12th HLRS Results and Review Workshop

Molecular modeling of hydrogen bonding fluids: vapor-liquid coexistence and interfacial properties

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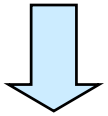
TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Technology Vision 2020: The US chemical industry

New Chemical Engineering Science and Technology	Supply Chain Management	Information Systems	Manufacturing & Operations

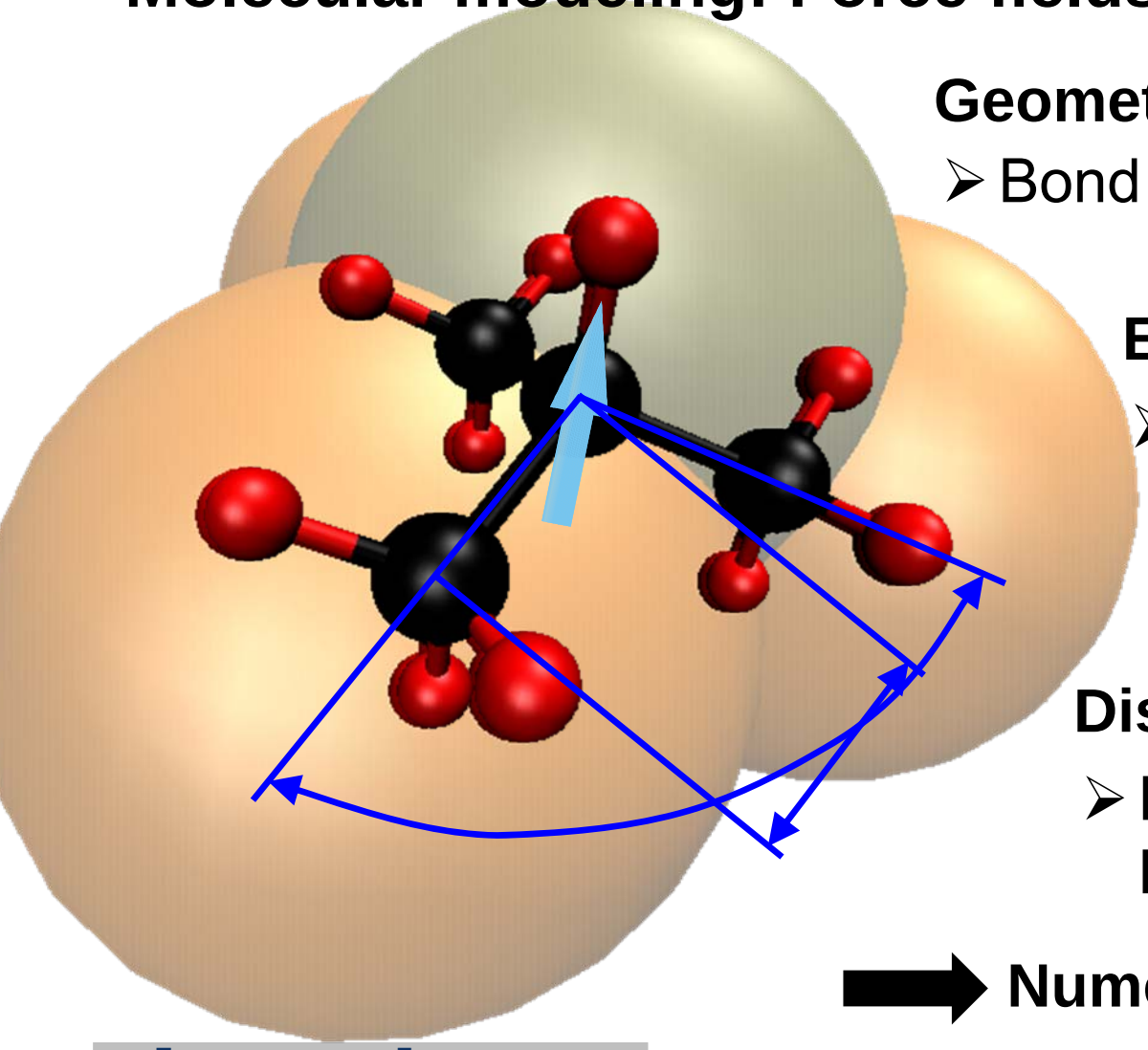


Engineering Computational Technologies

Computational Molecular Science	Computational Fluid Dynamics	Process Modeling & Simulation	Operations Simulation & Optimization

⇒ link between Engineering and Chemistry
⇒ new processes, products, materials

Molecular modeling: Force fields



Geometry

- Bond lengths and angles

Electrostatics

- Position and magnitude of dipoles, quadrupoles and partial charges

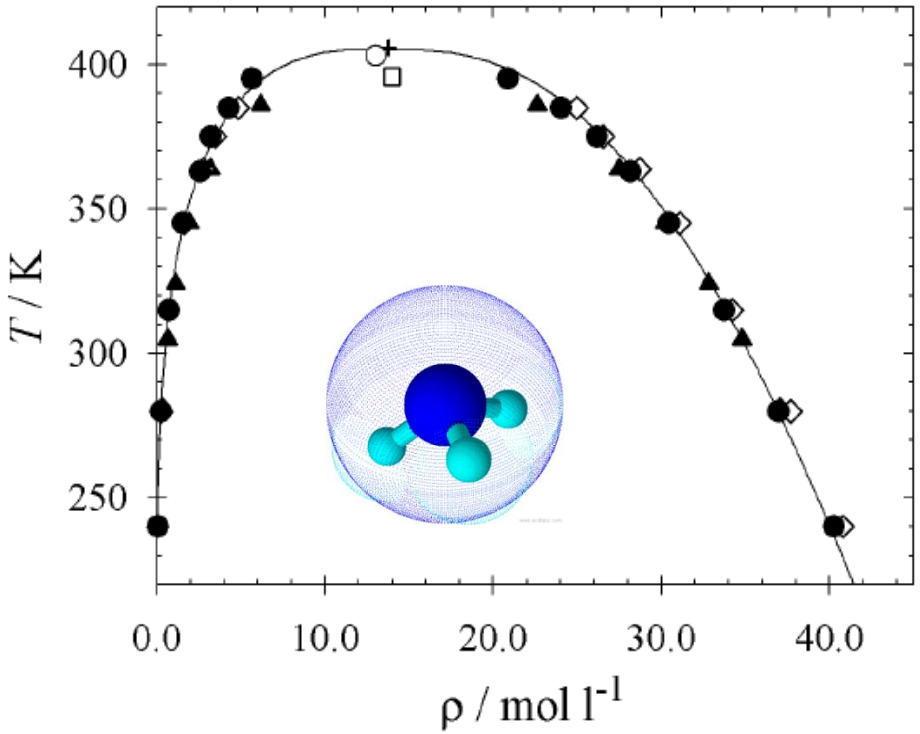
Dispersion and repulsion

- Parameters of Lennard-Jones potentials

➡ **Numerous parameters**

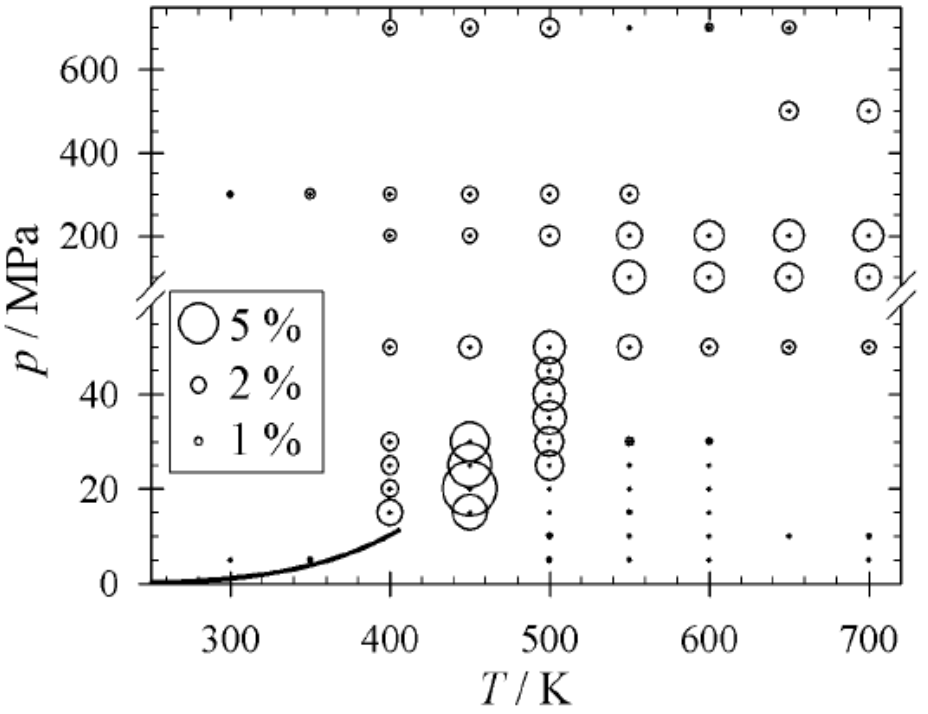
Modeling of hydrogen bonding fluids: Ammonia

Vapor-liquid equilibrium



- ● NH_3 model of Eckl *et al.*
- ◇ ○ ▲ Other models
- — Correlation of experimental data

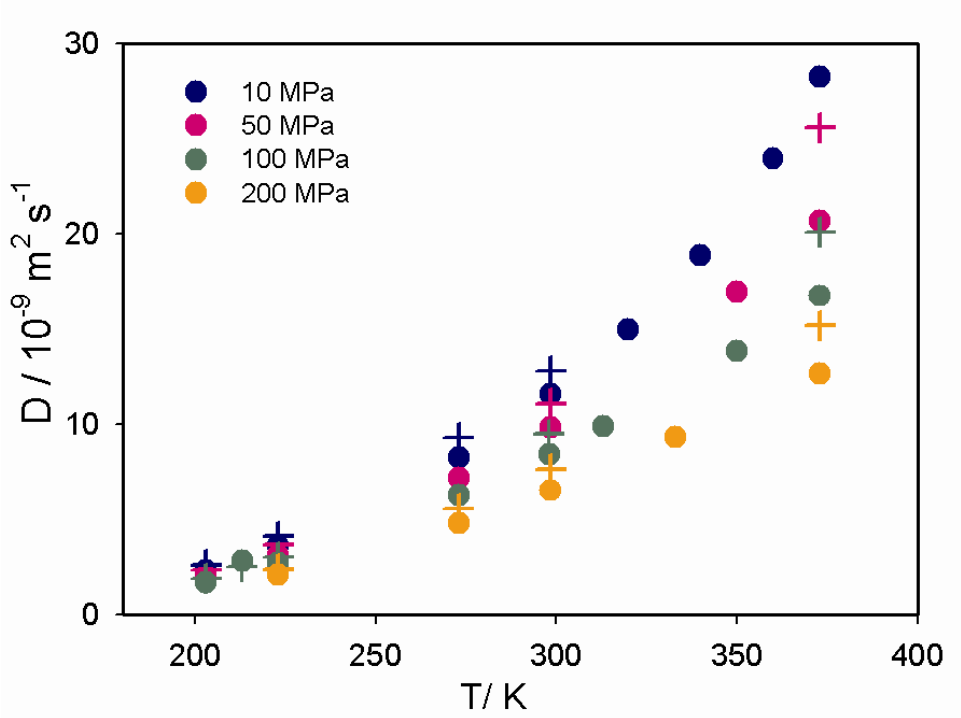
Supercritical fluid density



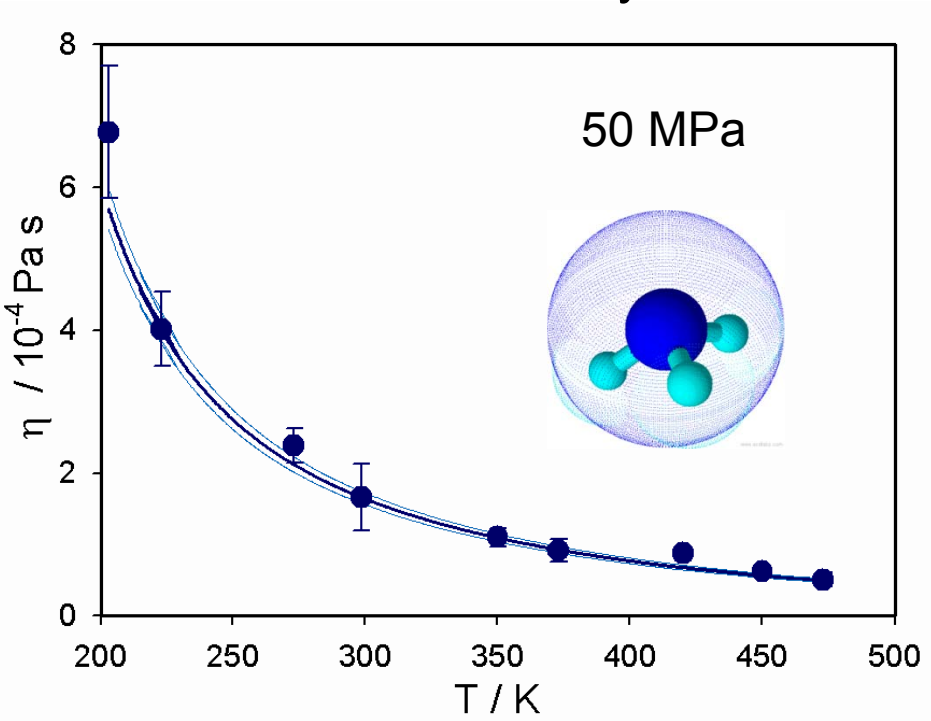
Excellent reliability for the extrapolation of thermo-physical properties

Ammonia: Predicted transport properties

Self-diffusion coefficient



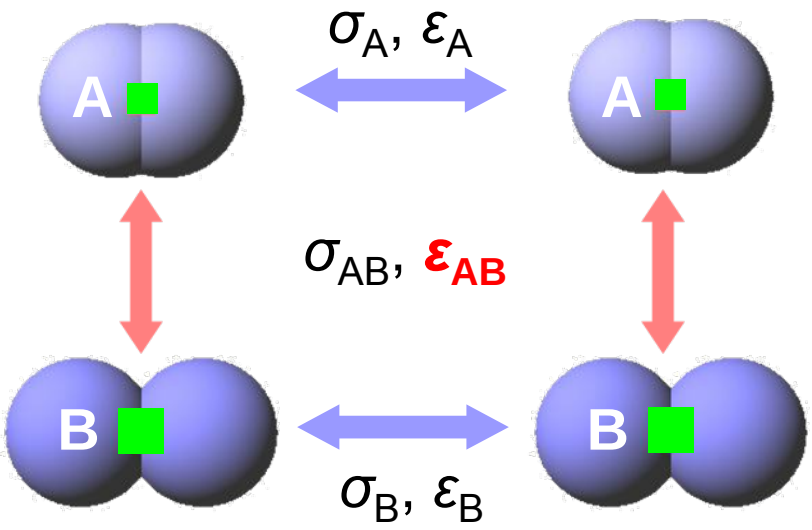
Shear viscosity



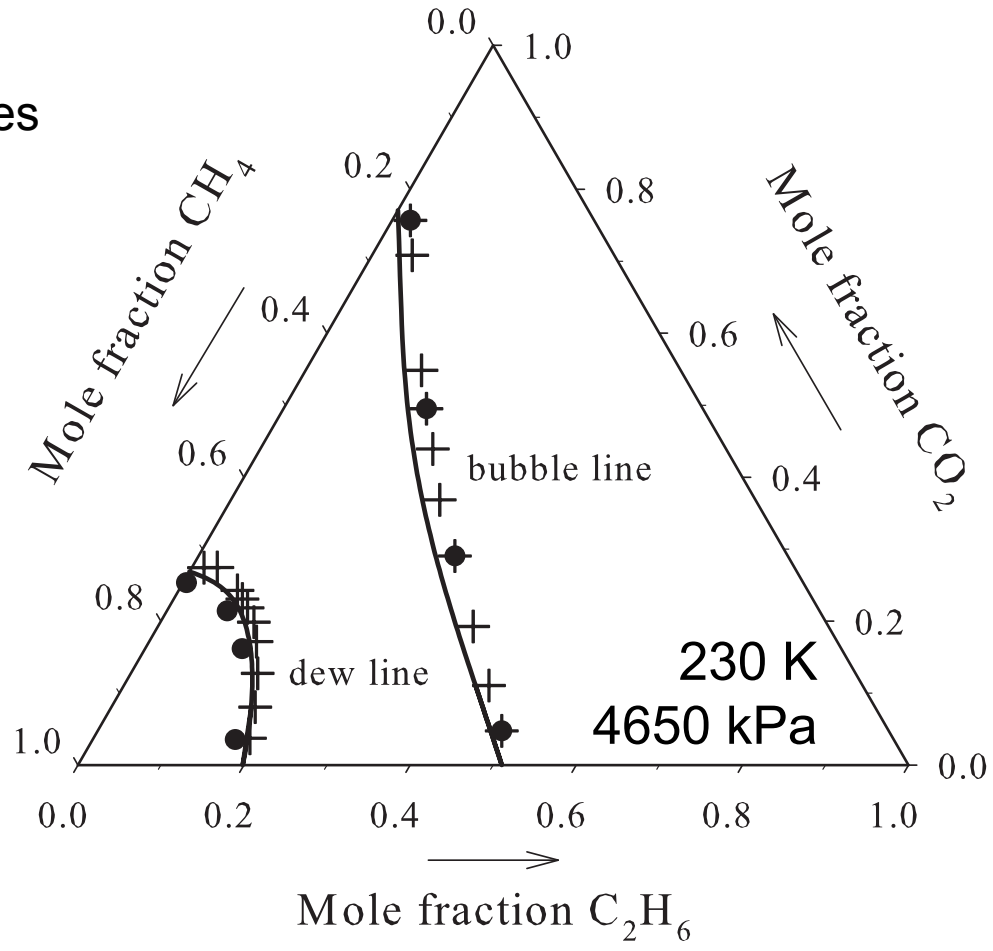
+ experimental data • simulation results

Molecular simulation of fluid mixtures

- Purely predictive electrostatics
- LJ parameters from combination rules

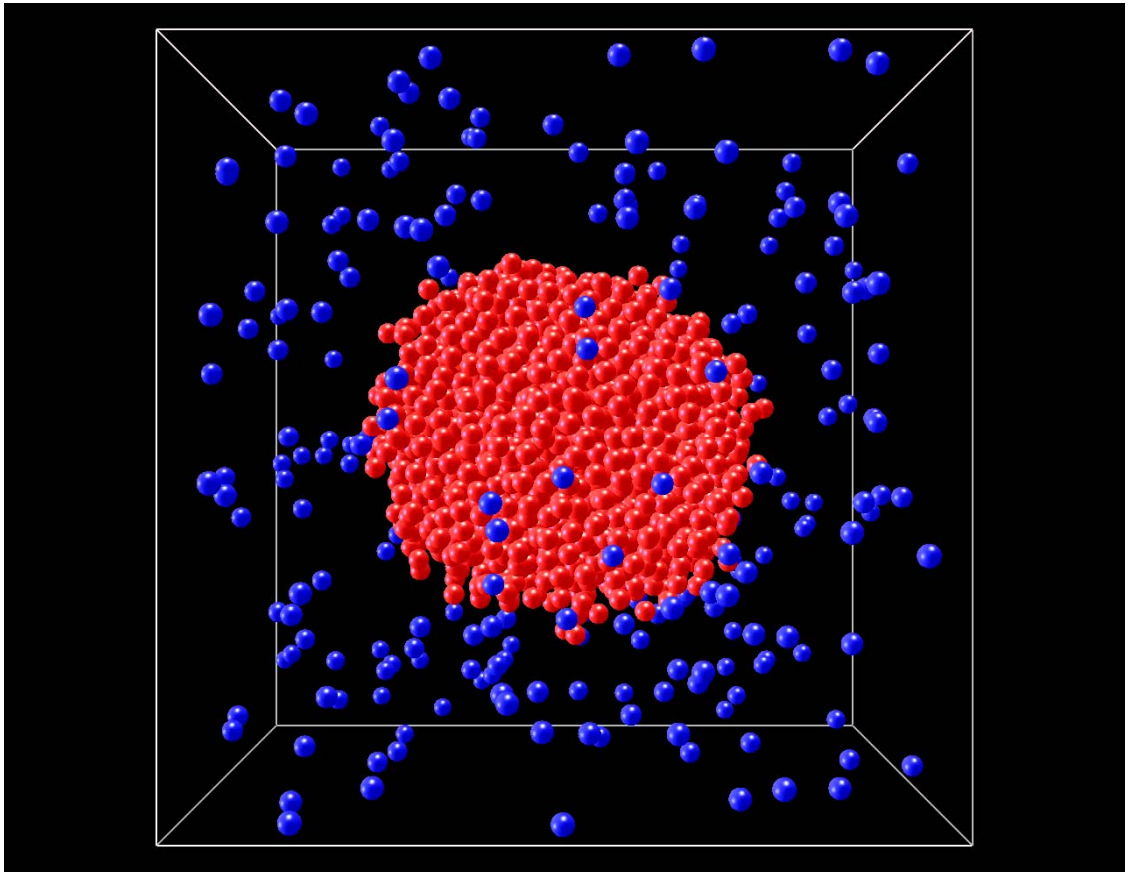


adjustment to a single experimental value
$p(T, \underline{x})$ or $\Delta h^v(T)$



MD simulation of a single droplet

- Vapor and liquid are equilibrated separately
- A small (n < 10000) droplet is inserted into the vapor
- If the droplet cannot evaporate completely, an equilibrium is established within a few nanoseconds

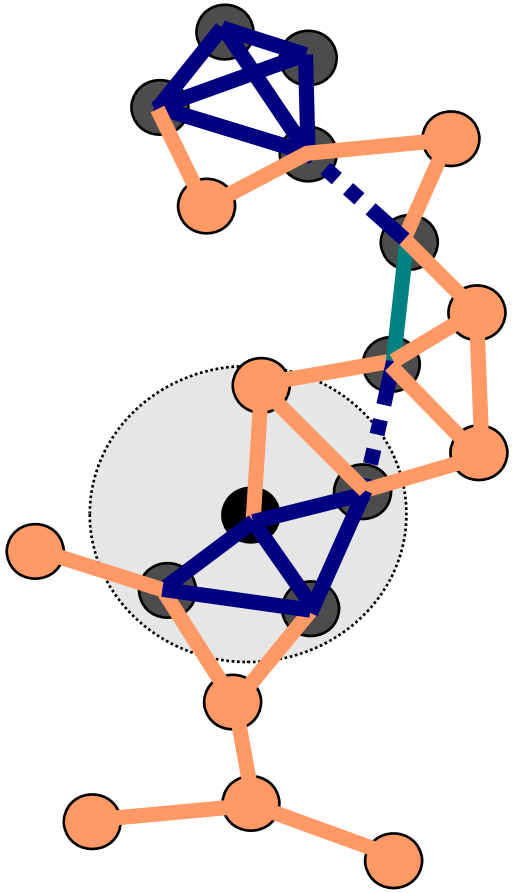


truncated-shifted LJ fluid (r_c = 2.5 σ)

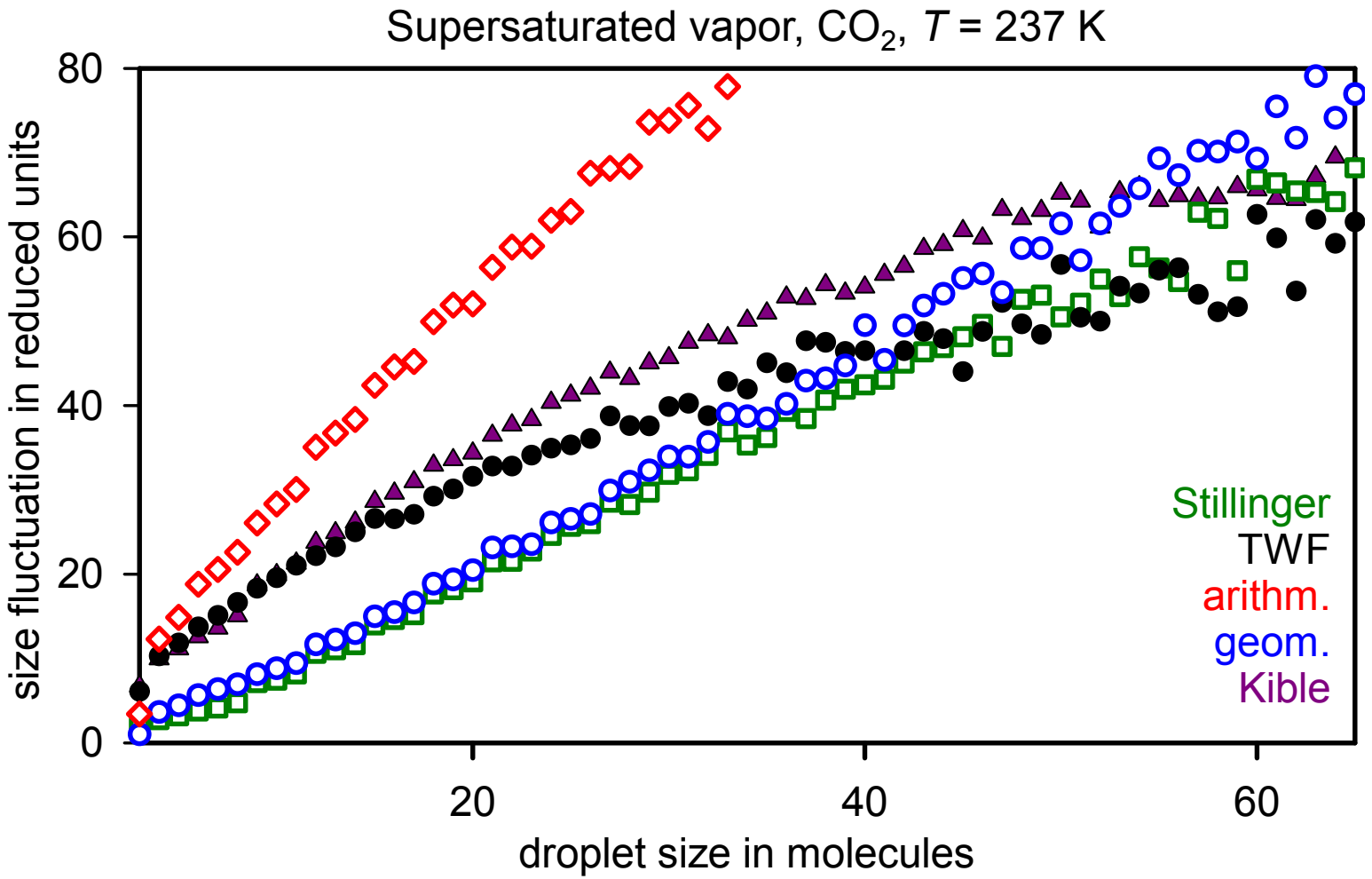
Vapor-liquid coexistence: Cluster criteria

Stillinger: molecules with a distance of 1.5σ or less are liquid.
Ten Wolde and Frenkel (TWF): molecules with at least four neighbors within a distance of 1.5σ are liquid.
Arithmetic mean, *n* neighbors (a_n): a molecule is liquid if the density in the sphere containing its *n* nearest neighbors exceeds $(\rho'+\rho'')/2$.
Geometric mean, *n* neighbors (g_n): analogous, the required density is $(\rho'\rho'')^{1/2}$.

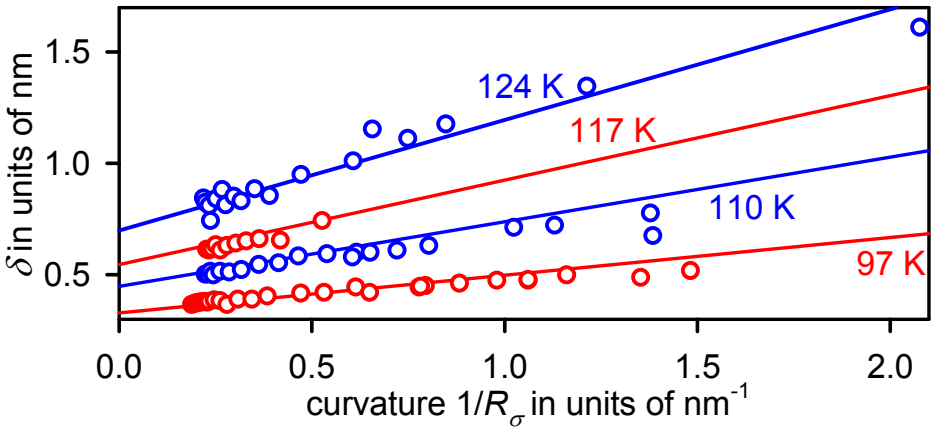
Nuclei can also be determined as **biconnected** (instead of connected) components, such that no nucleus can be separated by removing a single molecule (TWF' and g'_2 criteria).



Comparison of cluster criteria



Droplet interface properties



For small droplets, the Tolman length

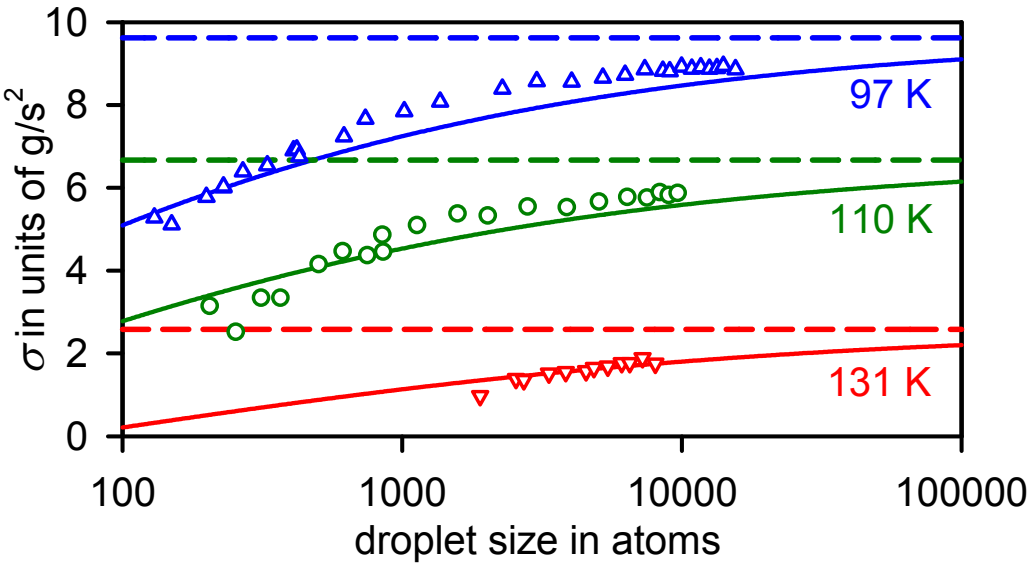
$$\delta = R_e - R_\sigma,$$

i.e. a characteristic interface thickness, increases significantly.

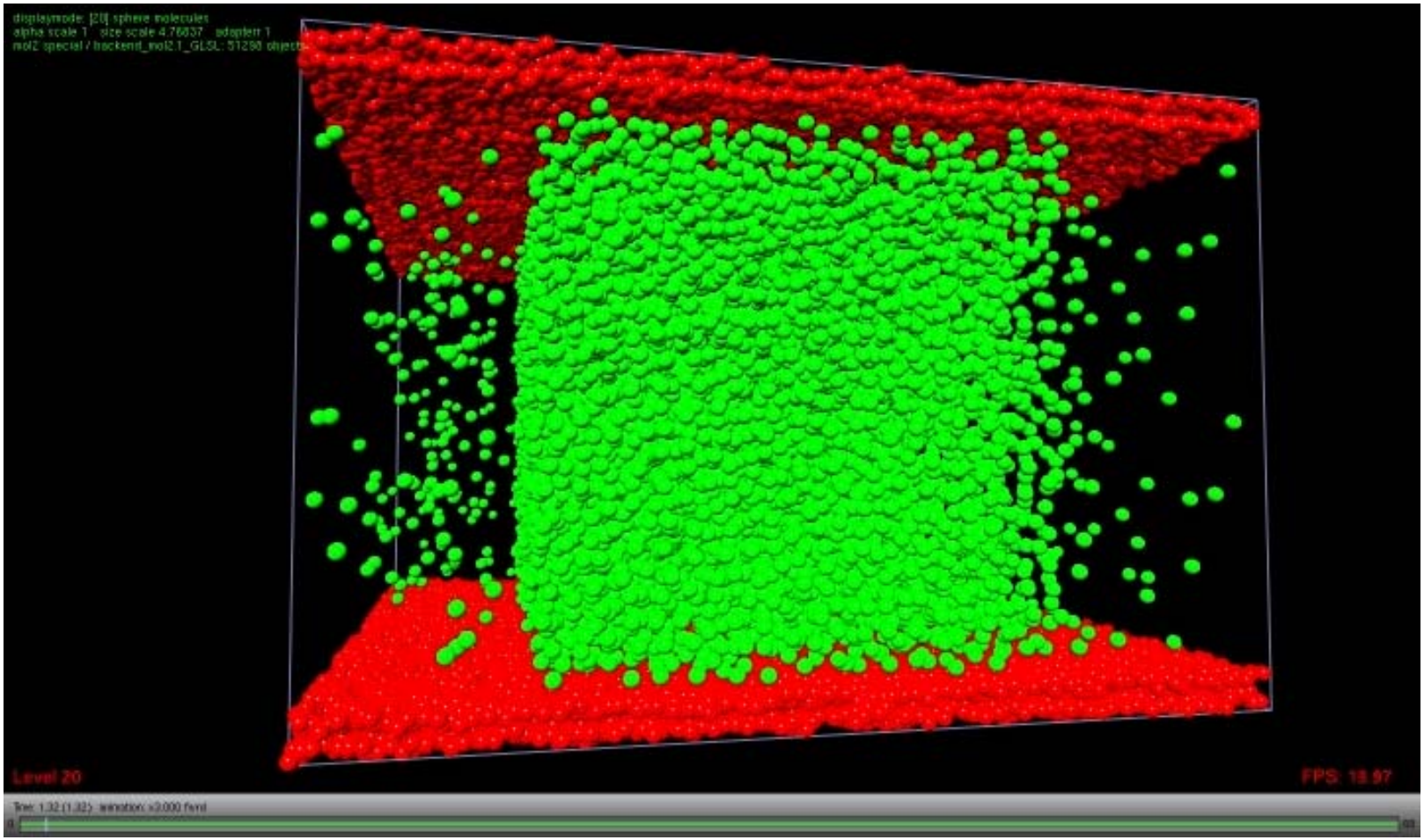
Surface tension (Tolman):

$$\frac{\sigma_\infty}{\sigma} \approx \frac{R_e + \delta_\infty}{R_e - \delta_\infty}$$

- ● simulation
- — Tolman equation
- - - planar interface

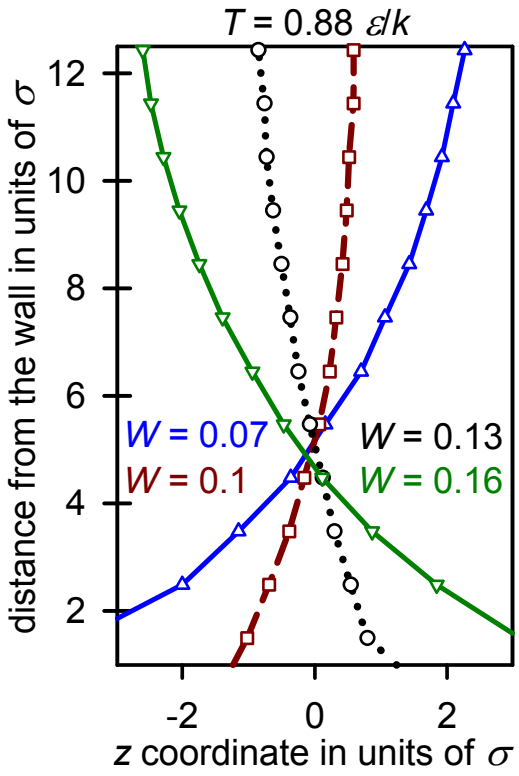


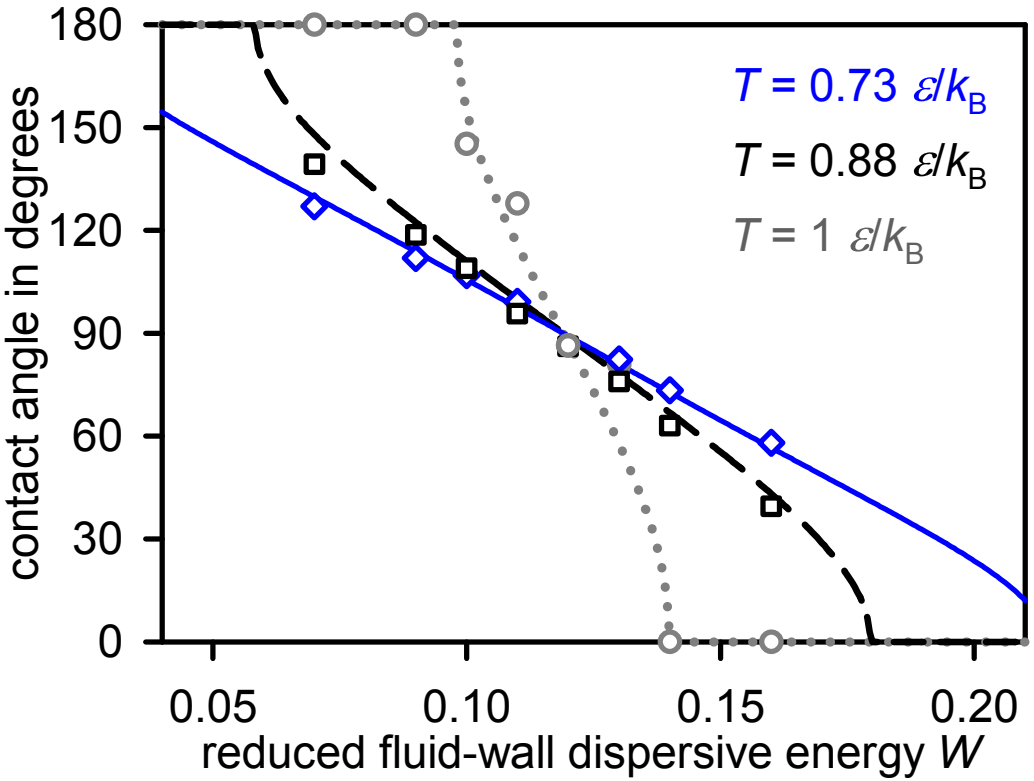
Contact angle: Simulation of a meniscus



Contact angle and fluid-wall dispersion

Methane meniscus (t. s. LJ fluid) between graphite walls





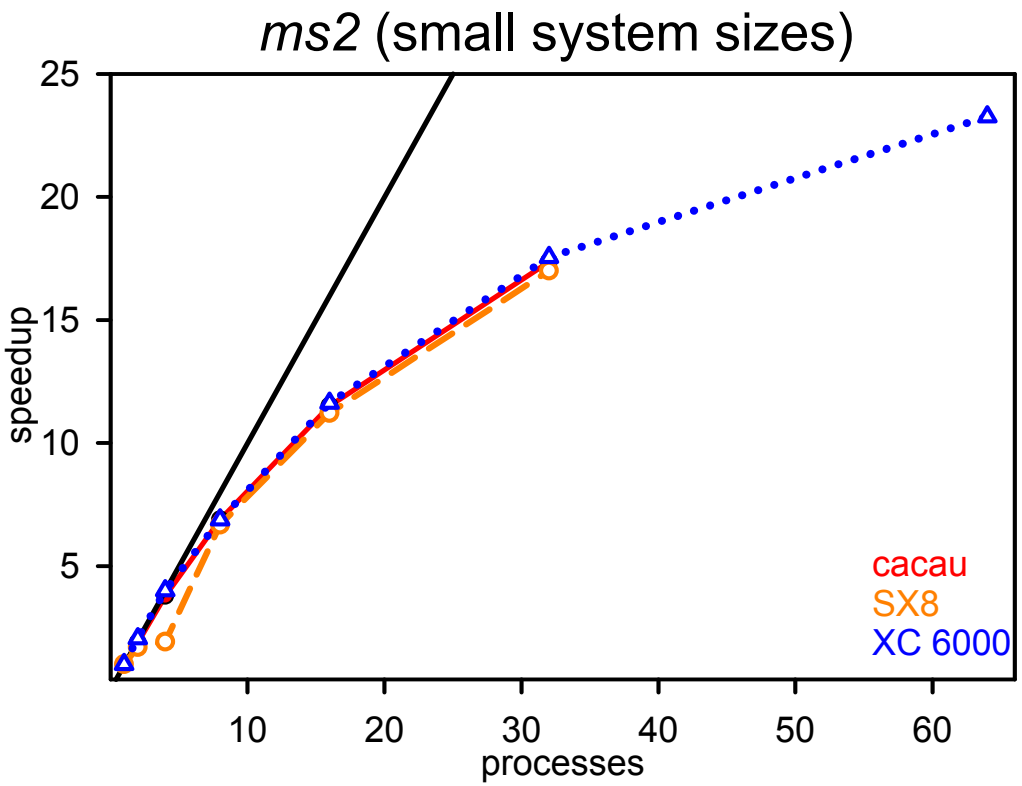
$$\cos\theta(T,E-\Delta W)=-\cos\theta(T,E+\Delta W)$$

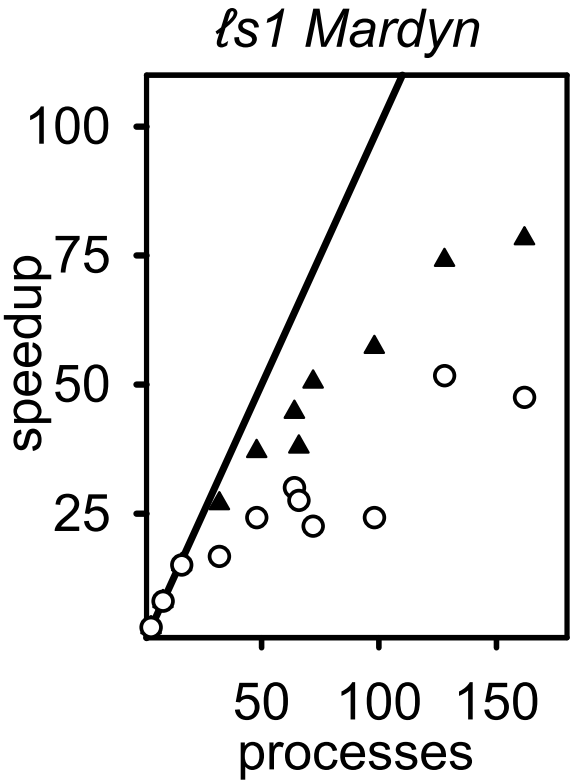
High performance computing


cacau


XC 6000


SX8





○ without load balancing
▲ static load balancing

Innovative HPC-Methoden und Einsatz für hochskalierbare Molekulare Simulation (IMEMO)

Bundesministerium
für Bildung
und Forschung

Project scheduled from
October 2008 to December 2011

Project associates:

HLRS

Technische Universität
Kaiserslautern

UNIVERSITÄT PADERBORN
Die Universität der Informationsgesellschaft

TUM

FhG

Industrial associates:

BASF
The Chemical Company

Bayer

EVONIK
INDUSTRIES

IBM

Conclusion

Molecular simulation for process engineering …

- is already applied in the industry
- raises high expectations
- is a common endeavor of engineers, natural scientists, and computer scientists
- relies on HPC: Hardware, software, and algorithms