Thermodynamic properties of ammonia by molecular simulation

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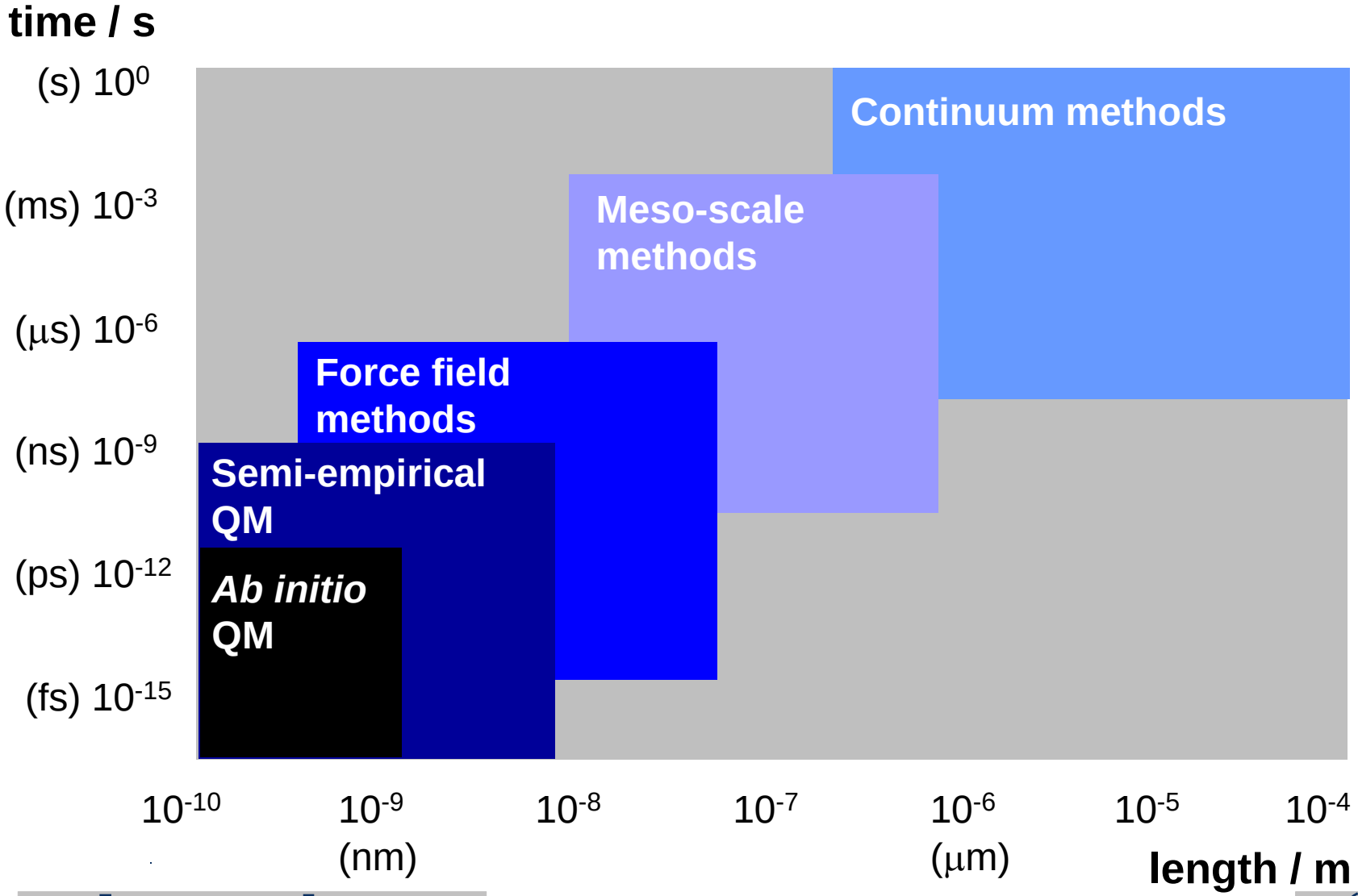
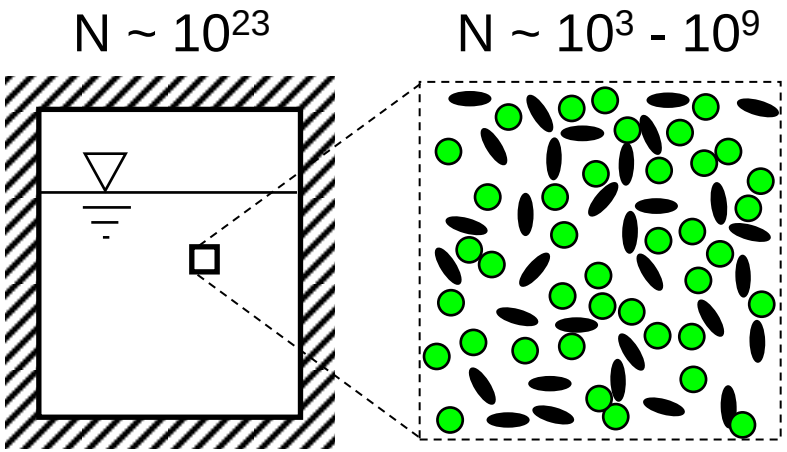
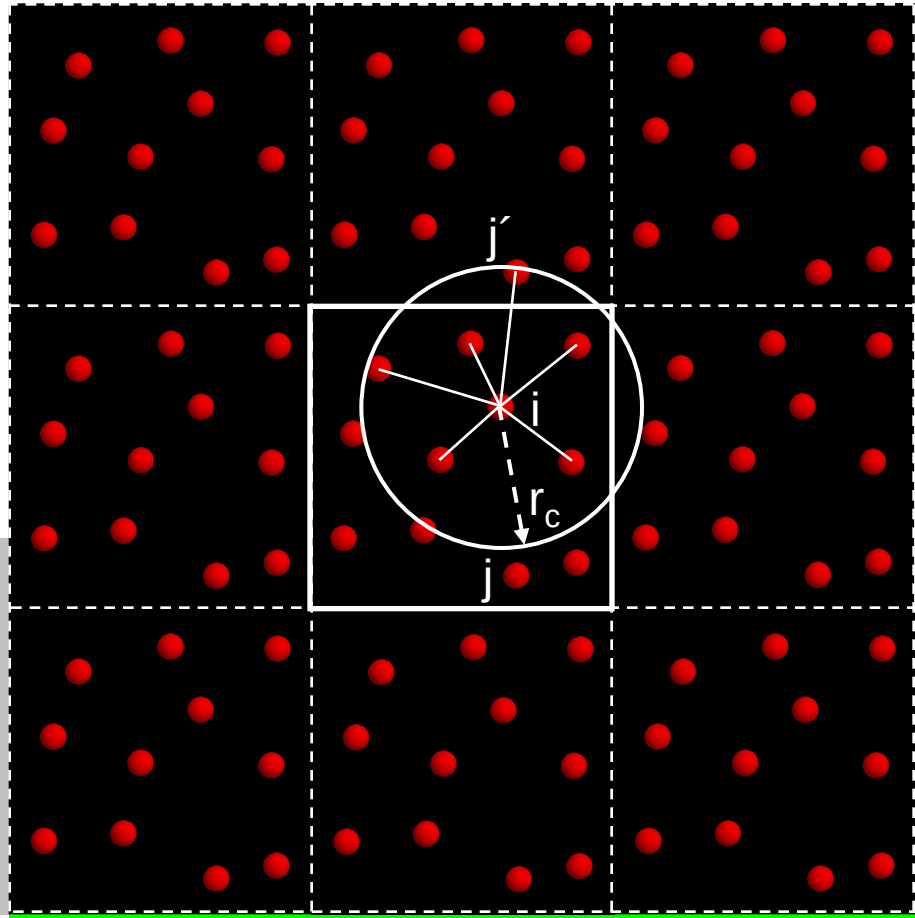
Overview on numerical methods



Molecular Simulation – Basic Idea





- Assumption of a force field u
- Explicit calculation of all interactions within r_C
- Corrections for $r > r_C$

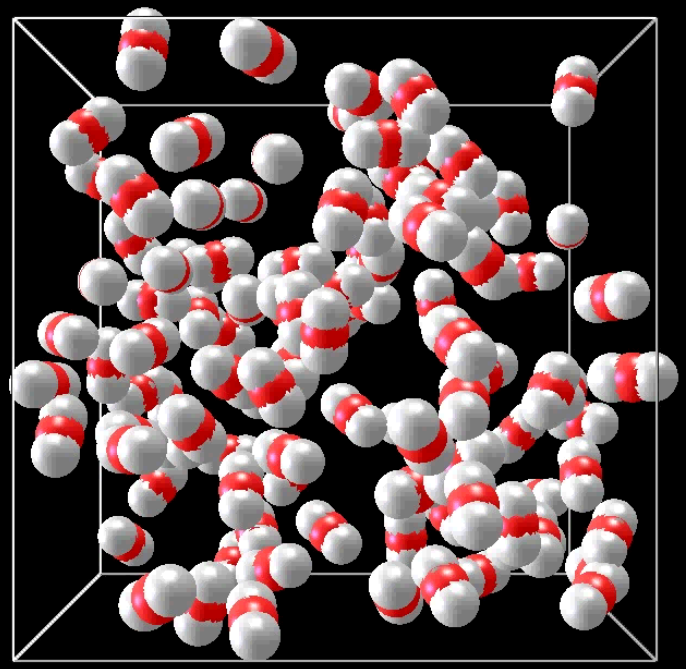
$$U = \left\langle \sum_{\substack{i<j \\ r<r_C}} u(\mathbf{r}_{ij}) \right\rangle + \frac{N\rho}{2} \int_{r_c}^{\infty} dV \cdot u(\mathbf{r})$$

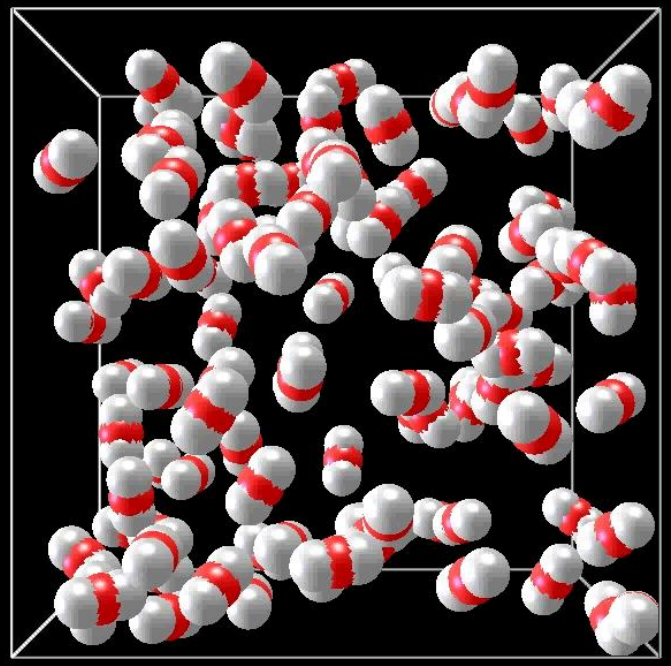
- Periodic boundary condition
- Minimum-image convention
- Cut-off radius r_C

Molecular simulation

- Molecular dynamics (MD)
  - deterministic system
  - static and dynamic properties
  - straightforwardly applicable to non-equilibria

- Monte-Carlo (MC)
  - statistical approach
  - energetic acceptance criteria
  - only static properties



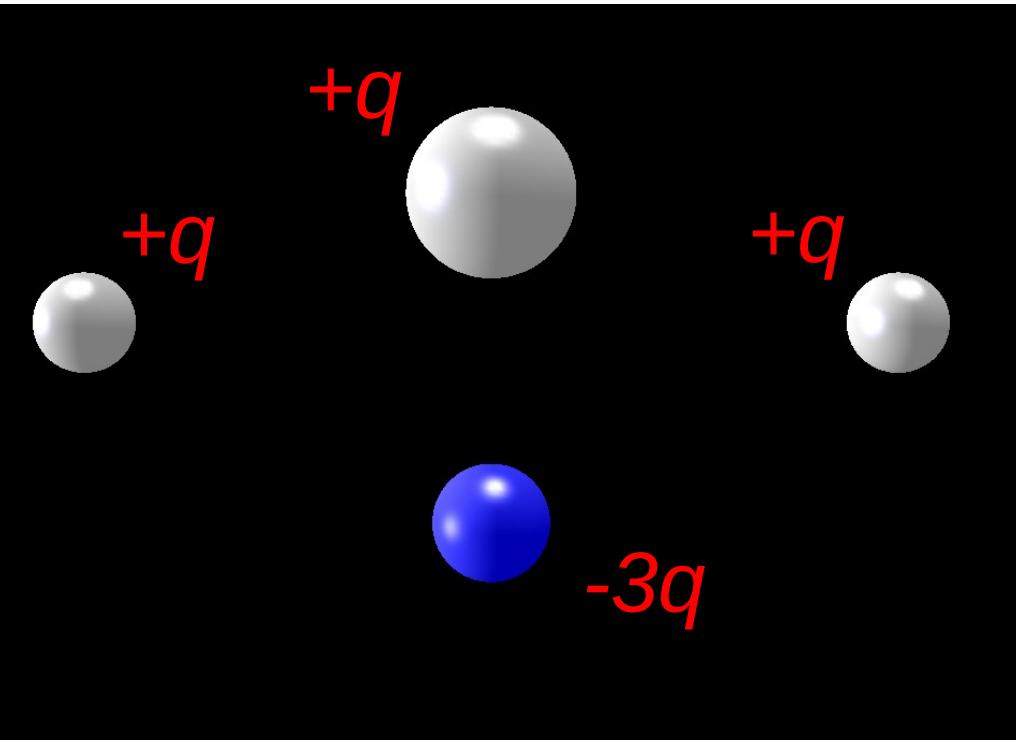


Thermodynamics with molecular approach

- Models of intermolecular interactions
  - Parameters can physically be interpreted
- Contain all thermodynamic properties
  - Static: thermal, caloric, entropic
  - Dynamic: viscosity, diffusion, thermal conductivity, …
  - Surface properties, e.g. surface tension
- Mixture properties well accessible
- Strong predictive and extrapolative capabilities
- Technical accuracies achievable

- Directly applicable to investigate fluid properties
  - in geometries, e.g. adsorption, zeolites, …
  - in dynamic processes, e.g. condensation, flow, …

Molecular models for intermolecular interactions



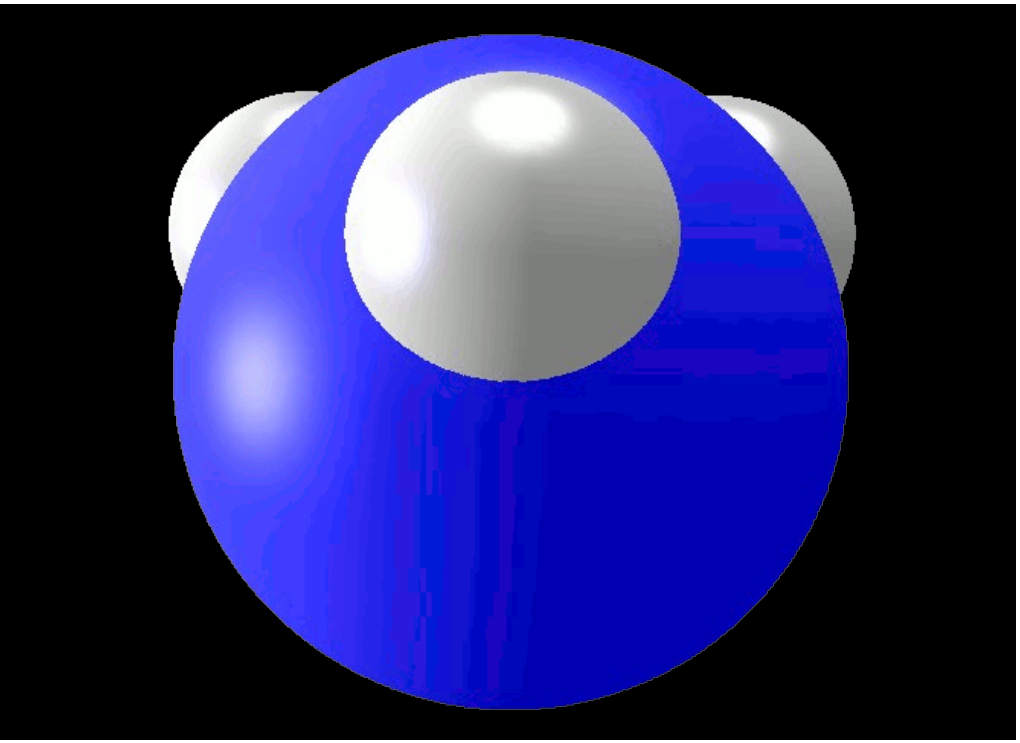
Geometry

- Bond lengths and angles

Electrostatics

- Magnitude of point charges

Molecular models for intermolecular interactions



Geometry

- Bond lengths and angles

Electrostatics

- Magnitude of point charges

Dispersion and repulsion

- Parameters e.g. of Lennard-Jones sites

Potentially, a large number of parameters

Molecular properties from quantum chemistry

Geometry

- Hartree-Fock with small basis set (e.g. 6-31G) or DFT methods

Electrostatics from electron density distribution

- Møller-Plesset2 with medium, polarizable basis set (e.g. 6-311+G**)
- Embedded in a dielectric cavity (COSMO) to account for a liquid (dense) phase

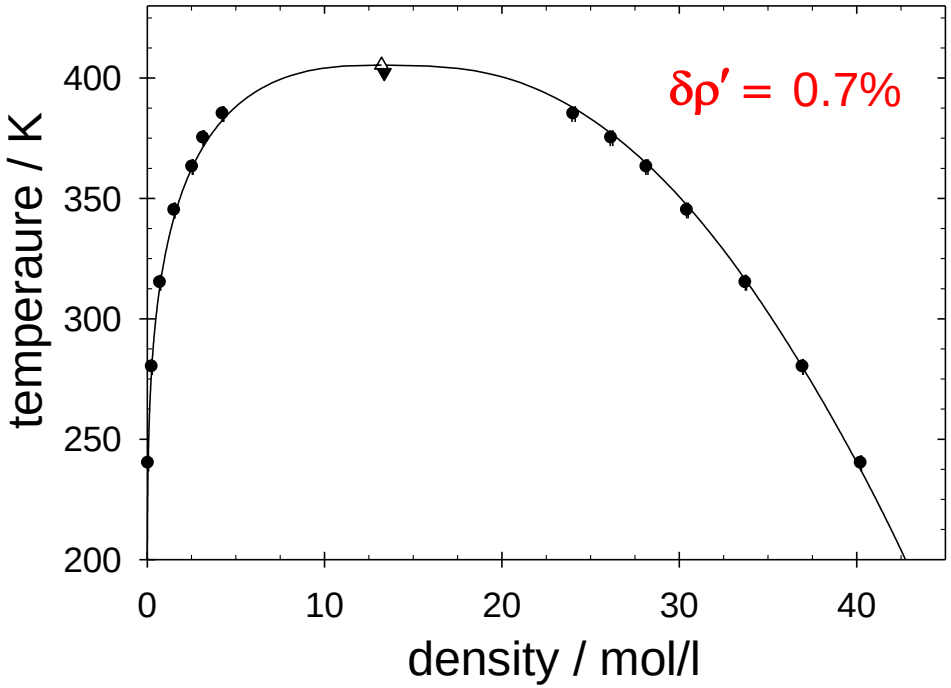
Dispersion and repulsion

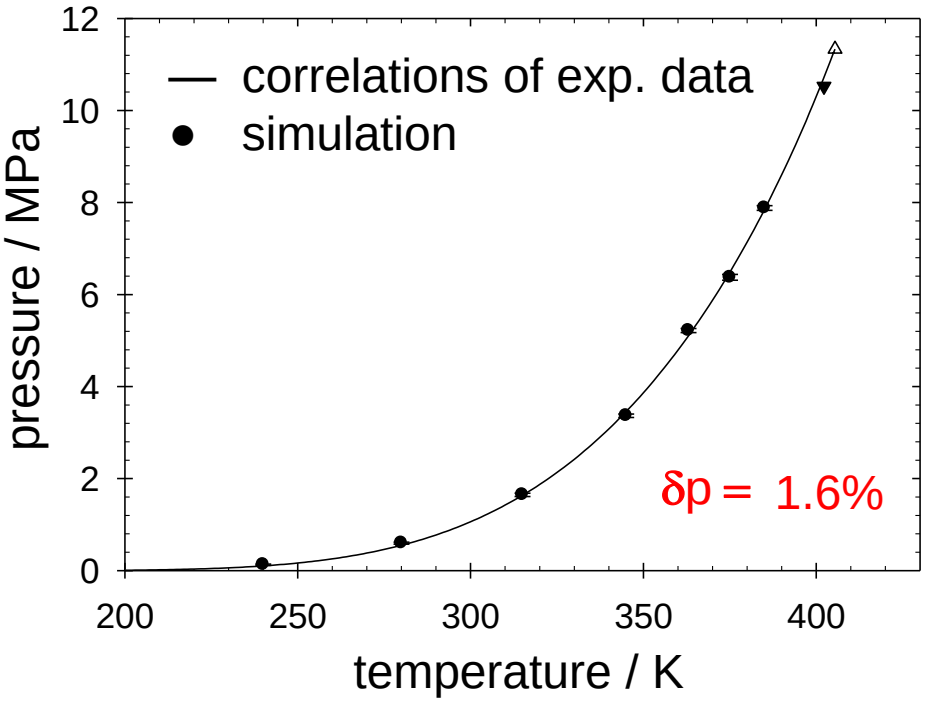
- At least dimers have to be regarded
- CCSD(T) or Møller-Plesset2 with large basis set (TZV or QZV)
- Large computational effort due to large basis set and accurate electron correlation

Better to be optimized to VLE data

Adjustment to experimental VLE data

- 2 Lennard-Jones parameters optimized to saturated liquid density and vapor pressure
- Optimization result:





Parameters of the ammonia model

Site	x Å	y Å	z Å	σ Å	ε/k_B K	q e
N	0	0	0.0757	3.376	182.9	0.9993
H(1)	0.9347	0	0.3164	–	–	0.3331
H(2)	0.4673	0.8095	0.3164	–	–	0.3331
H(3)	0.4673	0.8095	0.3164	–	–	0.3331

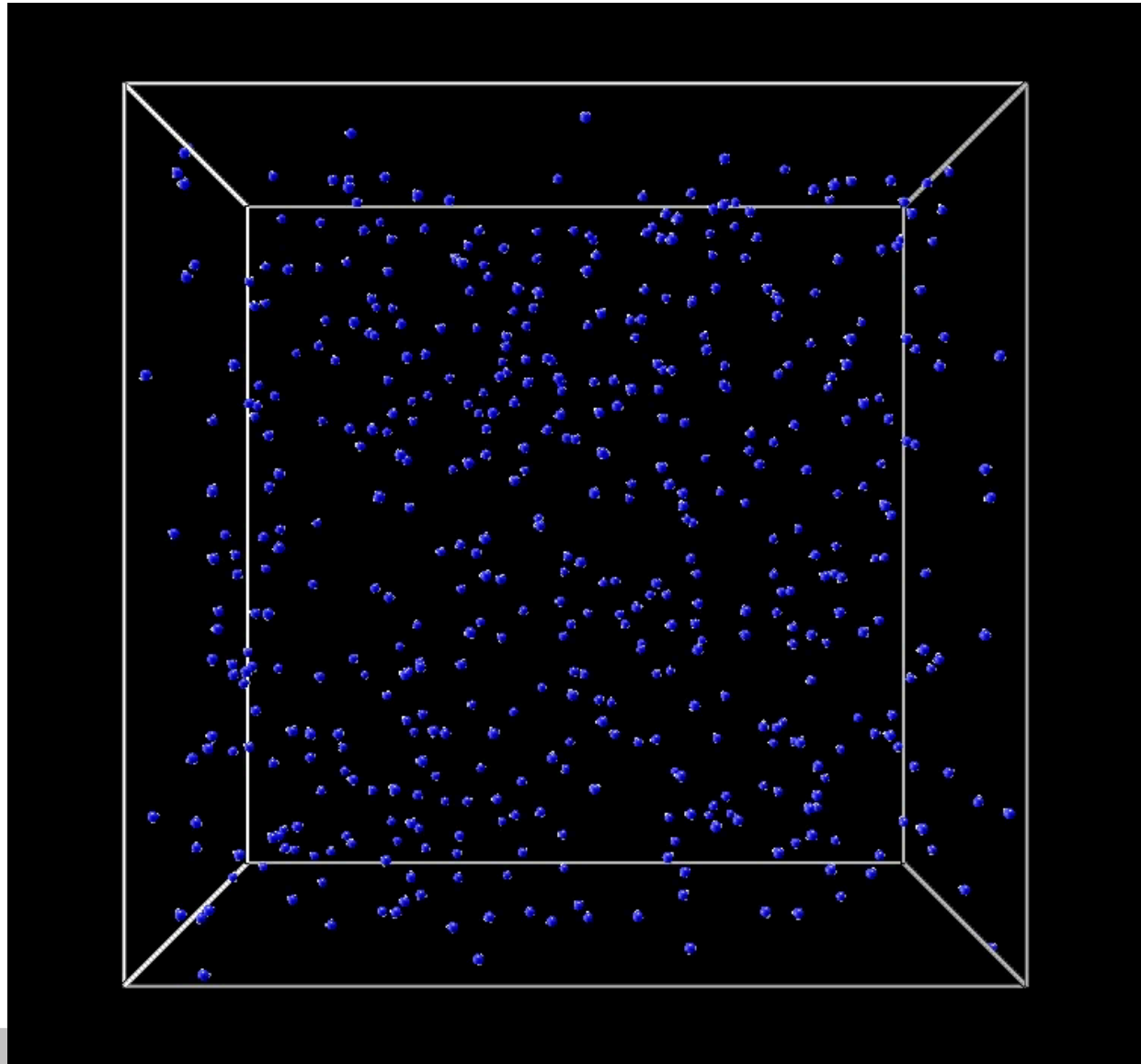
Five parameters

1 angle, 1 length, 1 charge magnitude
2 Lennard-Jones parameters

Molecular dynamics simulation (I)

Gas @

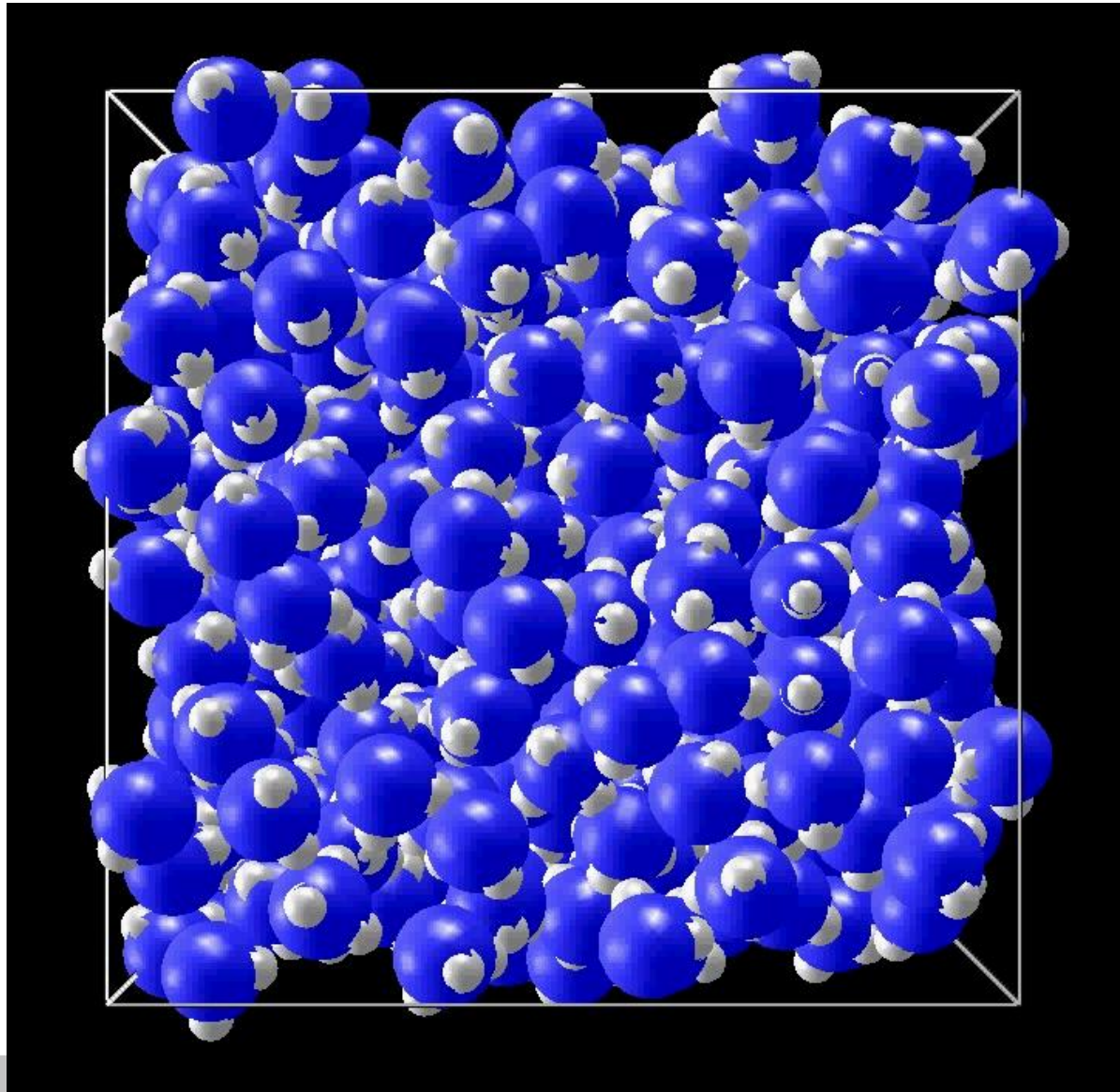
393 K and 0.1 MPa



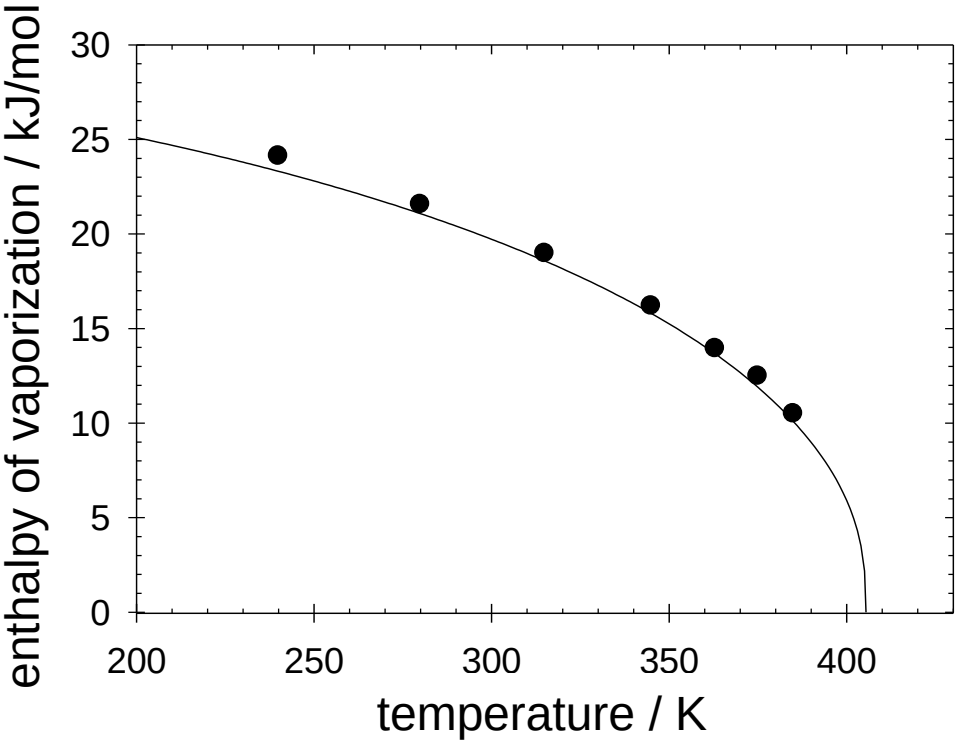
Molecular dynamics simulation (II)

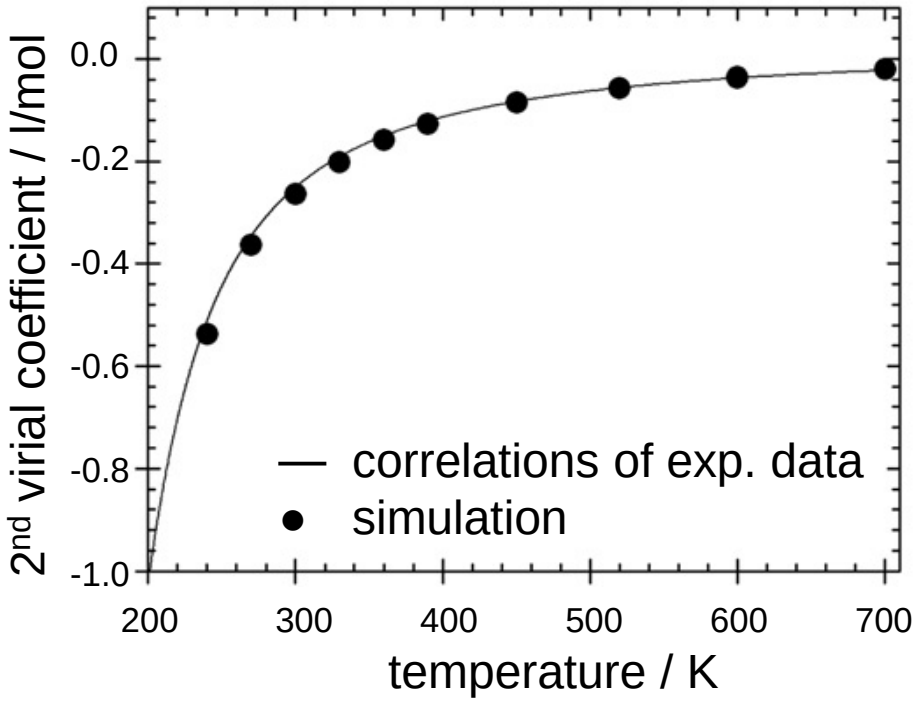
Liquid @

323 K and 3 MPa



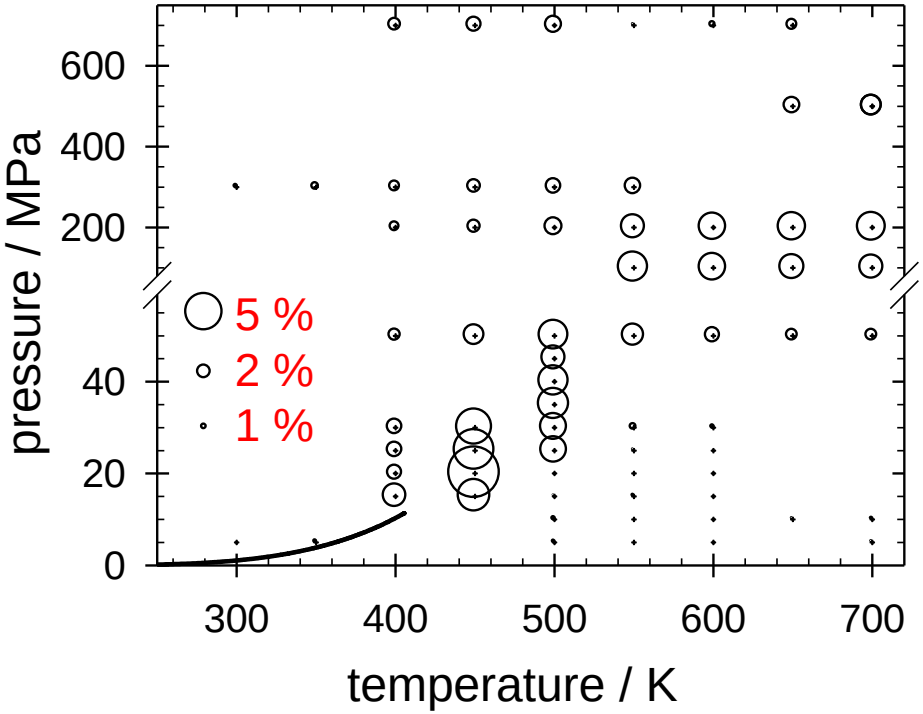
Prediction of second virial coefficient and enthalpy of vaporization



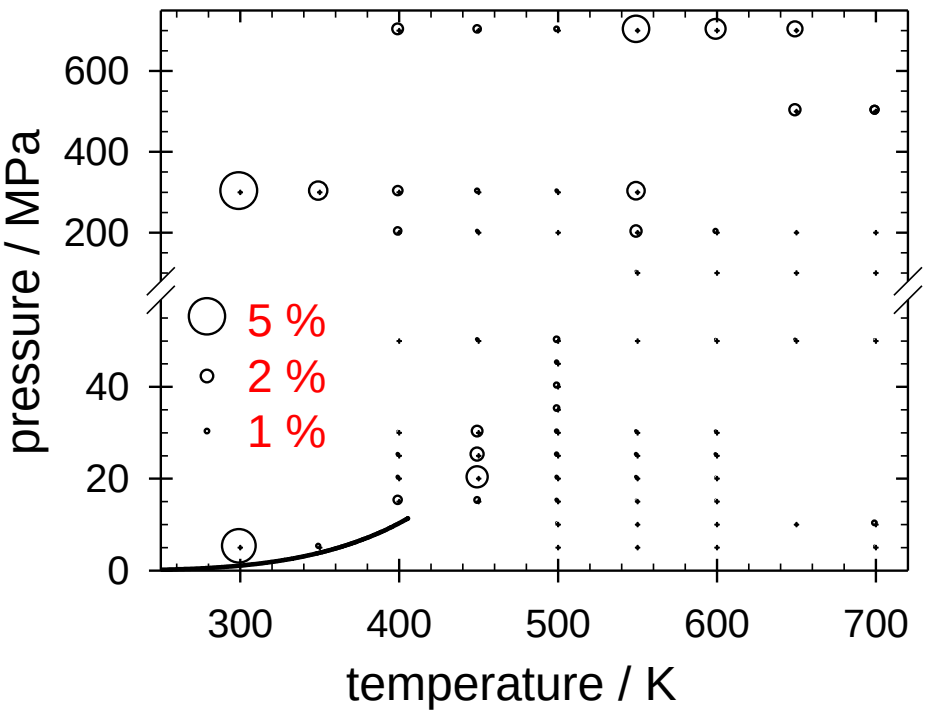


Prediction of density and enthalpy In the homogeneous region

density

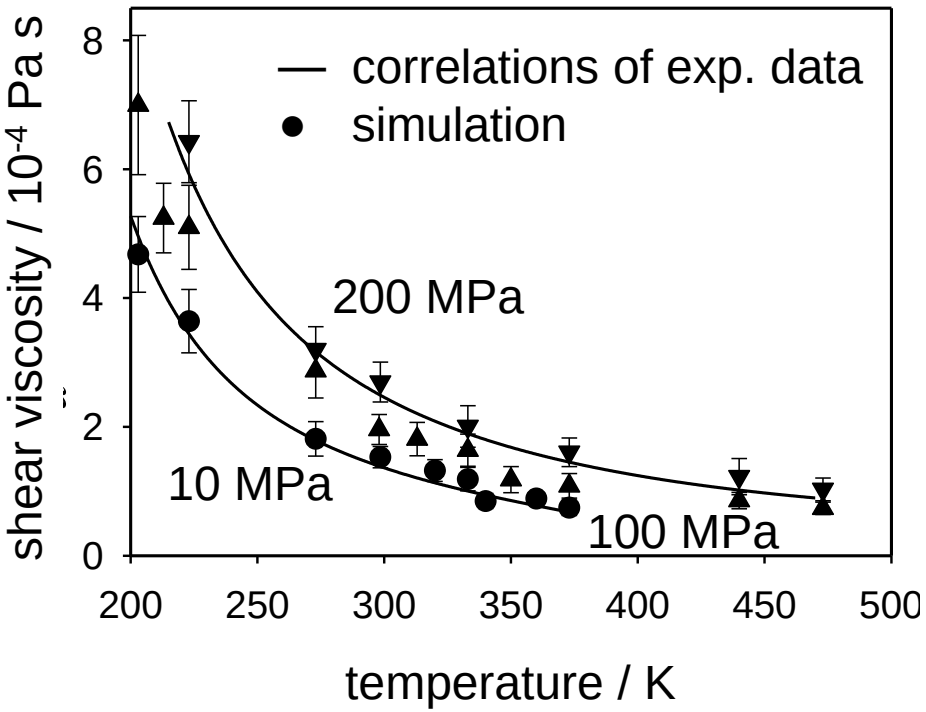


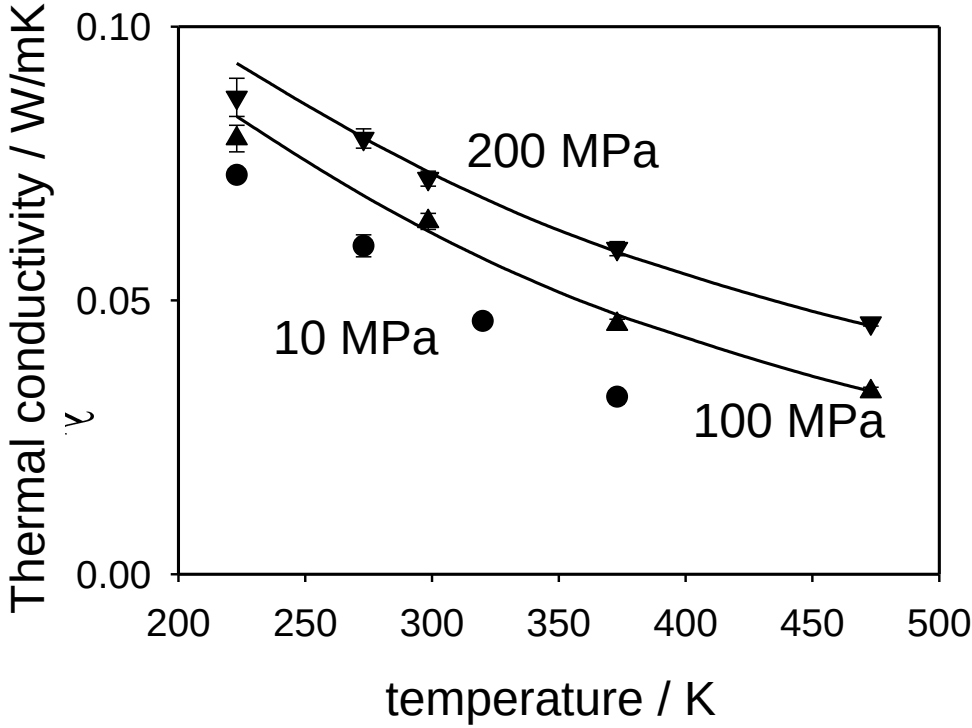
enthalpy



Deviations with respect to the equation of state by
Tillner-Roth, Harms-Watzenberg, Baehr: DKV-Tagungsbericht 20, 167 (1993).

Prediction of shear viscosity and thermal conductivity in the homogeneous region





Summary

- Molecular force fields are comprehensive models for thermodynamic properties with a strong predictive power
- Mixture properties are well accessible
- Molecular simulation is a versatile tool to investigate the behavior of fluids, which is about to be transferred to industry
- Using parallel simulation codes and appropriate computing equipment, acceptable response times may be achieved

*ms*2: molecular simulation tool

- Molecular dynamics / Monte Carlo
- Arbitrary mixtures of rigid molecules
- Several ensembles
- Grand Equilibrium method for VLE calculations

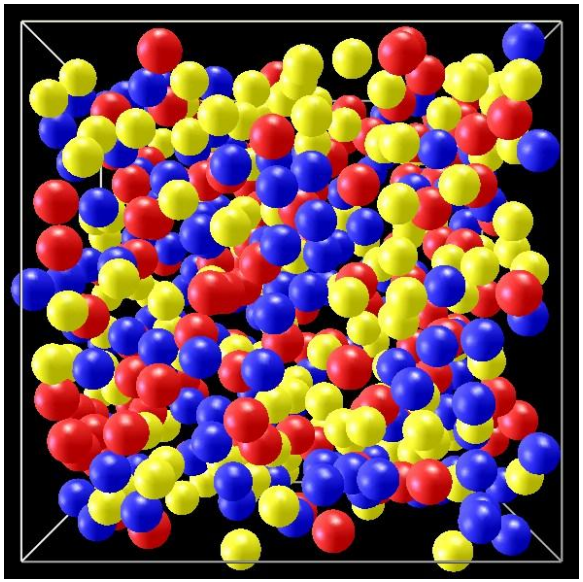
- Many static properties (thermal, caloric, entropic)
- Transport properties (Green-Kubo)

- Consistent FORTRAN90 code
- Reasonably object oriented
- Distributed memory parallelization by MPI
- All relevant loops vectorized
- Interface to 2,5D (OpenGL) and 3D Virtual Reality visualization

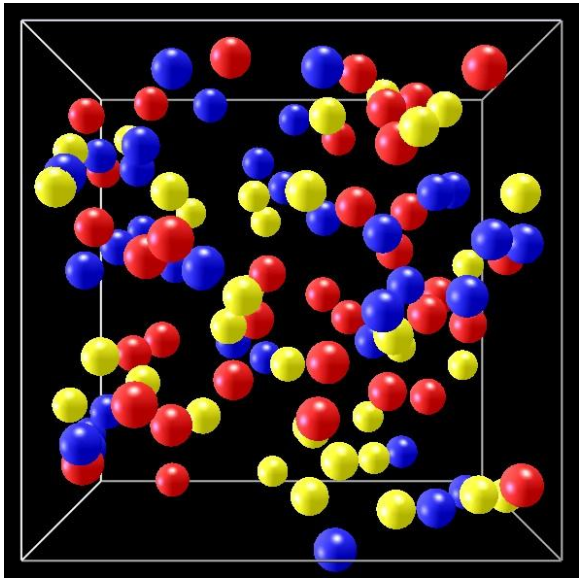
Phase equilibrium from Grand Equilibrium method @ *ms2*

Specs: T, x

Liquid



Vapor



Simulation:
- Chemical potentials
- Partial molar volumes

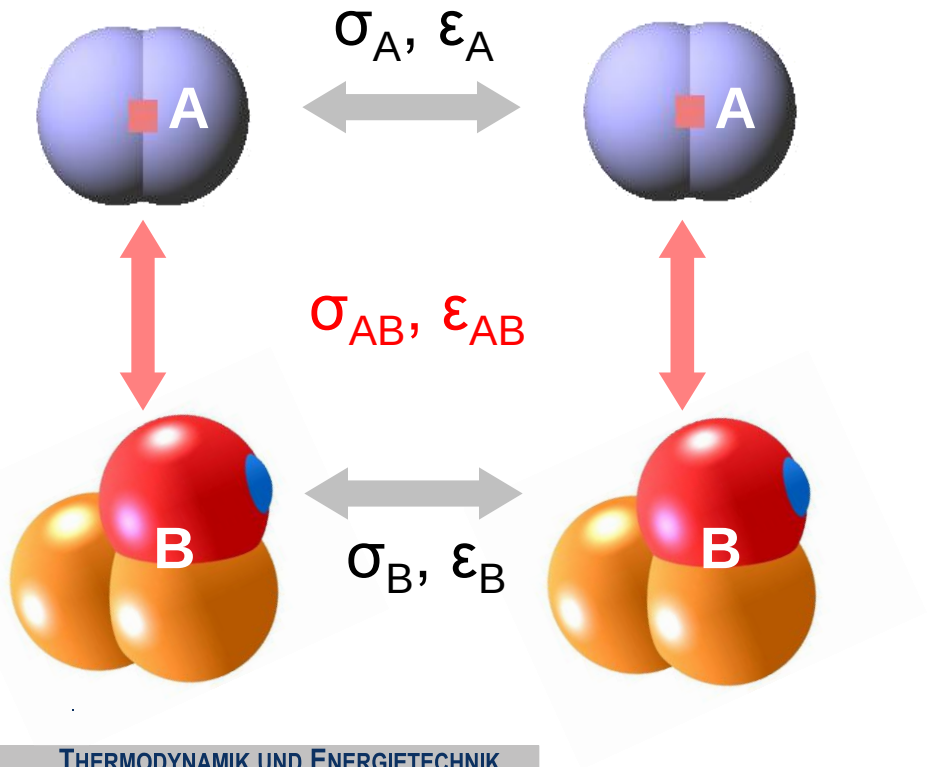
$$\mu_i^l(p) \approx \mu_i^l(p_0) + v_i^l \cdot (p - p_0)$$

Pseudo grand canonical simulation
(Specification of $\mu_i^l(p)$, V, T)

Result: p, y

Transferability to mixtures

- Assumption: pairwise additivity
- Unlike electrostatics straightforward
- Unlike dispersion a priori not known

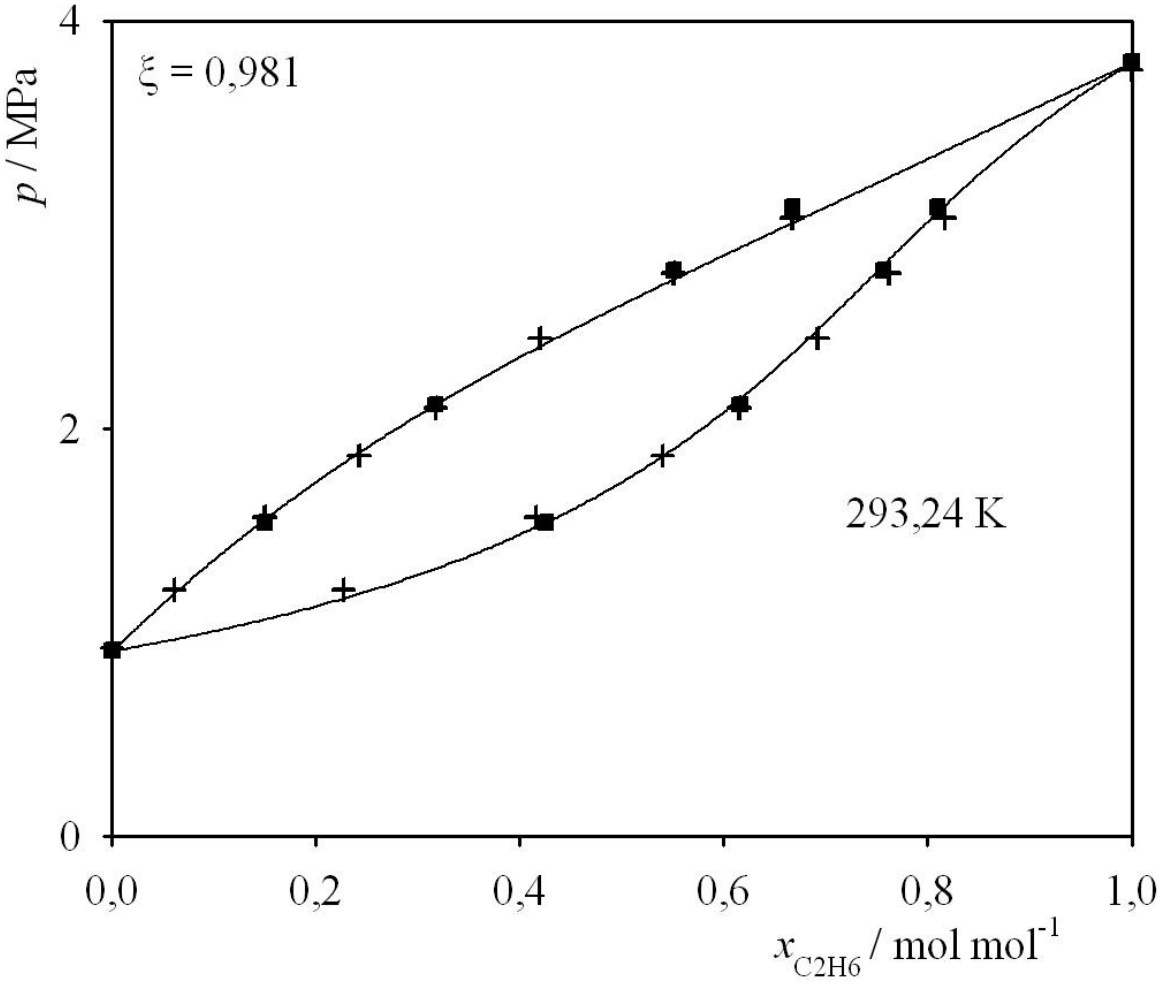


Unlike Lennard-Jones parameters

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2$$

$$\varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}$$

Binary VLE of C_2H_6 + R22



+ experiment

PR-EOS, k_{ij} adjusted

simulation, ξ = 1

simulation, ξ = 0,95 to 1,05

simulation, ξ adjusted

Vapor-liquid equilibria of binary mixtures

- Strategy applied to >350 binary mixtures regarding different types