TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

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

Molecular thermodynamics of fluids at interfaces

Martin Thomas Horsch

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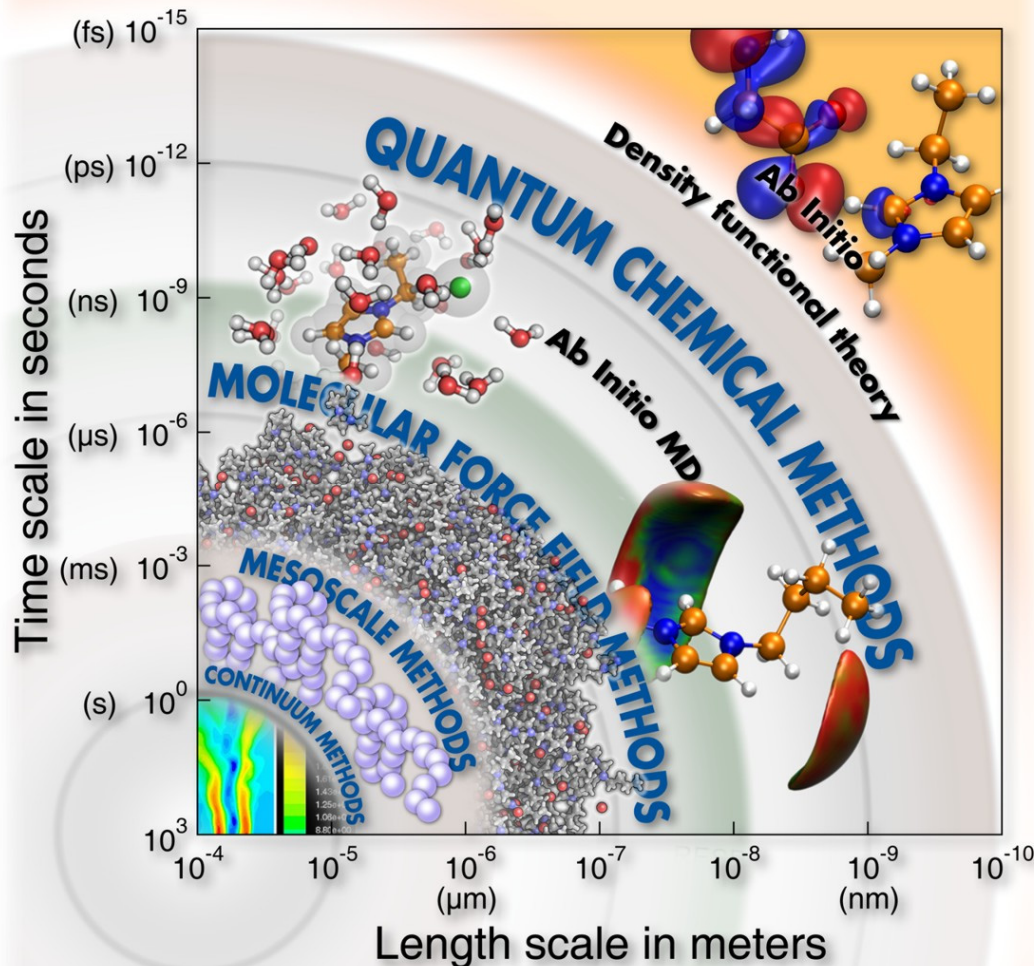
TU Kaiserslautern

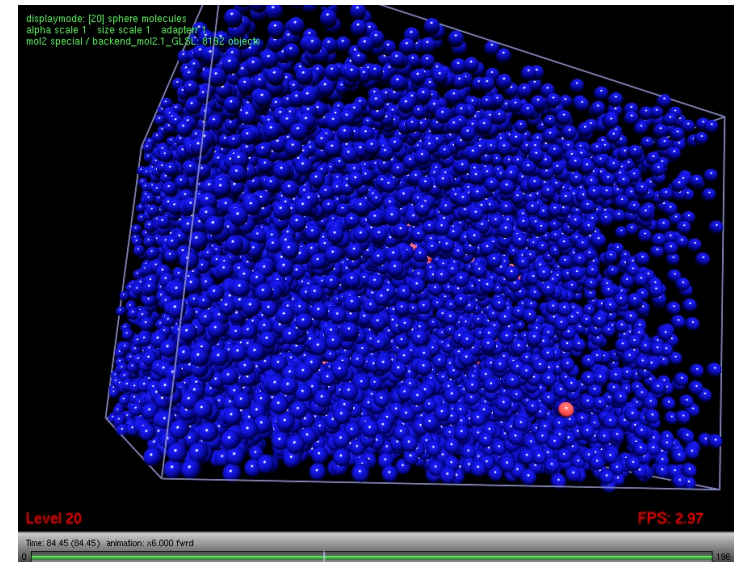DFH / UFA Workshop, 5th November 2012
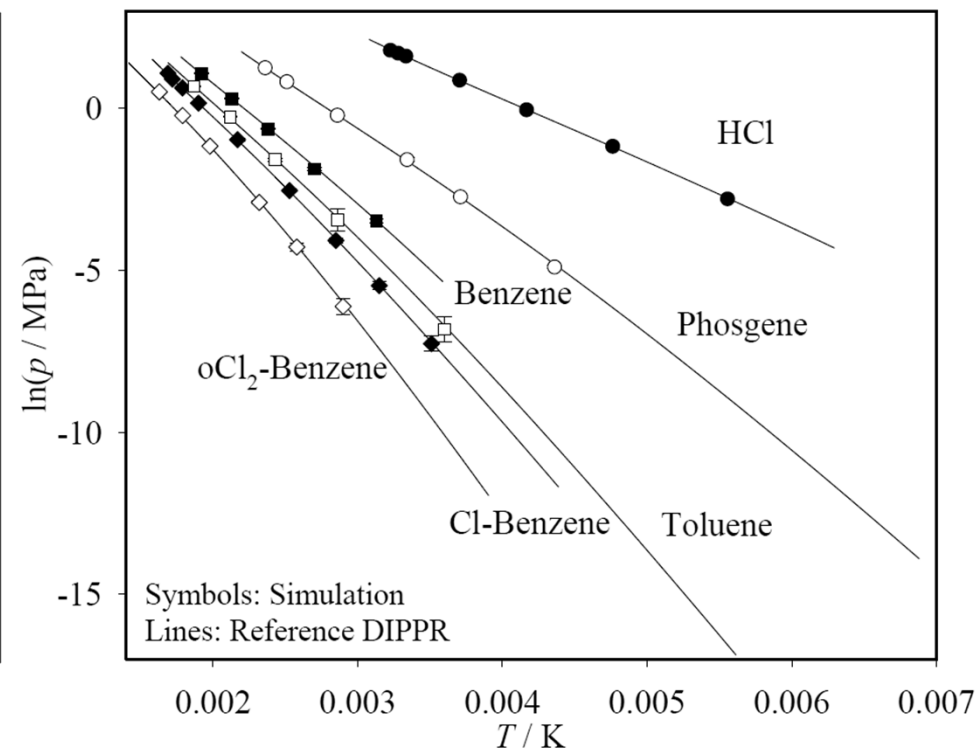
Computational
Molecular Engineering

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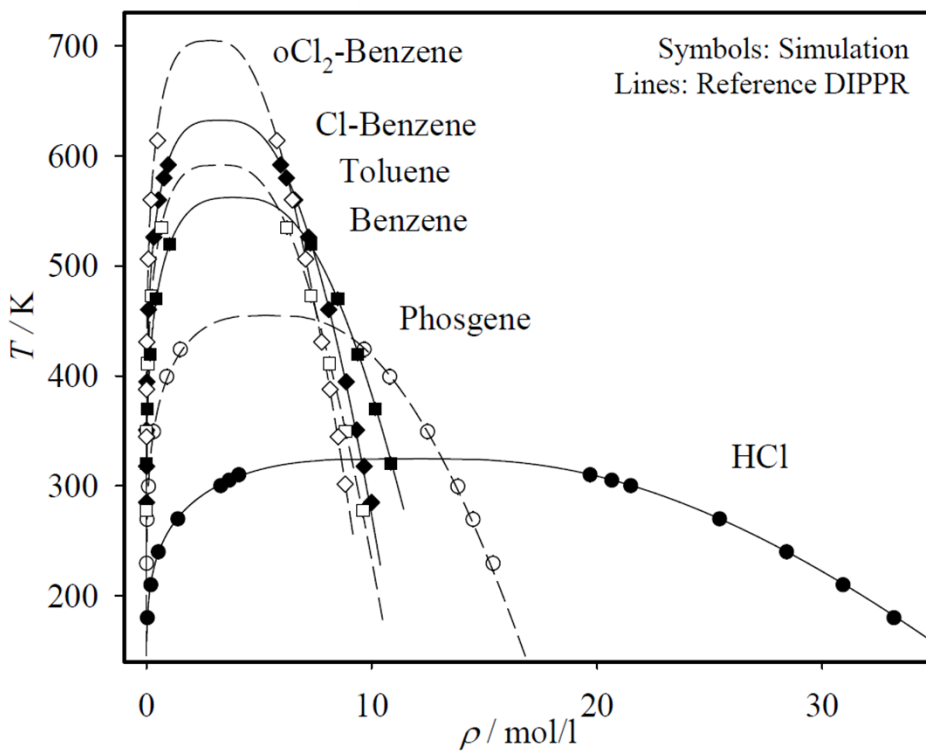Lehrstuhl für Thermodynamik
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Molecular force field methods

- Classical force fields

- From nano- to microscale

- Molecular-level precision

- Quantitative reliability

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Molecular modelling of real fluids

Approach: Lennard-Jones (dispersion, repulsion) + point charges/multipoles

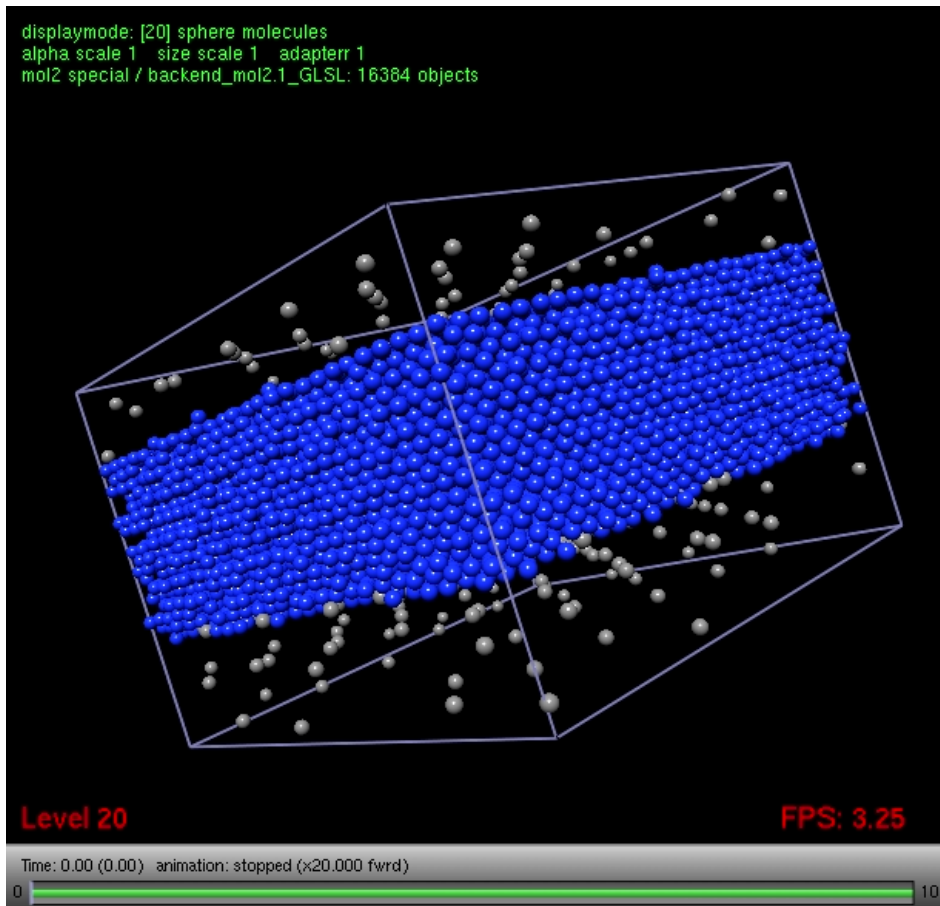High accuracy for interfacial and transport properties, for mixtures, etc.

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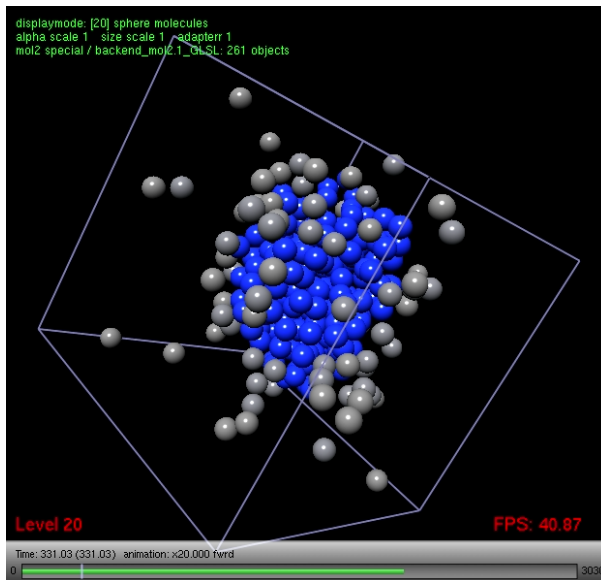# Fluid interfaces at molecular resolution

Argon at T = -150.6 °C

- For the density and other fluid properties, continuous profiles across the interface are obtained.

- The interfacial thickness typically is on the Å to nm length scale. However, it diverges at $T \to T_c$.

- Fluctuations, capillary waves, and configurations away from mechanical equilibrium occur.

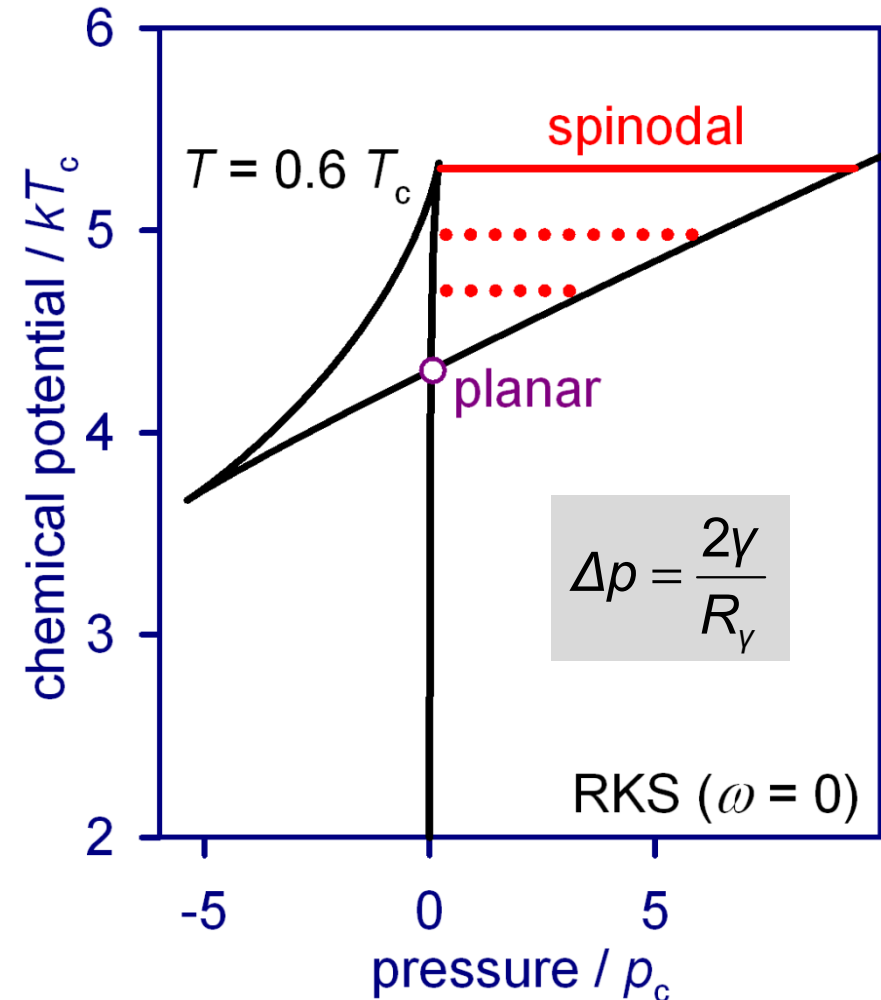- Finite size effects: Nanoscale liquid slabs have a lower density and surface tension.

Spherical vapour-liquid interfaces
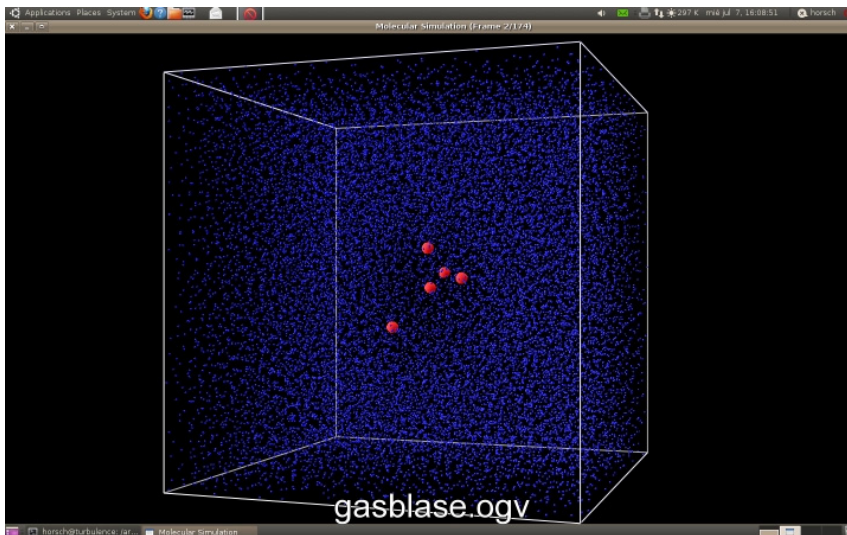
- Droplet + metastable vapour

Spinodal limit: For the external phase, metastability breaks down.

$$\Delta p = \frac{2\gamma}{R_\gamma}$$

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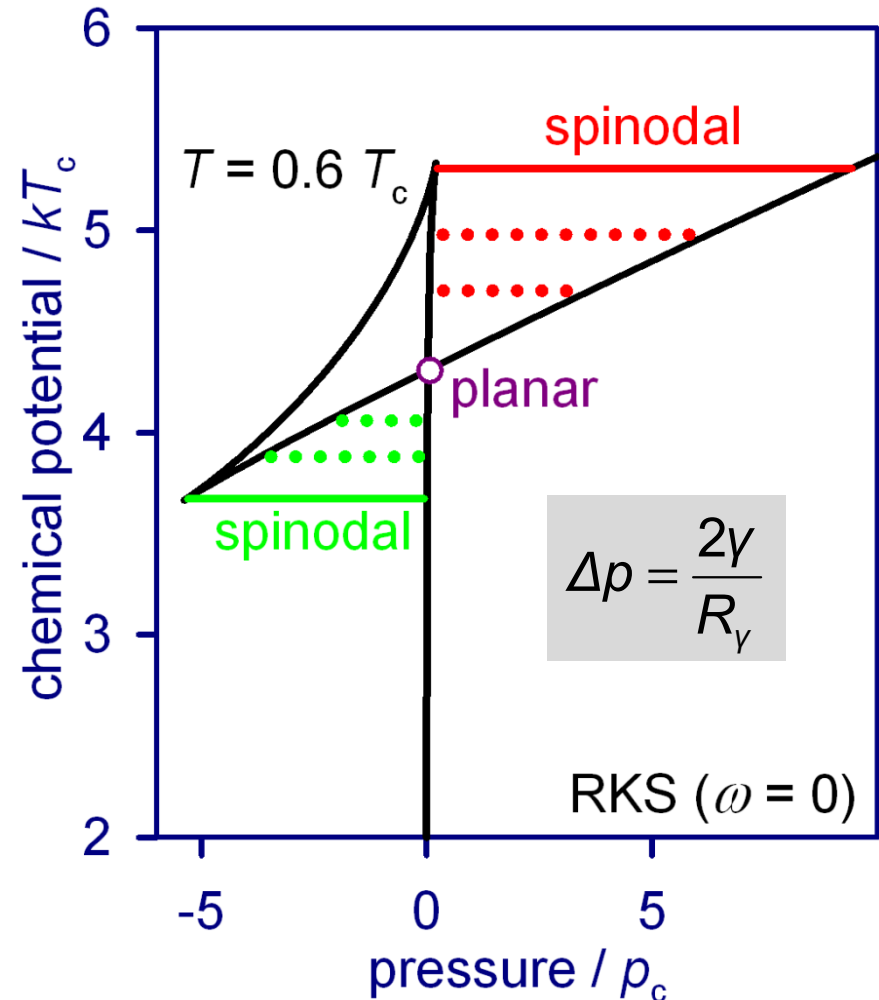Lehrstuhl für Thermodynamik
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Spherical vapour-liquid interfaces

- Droplet + metastable vapour
- Bubble + metastable liquid

Spinodal limit: For the external phase, metastability breaks down.
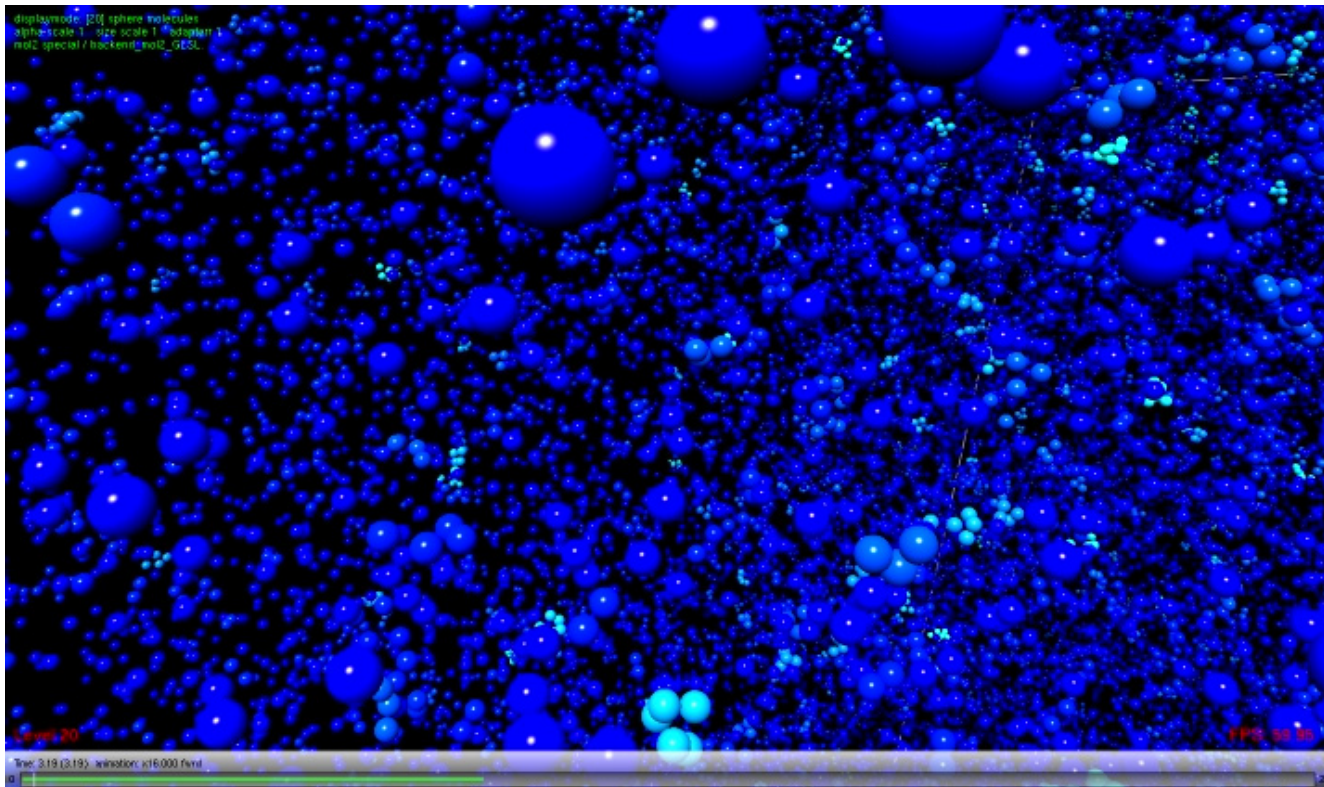
Planar limit: The curvature changes its sign and the radius R_γ diverges.

$$\Delta p = \frac{2\gamma}{R_\gamma}$$

Non-equilibrium molecular dynamics

By molecular-level interventions (of a Maxwell dæmon) a non-equilibrium state is stabilized, and the relaxation rate of the system can be computed.
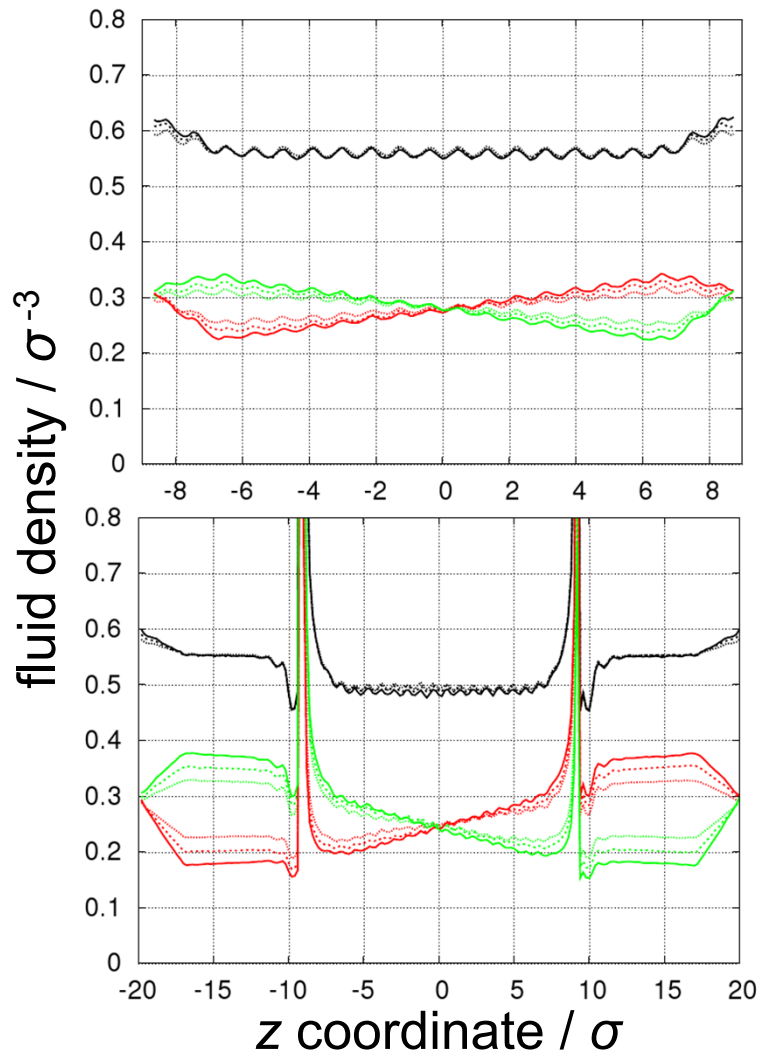

Scenario:

Nucleation in a supersaturated vapour

Interventions of McDonald's dæmon remove sufficiently large droplets.
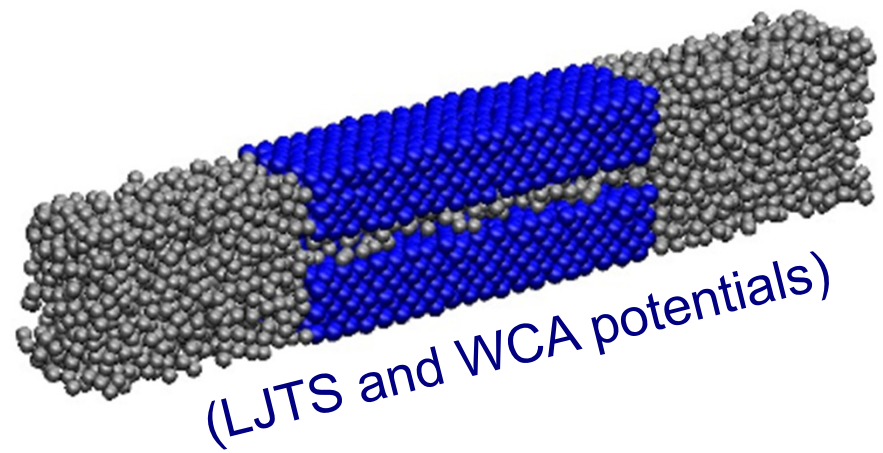
The nucleation rate is computed.

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Pore permeability (Avendaño's dæmon)

By comparison between fluxes in

- an infinite (i.e. periodic) channel

- an "open" system including a bulk section …
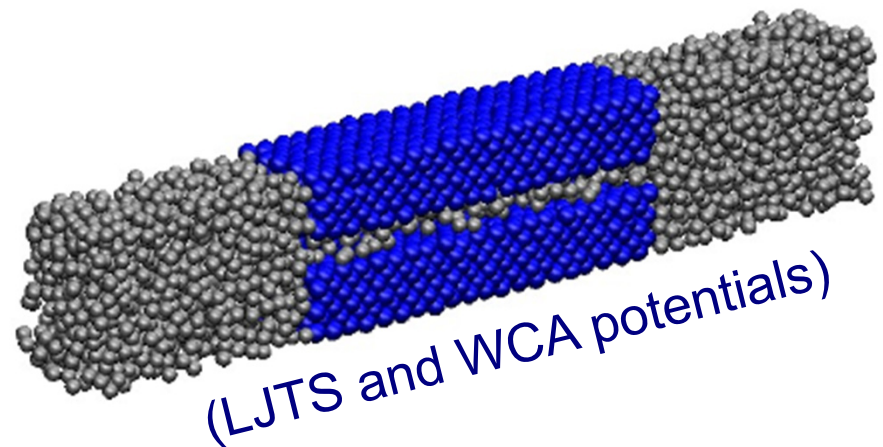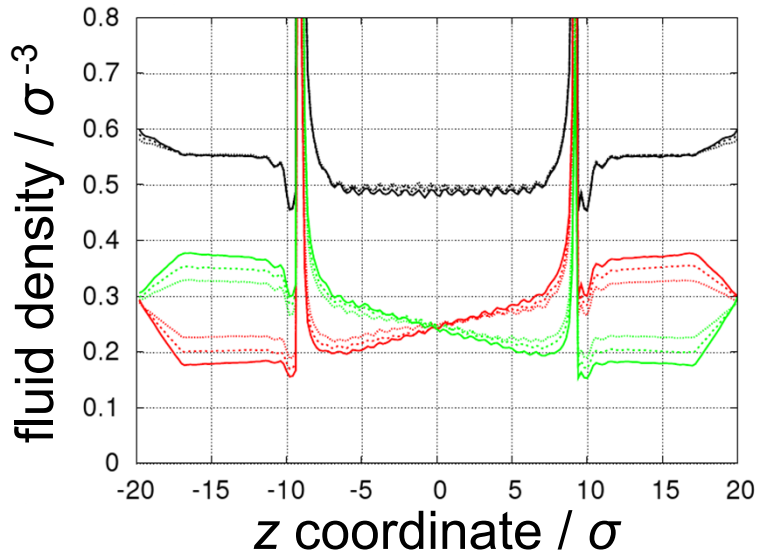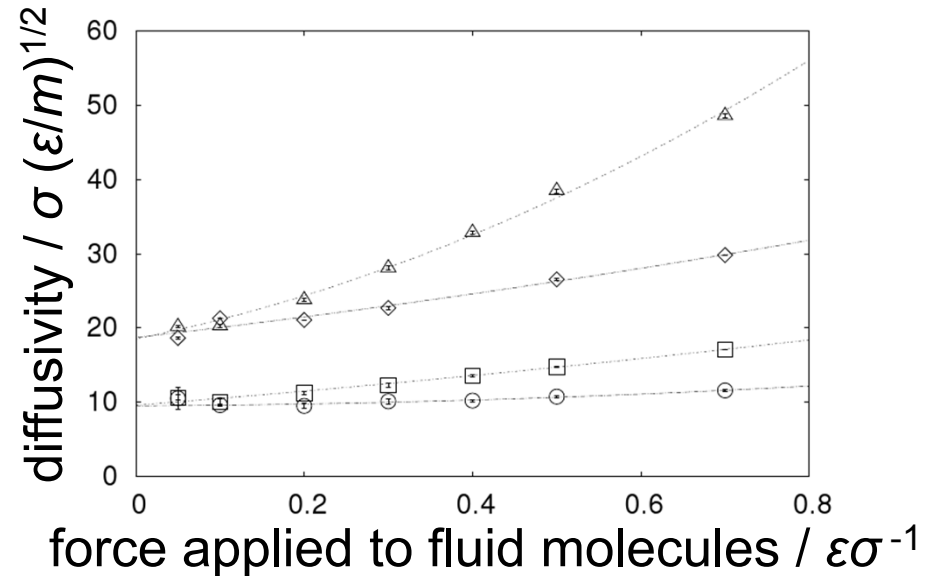
… the influence of the channel entrance and exit regions on the overall effective diffusivity can be isolated.

(LJTS and WCA potentials)

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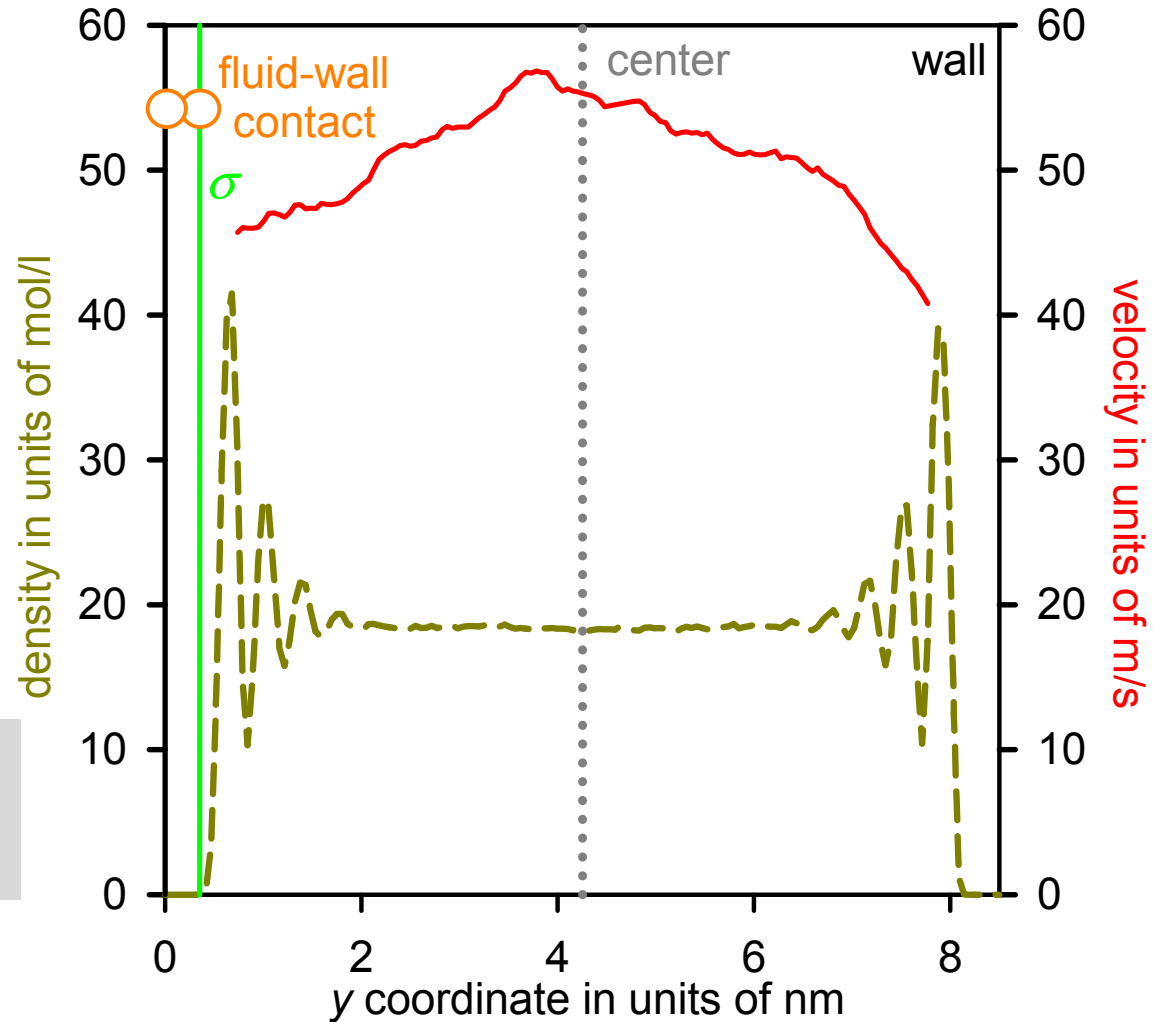Lehrstuhl für Thermodynamik
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Effective diffusivity

Diffusivities are obtained as linear response coefficients, i.e. in the limit where the accelerating force, which perturbs the equilibrium state of the system, approaches zero

(LJTS and WCA potentials)

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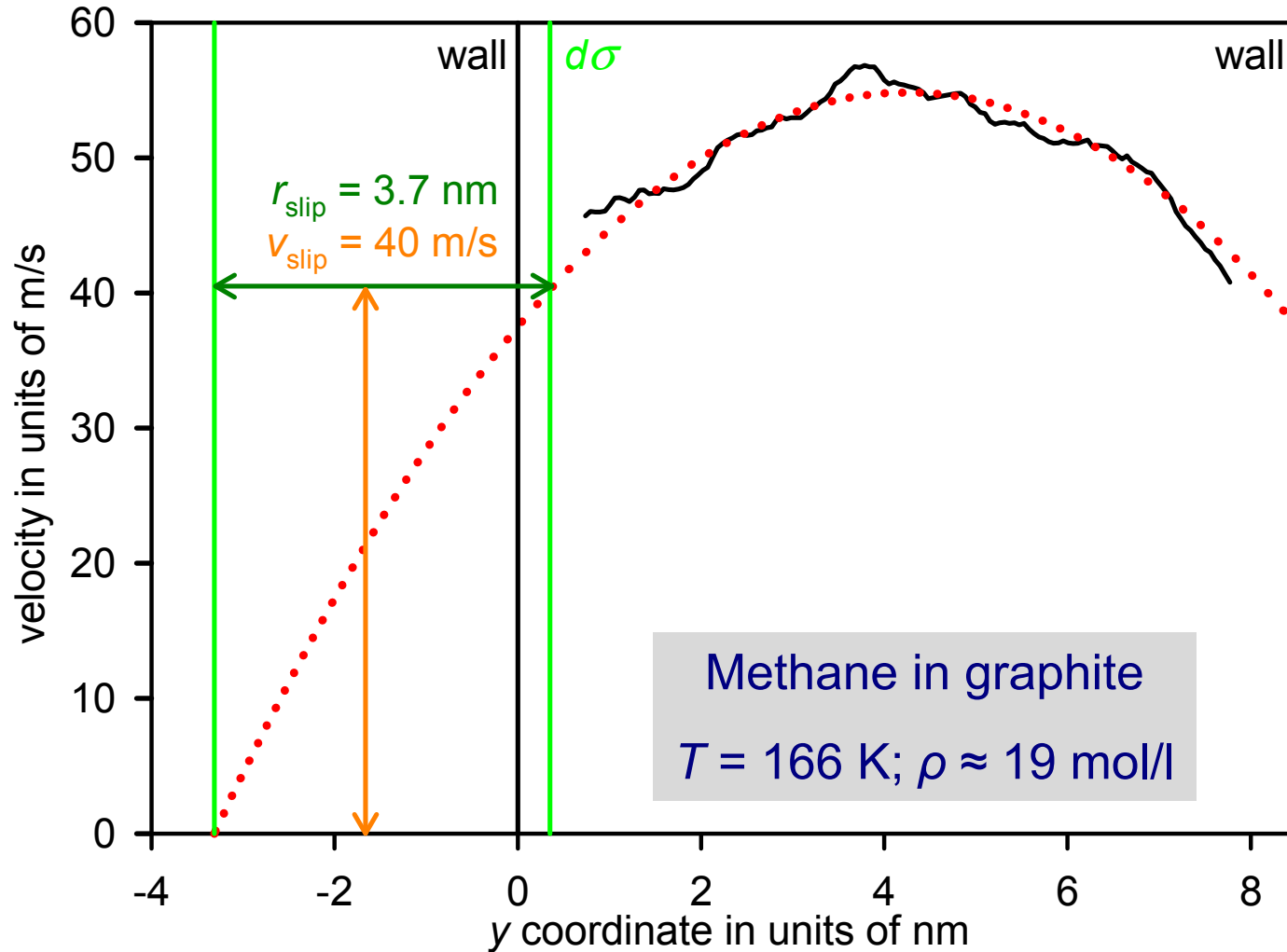KAISERSLAUTERN

Velocity profile and boundary slip

Methane in graphite

T = 166 K

Velocity profile and boundary slip

Conclusion

- High accuracy and predictive capacity of the employed molecular models and simulation methods

- Experimental data on the vapour-liquid coexistence in equilibrium are accurately reproduced, and the structure of fluid interfaces is resolved at molecular level precision.

- Non-equilibrium molecular dynamics simulation permits the analysis of complex and coupled transport processes, even beyond the linear response regime, on the basis of the intermolecular interactions.

- Extremely wide spectrum of possible applications within mechanical and process engineering (focus on fluid systems)

- Massively parallel molecular dynamics promises to make a molecular analysis of microfluidics feasible within the present decade.