, 10th March 2017

Homogeneous liquid to vapour nucleation

Bubble formation



Carbon dioxide

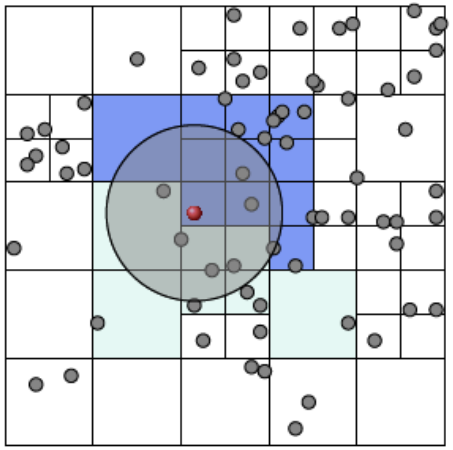


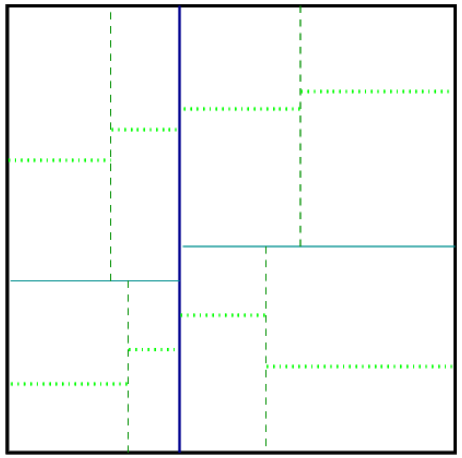
MD simulation of nucleation requires large systems and performant codes.

Scalable molecular dynamics simulation

Collaboration within

IMEMO (2008 – 2011)
SkaSim (2013 – 2016)
TaLPas (2017 – 2020)





Bundesministerium für Bildung und Forschung

BASF The Chemical Company

SkaSim

Lehrstuhl für Thermodynamik
Prof. Dr.-Ing. H. Hasse

Technische Universität München

ThEt UNIVERSITÄT PADERBORN
Die Universität der Informationsgesellschaft

HLRS

Scalable molecular dynamics simulation

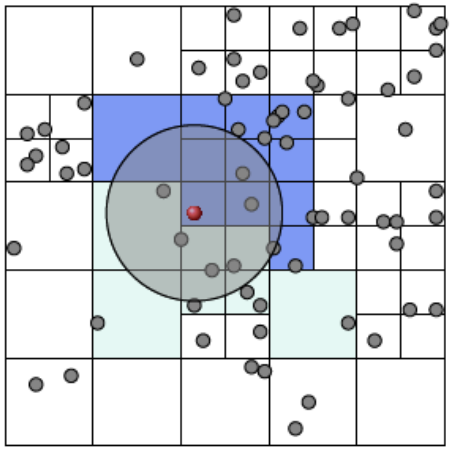
Spatial domain decomposition

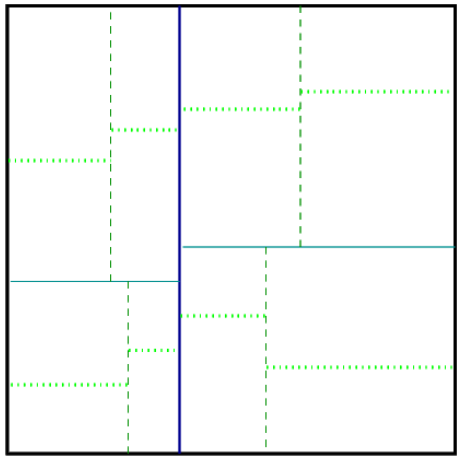
Dynamic load balancing

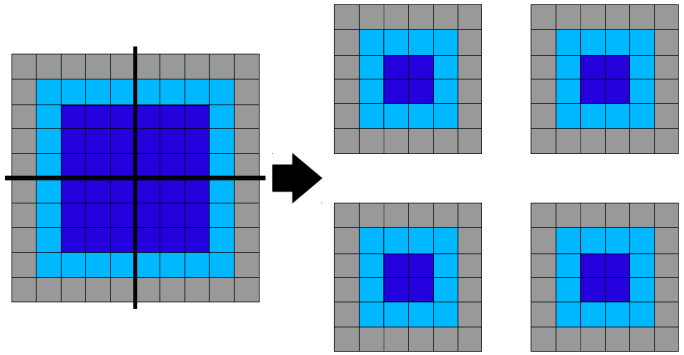
Communication (almost) only with neighbour processes

Linked-cell data structure near-field pair potentials

Summation techniques, e.g. Janeček, FMM, for far field







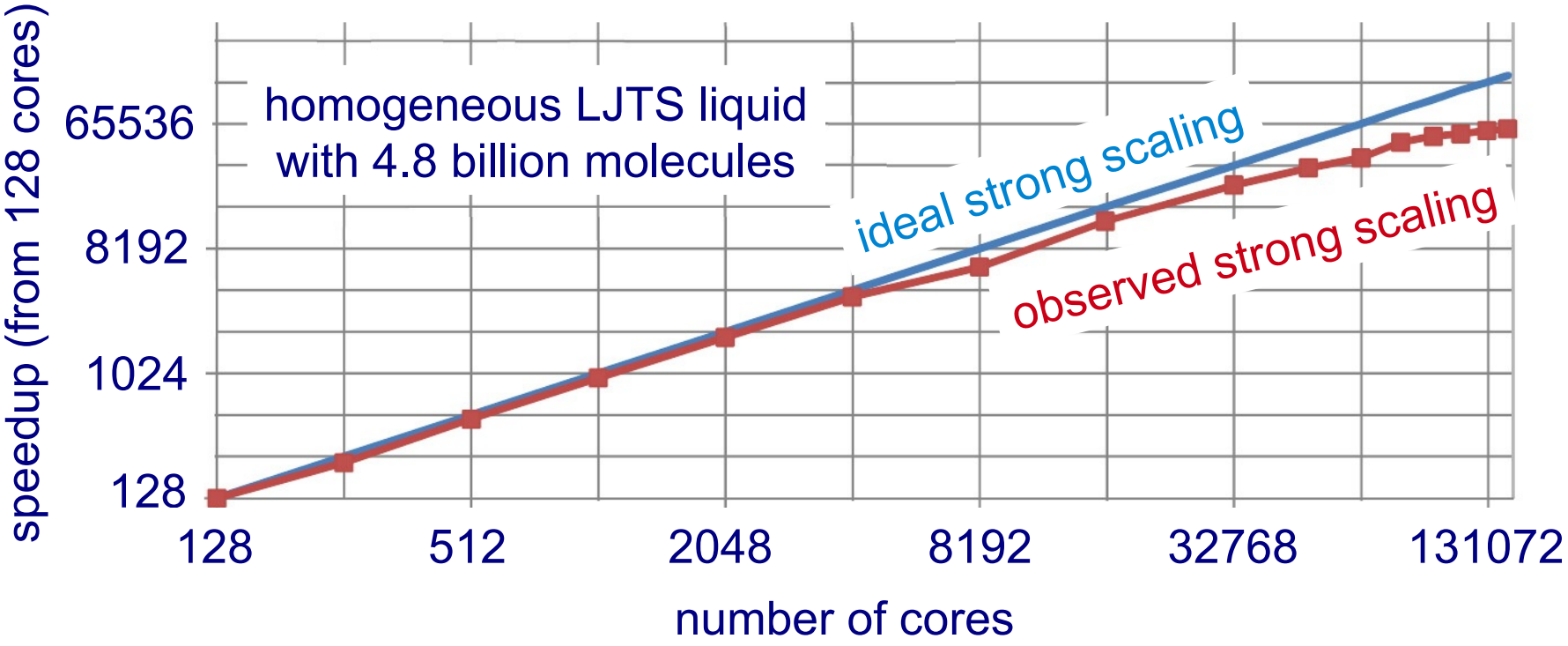
(non-blocking, overlapping MPI send/receive operations)

large systems “1”: molecular dynamics

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

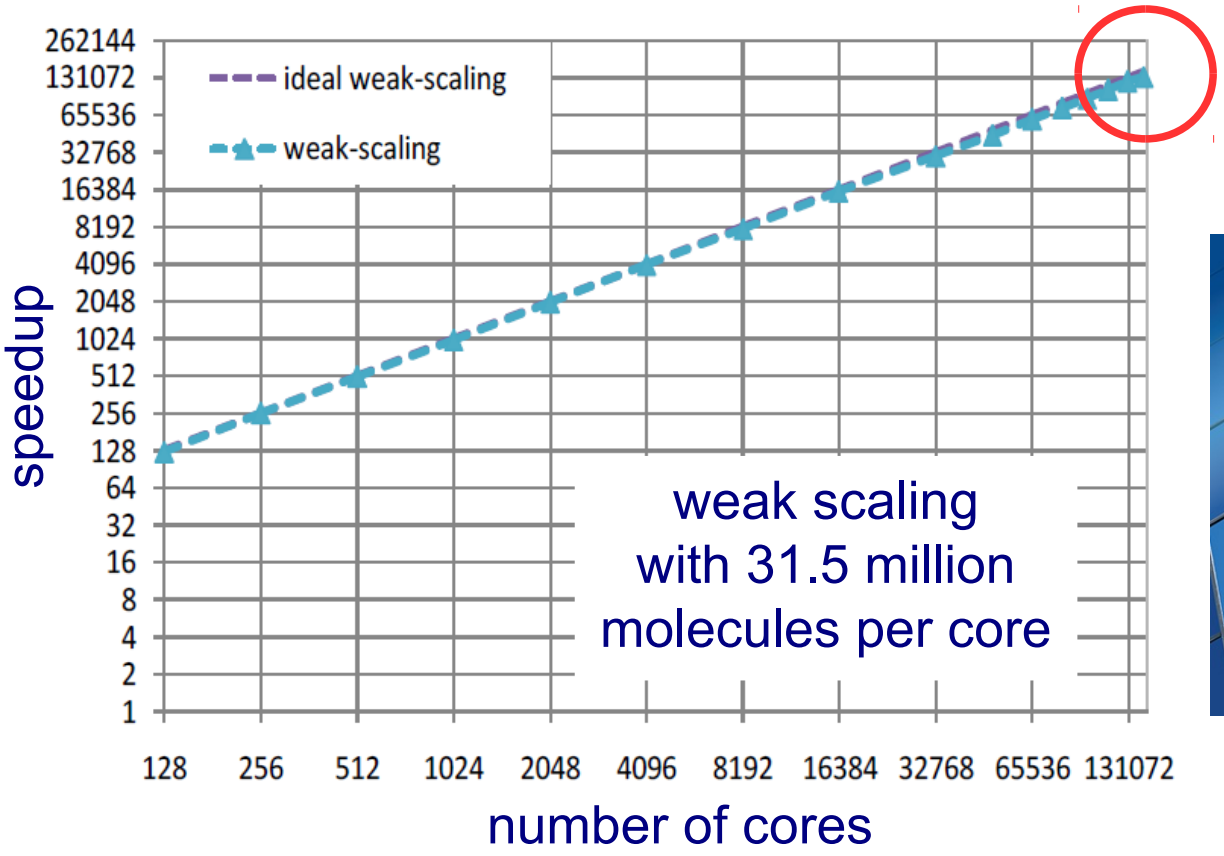
Scalable molecular dynamics simulation

Scaling of *ls1 mardyn* examined on SuperMUC up to 146 016 cores.[1]



[1]W. Eckhardt, A. Heinecke, *et al.*, *Proceedings of ISC 2013*, Springer, LNCS 7905, 1 – 12, **2013**.

Scalable molecular dynamics simulation



Up to $N = 4 \cdot 10^{12}$ on SuperMUC[1]

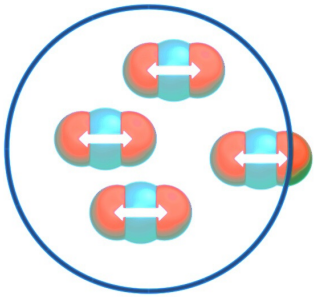
[1]Eckhardt *et al.*, *ISC 2013*, LNCS 7905, 1 – 12, **2013**.

MD simulation world record achieved for a liquid Lennard-Jones system.[1]

Bubble formation in metastable liquid CO_2

Canonical MD simulation of cavitation in carbon dioxide.

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

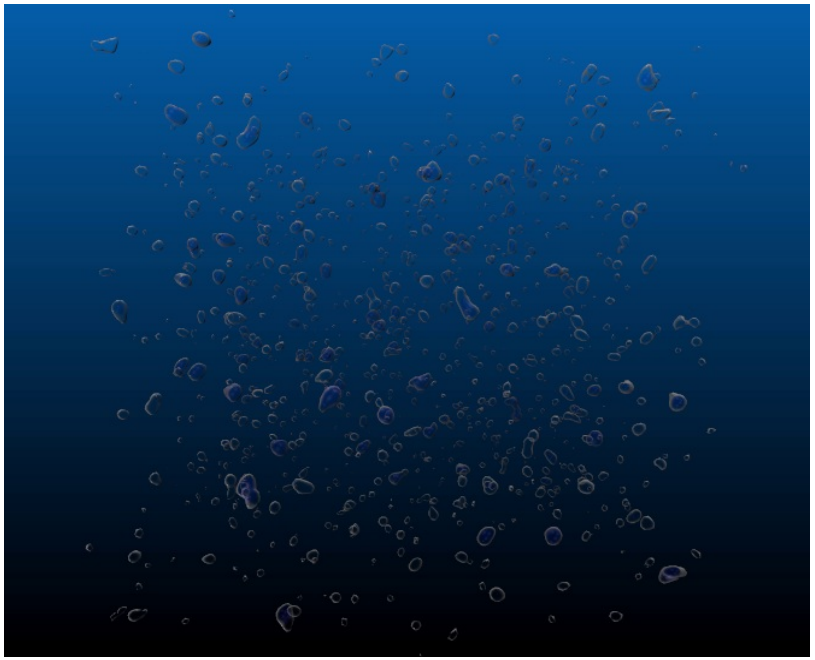


≤ 5 ?

(6 mol/l)

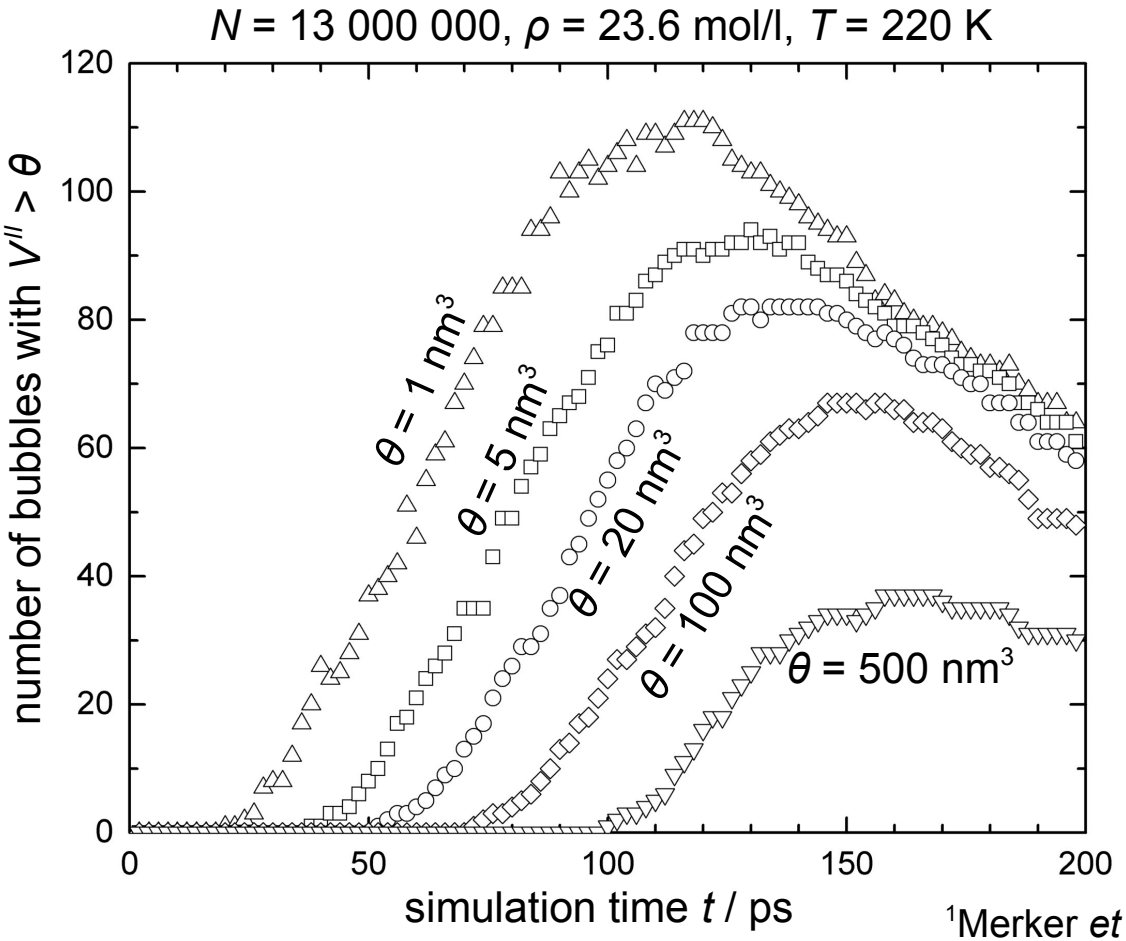
Liquid phase: More than five neighbours present within a radius of 6.9 Å around the grid point.

metastable liquid carbon dioxide



up to 100 million interaction sites

Nucleation rate from population statistics



Observation of

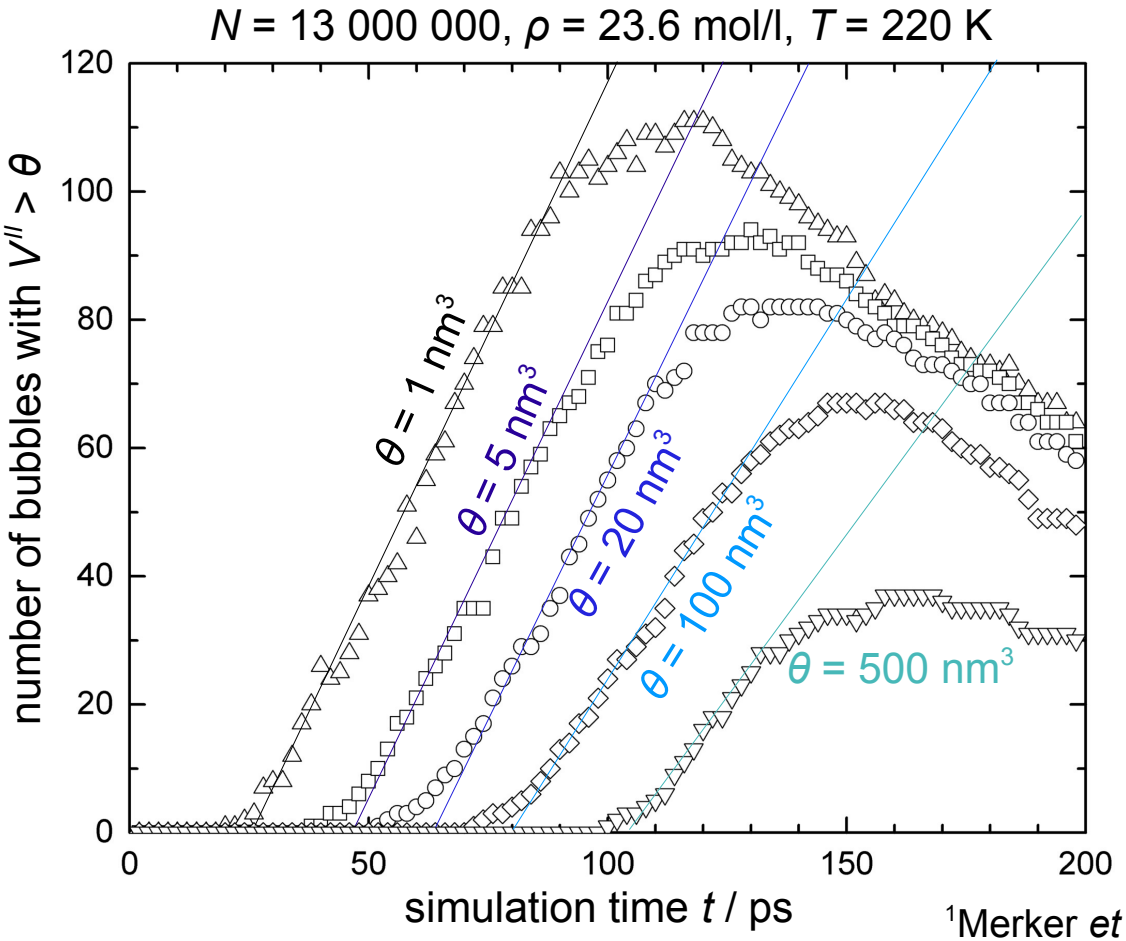
- metastable relaxation,
- nucleation,
- growth of supercritical bubbles,
- ripening / coalescence

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**.

Nucleation rate from population statistics[2]



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

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

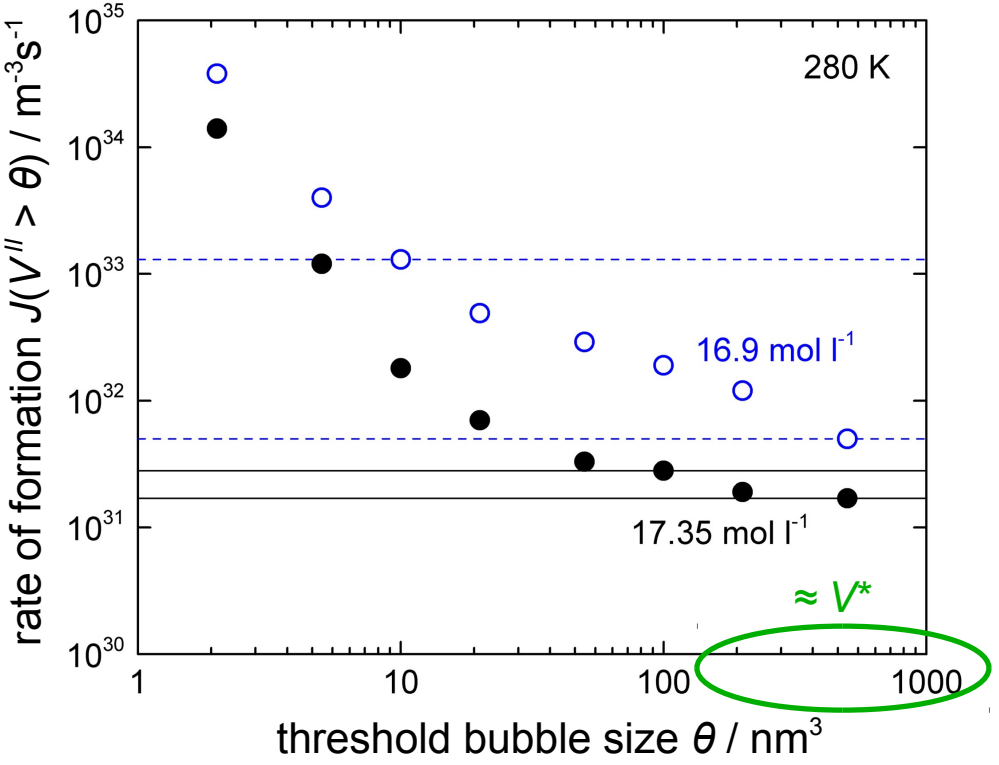
[2]Yasuoka and Matsumoto, *J. Chem. Phys.* 109, 8451, **1998**.

Nucleation rate from population statistics

Objective: Determine the macroscopic nucleation rate *J*.

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

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



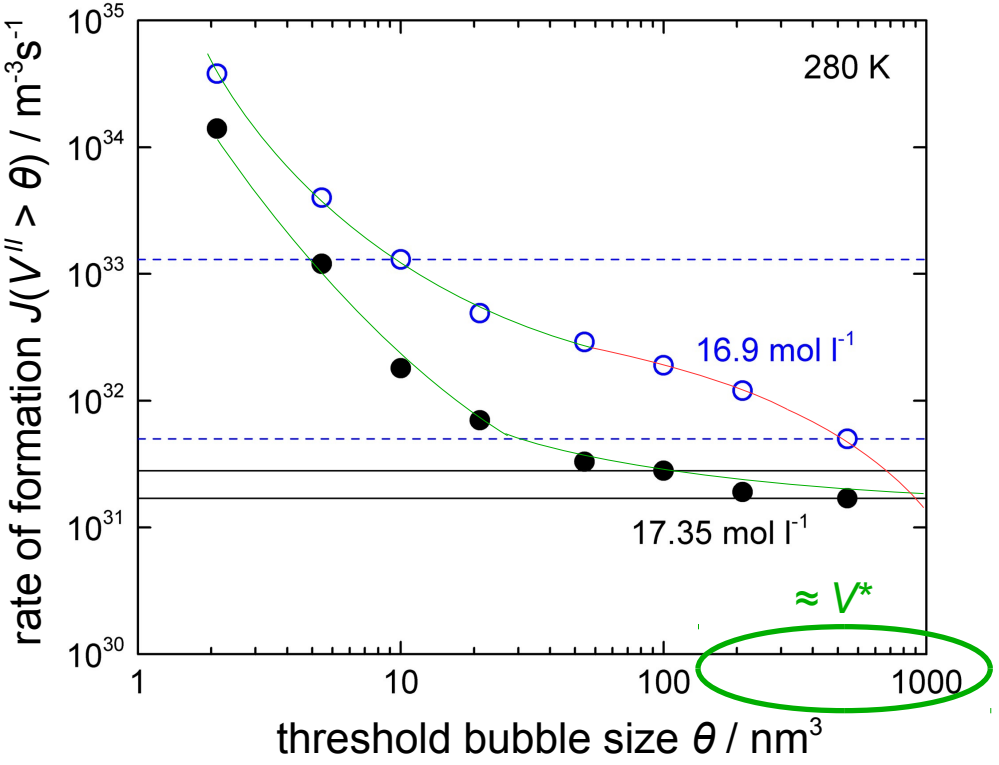
Nucleation rate from population statistics

Subcritical bubbles are formed at a higher rate.

Objective: Determine the macroscopic nucleation rate J.

The rate of formation $J(V'' > \theta)$ from the method of Yasuoka and Matsuomoto depends on the threshold size θ.

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

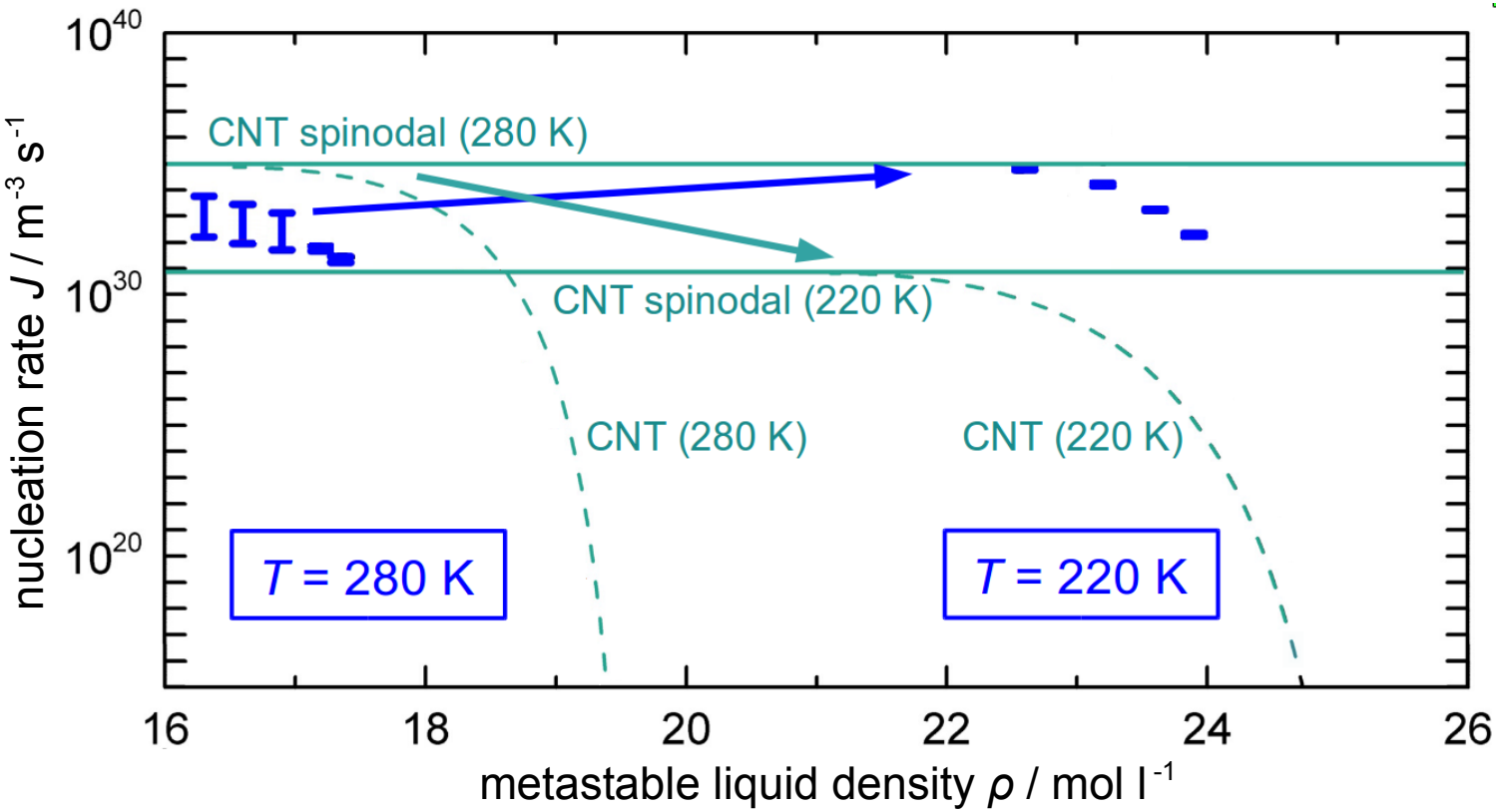


For large bubbles, the rate of formation is limited by the system volume.

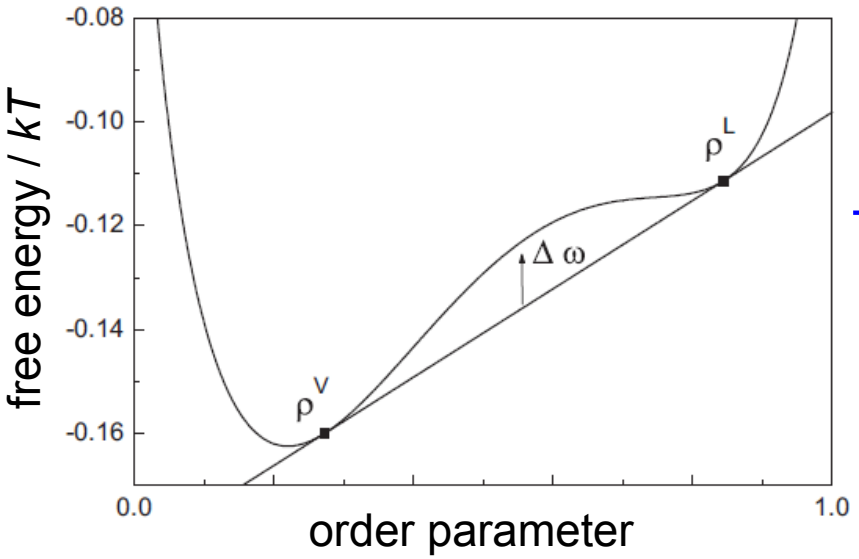
Comparison to classical nucleation theory

CNT → capillarity approximation

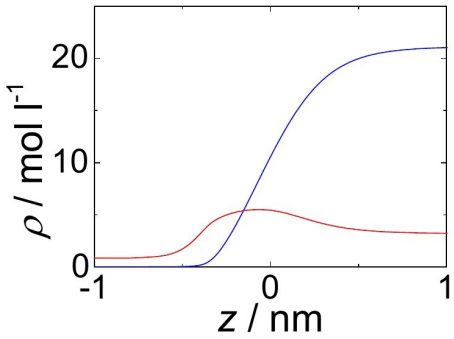
$\gamma = \gamma_{planar}(T)$ independent of the bubble radius

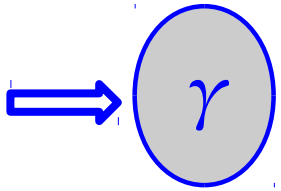


Density gradient theory



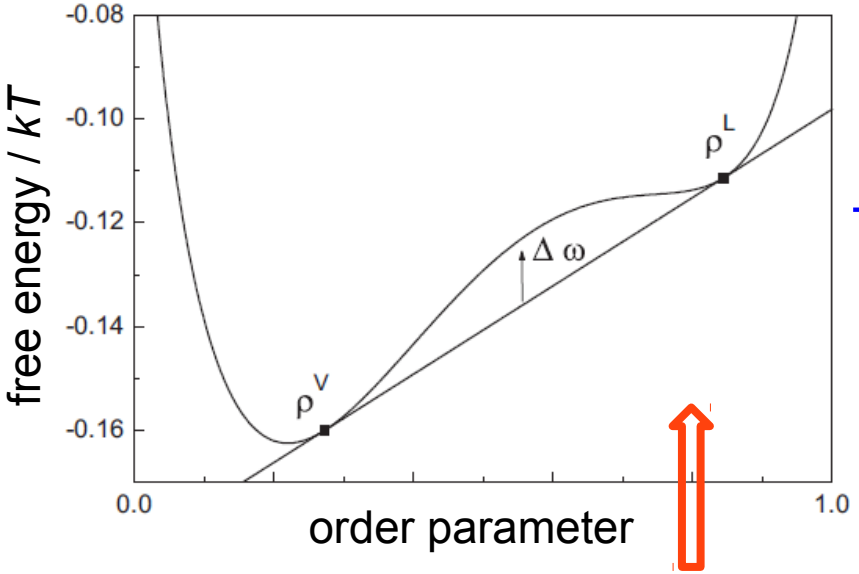
$+\kappa(\nabla\rho)^2$





[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**.

Density gradient theory + PC-SAFT EOS



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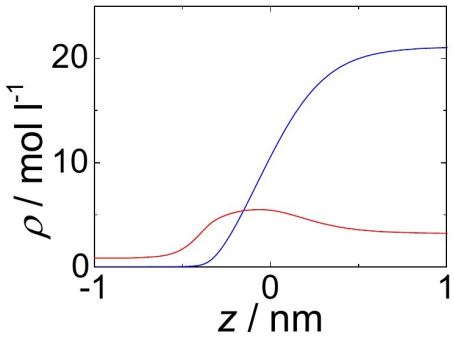

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[1] L. D. Landau, E. M. Lifshitz, *Phys. Z. Sowjet.* 8, 153, **1935**;
[2] J. W. Cahn, J. E. Hilliard, *J. Chem. Phys.* 28, 258, **1958**;
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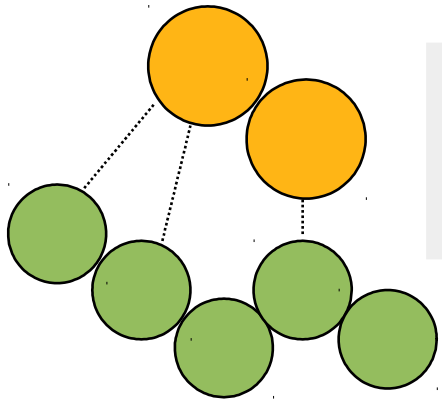
[5] H. Kahl, S. Enders, *Phys. Chem. Chem. Phys.* 4, 931, **2002**.

Perturbed-Chain Statistical Associating Fluid Theory

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



adjusted to model properties

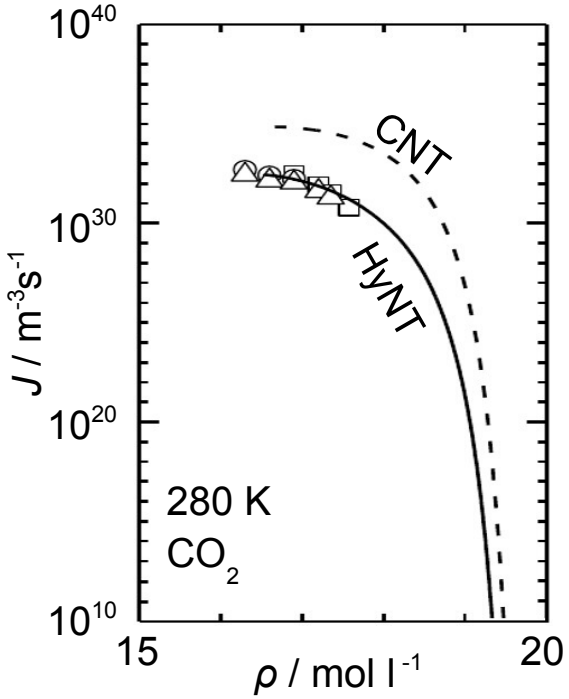
[6] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 40, 1244, **2001**;
[7] J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.* 41, 5510, **2002**.

Hybrid Nucleation Theory

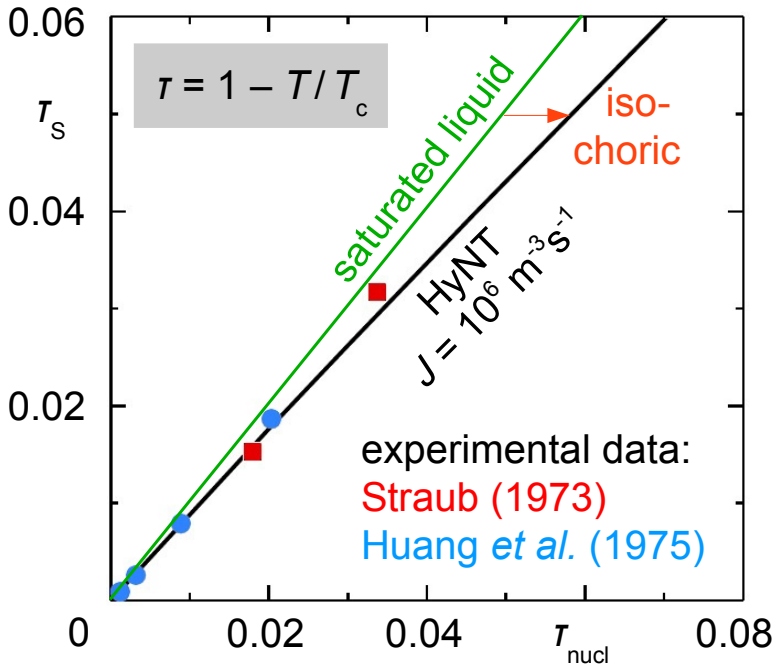
$$J = J_0 \exp\left(-\frac{\Delta A^*}{kT}\right)$$

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

kinetic factor from molecular dynamics



extrapolation by the hybrid nucleation theory



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.

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We create chemistry

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The **classical nucleation theory** predicts an unphysical temperature dependence of the thermodynamic factor which determines the nucleation rate in the spinodal limit.

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