# Orientational Effects of Multipoles on Simple Fluids

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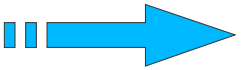
Process Energy Laboratory, Delft University of Technology

ESAT 2009

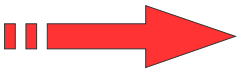
# Introduction

SAFT equation of state:

- mean field description
- geometry reduced to chains



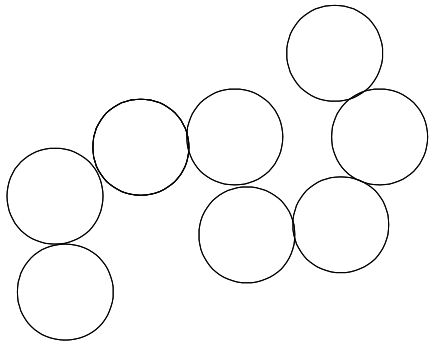
Orientation between multipoles and molecule geometry is lost !



Consequences ?

# Representation of Multipoles in SAFT EoS

PC-SAFTP1



PCP-SAFT-2008

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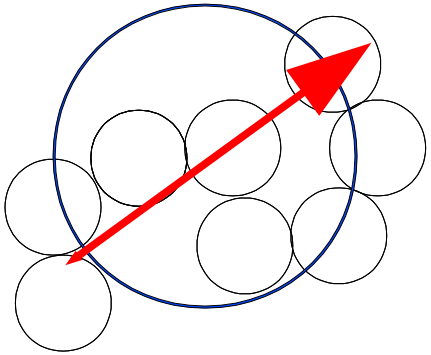

spherical reference particle
arbitrary multipoles

## PCP-SAFT-2008

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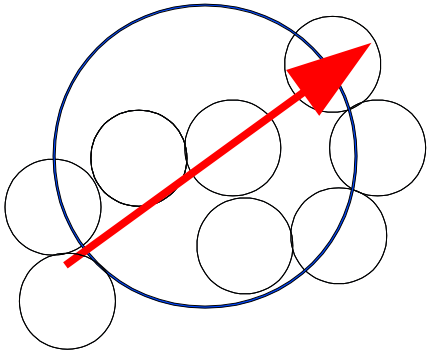

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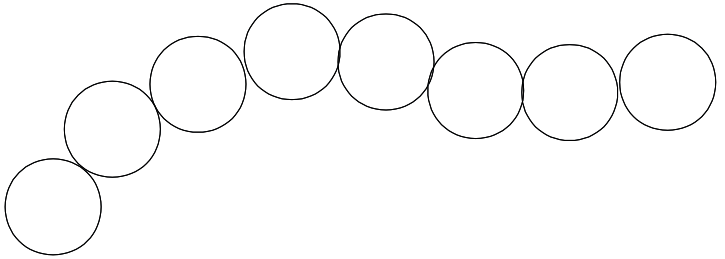

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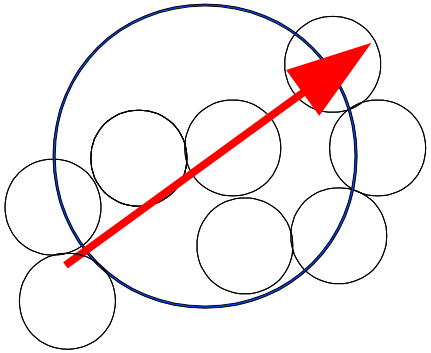

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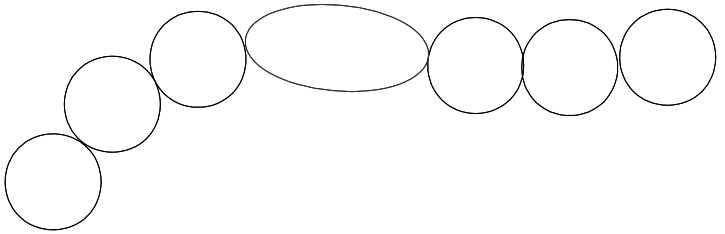

two-center Lennard-Jones particle

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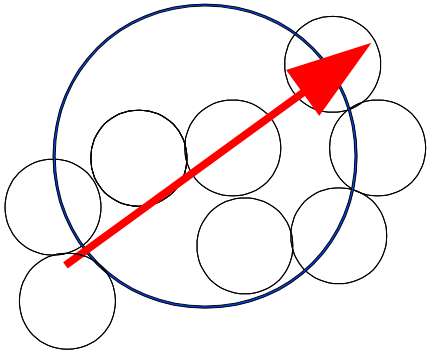

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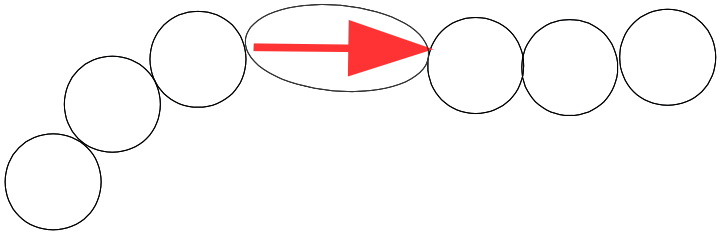

two-center Lennard-Jones particle
as reference for
axially symmetric multipoles

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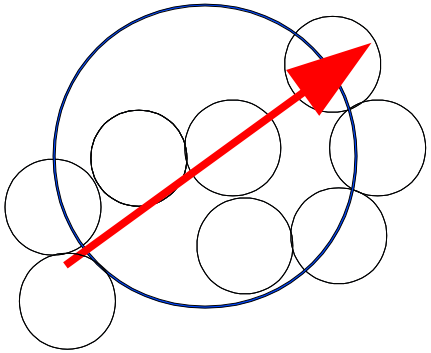
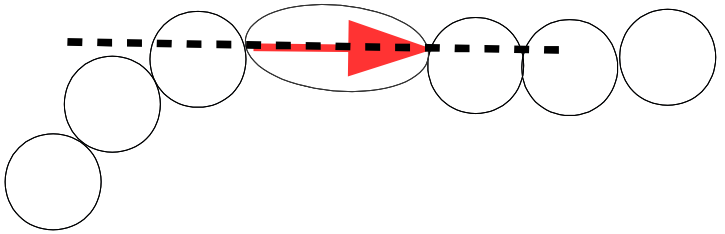


spherical reference particle
arbitrary multipoles

- deflection angle: undefined
- multipoles from quantum mechanics
- no association term

## PCP-SAFT-2008



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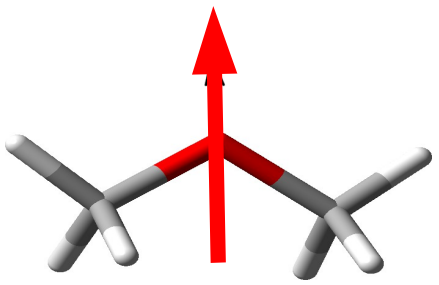
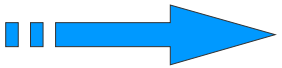
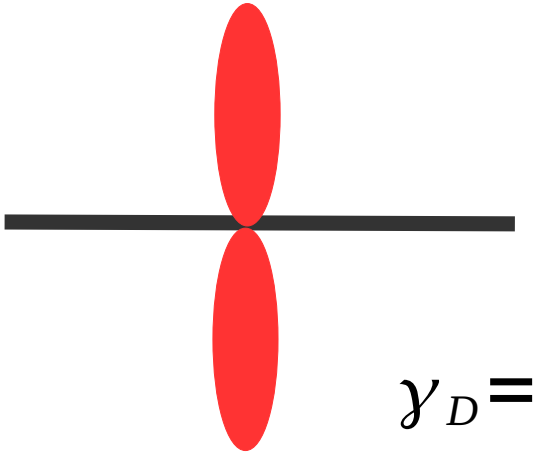
$$\gamma_D = 0\,°$$

# Geometry + Multipoles

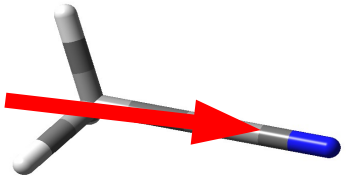


dimethylether

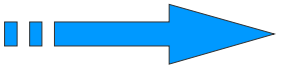




$\gamma_D = 90°$

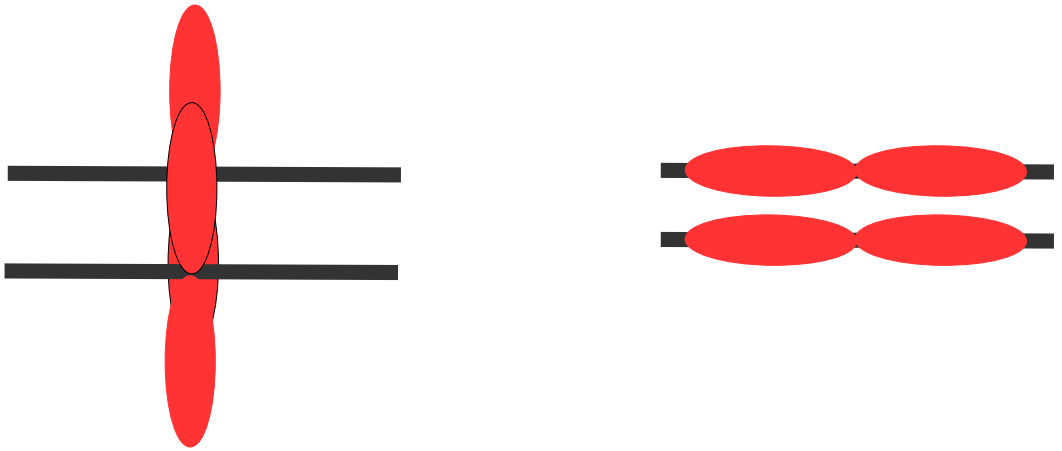


acetonitrile



$\gamma_D = 0°$

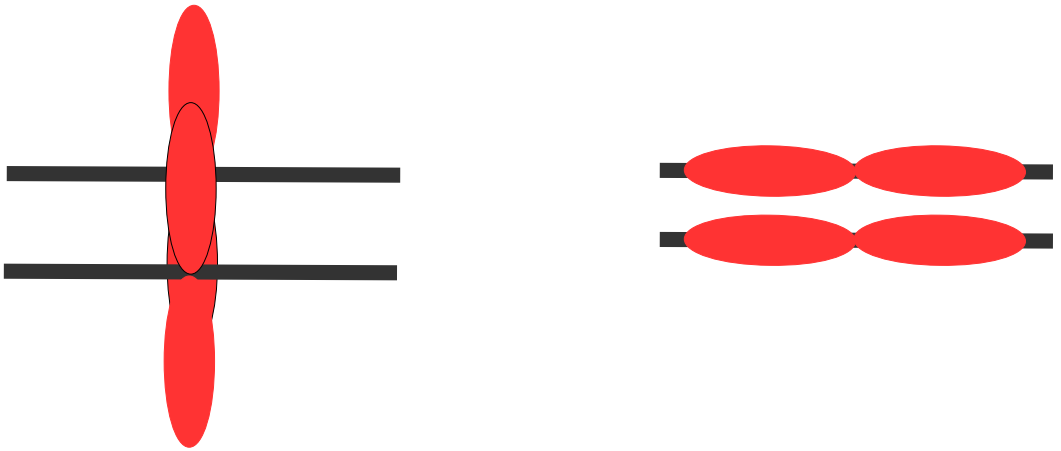
# Geometry + Multipoles



Multipoles in fluids:

- hindered by geometry
- the interaction energy for the 90° deflection angle is larger than for 0°.

# Geometry + Multipoles



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<u>Interaction energy:</u> P1 $\geq$ true value $\geq$ PCP

# Possible Solutions

1. Wertheim's perturbation theory to 2'nd order

   ⇢ not here !

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2. New EoS for 2CLJ particle + deflection angle perturbation theory / simulations

   ⇢ additional parameters ! $\gamma_D, \gamma_Q$

# Possible Solutions

1. Wertheim's perturbation theory to 2'nd order

   ⇢ not here !

2. New EoS for 2CLJ particle + deflection angle
   perturbation theory / simulations

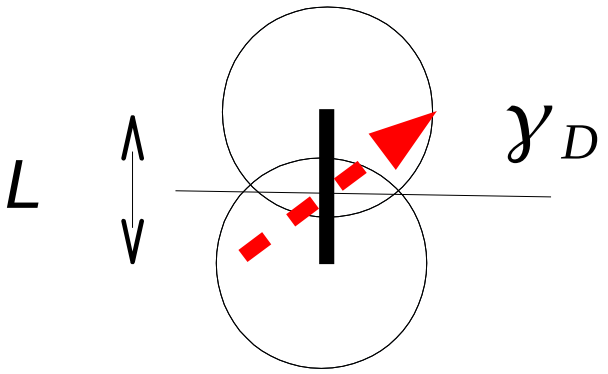
   ⇢ additional parameters ! $\gamma_D, \gamma_Q$

3. Rescaling of multipoles
   no new parameters,

   ⇢ less accurate than solution 2.!

# Perturbation Theory

- one-phase MC simulations: $g_2(r_{1,}r_2)$
- $\Phi_{DD}, \Phi_{DQ}, \Phi_{DDD} \ldots \Phi_{QQQ}$
- integrating $g * \Phi$ numerically
- parametrizing in *L*, *T*, *n*, *D*, *Q*, $\gamma_D, \gamma_Q$



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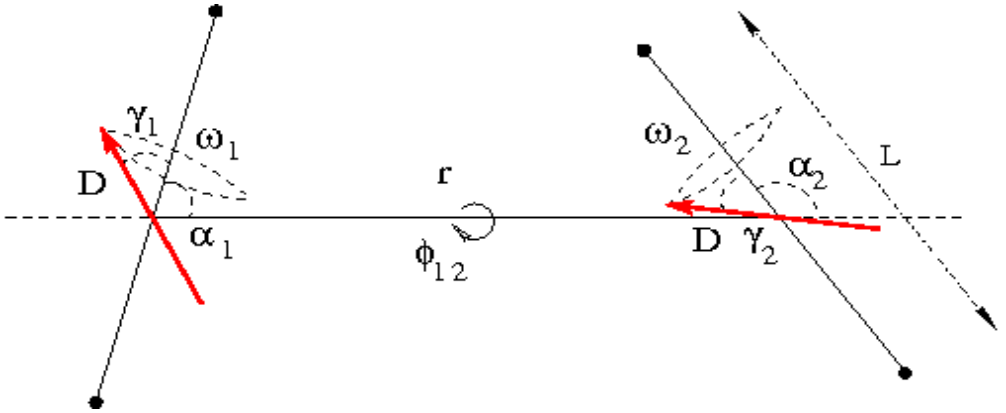



dipole - dipole interaction of 2CLJ:

L, D, $\gamma_D$

$\alpha_1, \alpha_2, \omega_1, \omega_2, \phi_{12}$

$r_{12}$

# Perturbation Theory

Approach is problematic:

- strong and long ranged interactions
- coordinate space: 6 … 13 dimensional
- parameter space: 7 dimensional
- Integration of singular functions

- $\gamma_D, \gamma_Q$ : new paramters of EoS

# Simulations

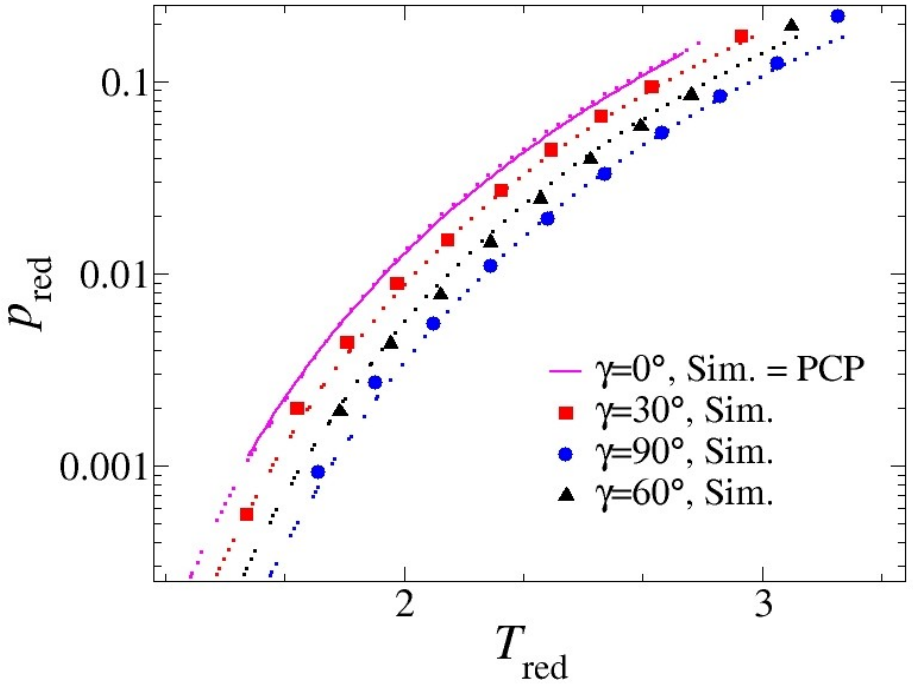
- VLE simulations with the "grand canonical equilibrium method"
- data points: L = 0, 0.2, 0.4, 0.6, 0.8, 1

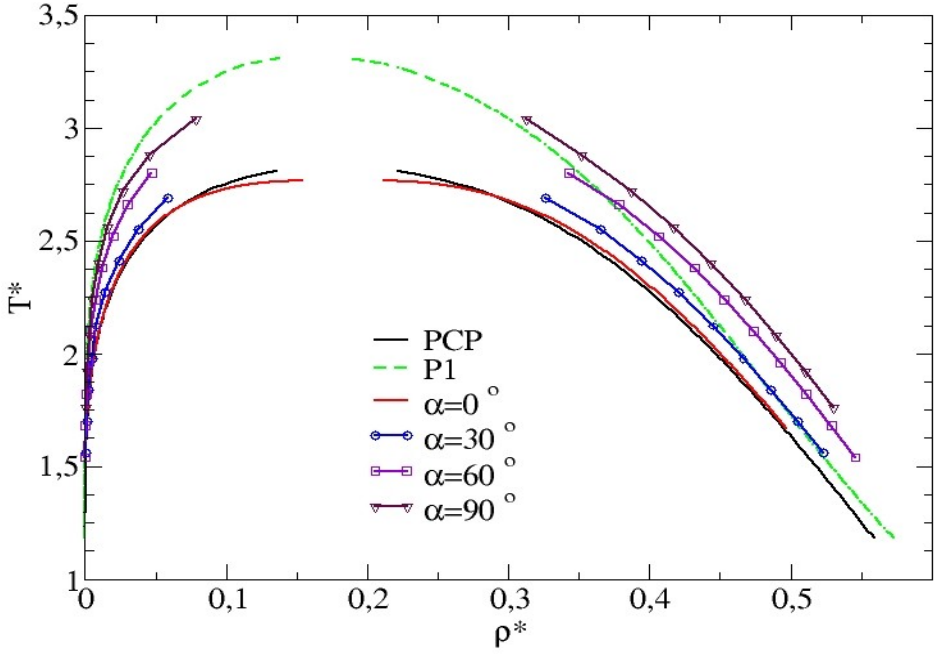
$\gamma_D$ = 0°, 30°, 60°, 90°

$D^2$ = 2, 4, 6, 12

$Q^2$ = 2

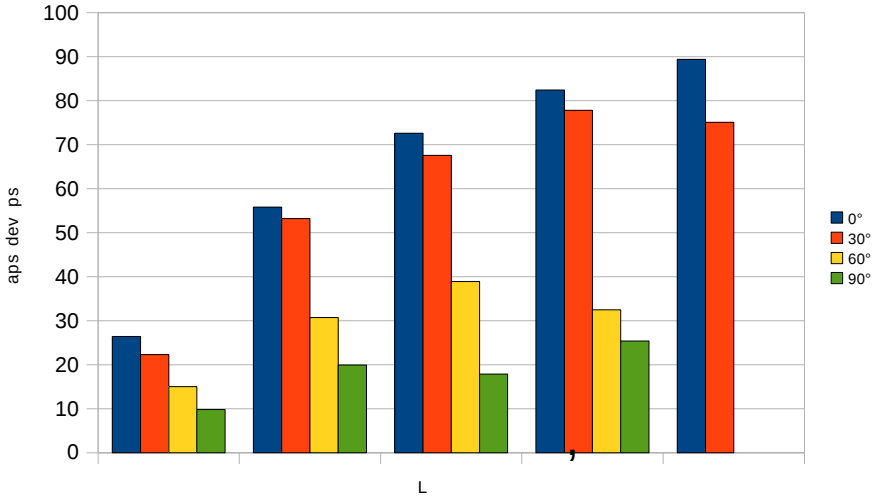
# Simulations

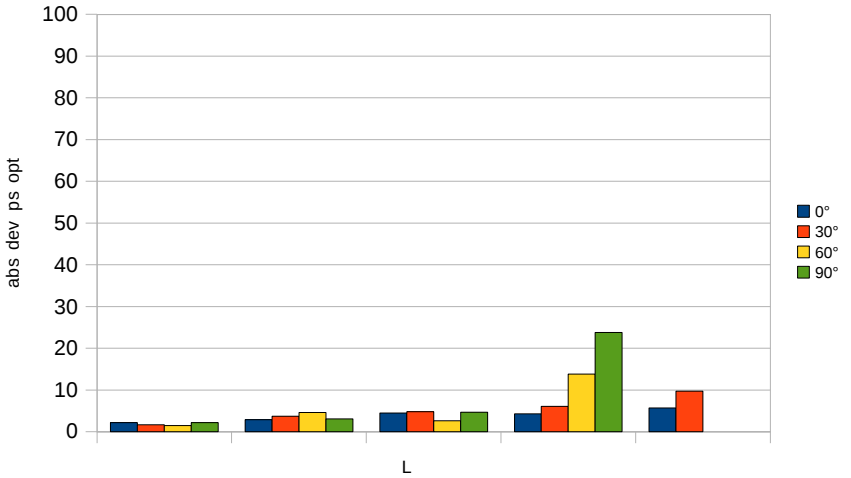



VLE data: change continuously with L and $\gamma_D$.

# Continuum Model




absolute deviation of saturation pressure / %
for P1 EoS

error reduction by adjusting $D_{eff}, Q_{eff}$

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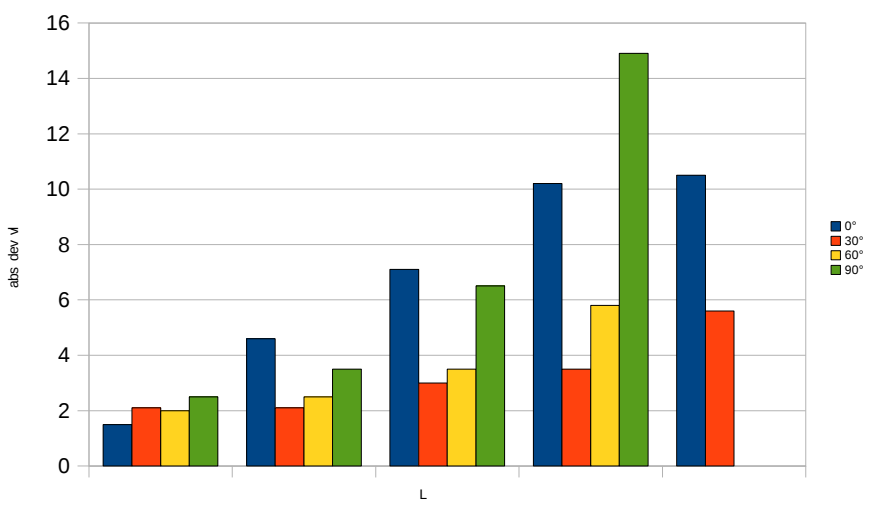
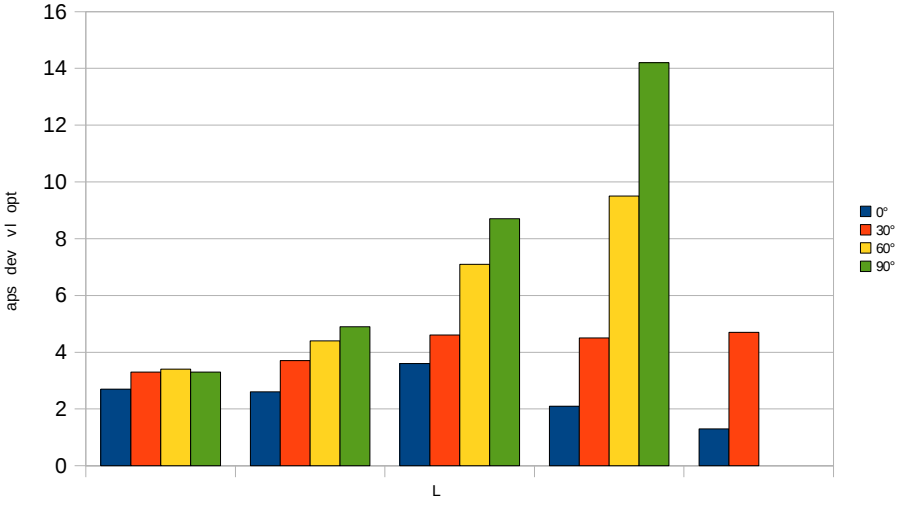


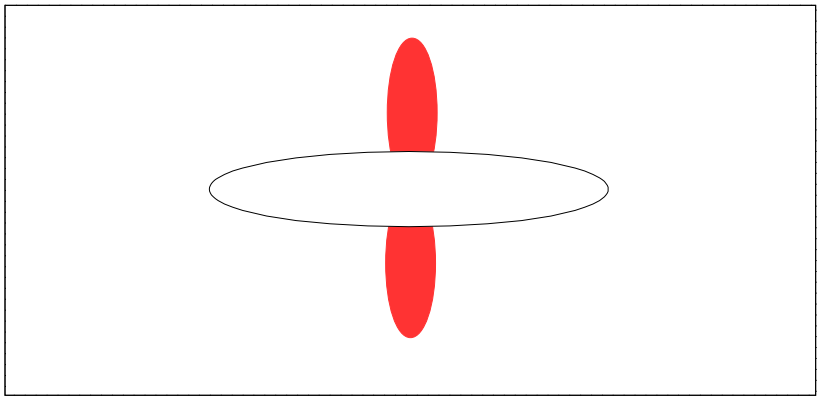




absolute deviation of specific volume / %
for P1 EoS

error reduction by adjusting $D_{eff}, Q_{eff}$

specific volume is dominated by $\sigma$

# Continuum Model

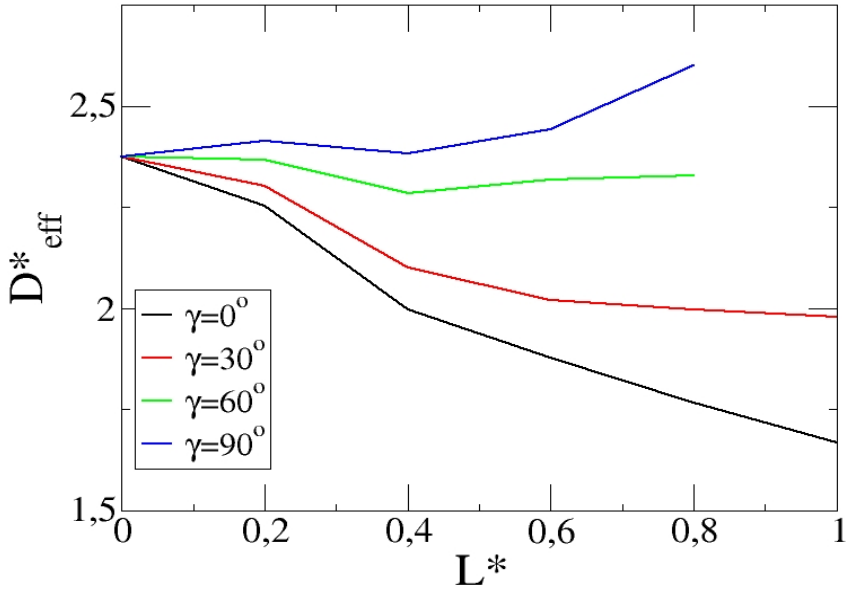


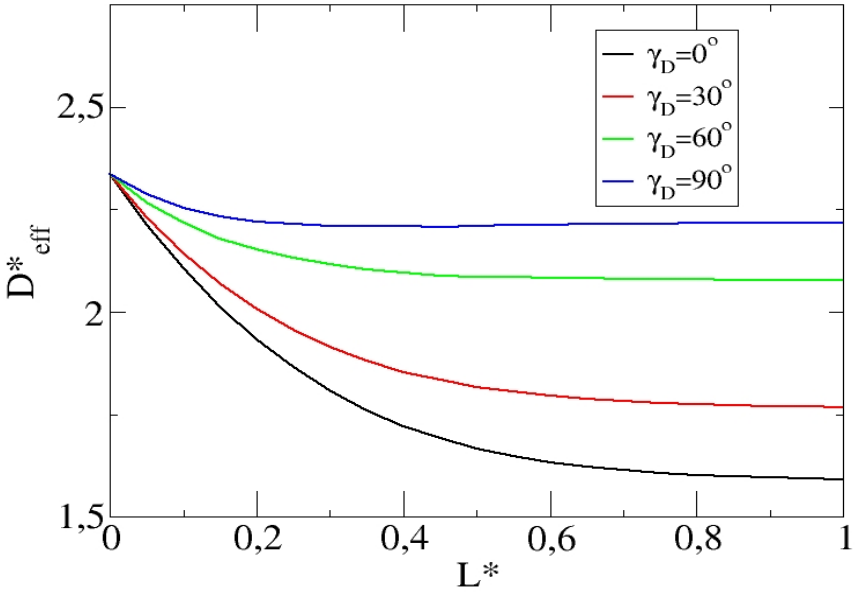
Assumption:

- electrostatic energy of N particles = dielectric energy of 1 dipole in dielectricum
- correlating the dielectric energy of spherical particles to that of 2CLJ

$$da = \left(P\,\rho^{-2} + \alpha/2 * \rho^{-1} E^2\right) d\,\rho - s\,dT$$

# Continuum Model




$D_{eff}$ and $D_{mopac}$ for axially symmetric dipole in dielectric cavity. Calculation done with:

Mopac: point-charge-COSMO program, A. Klamt

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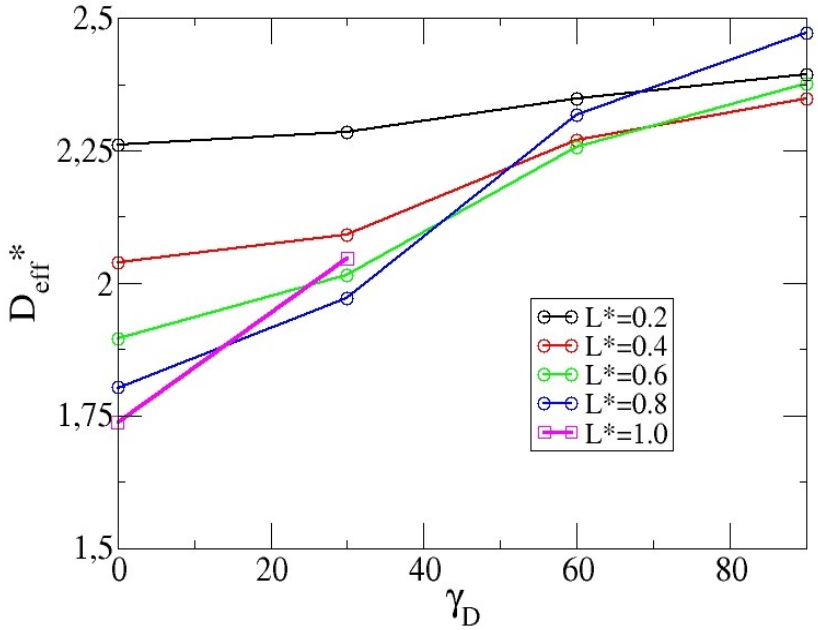


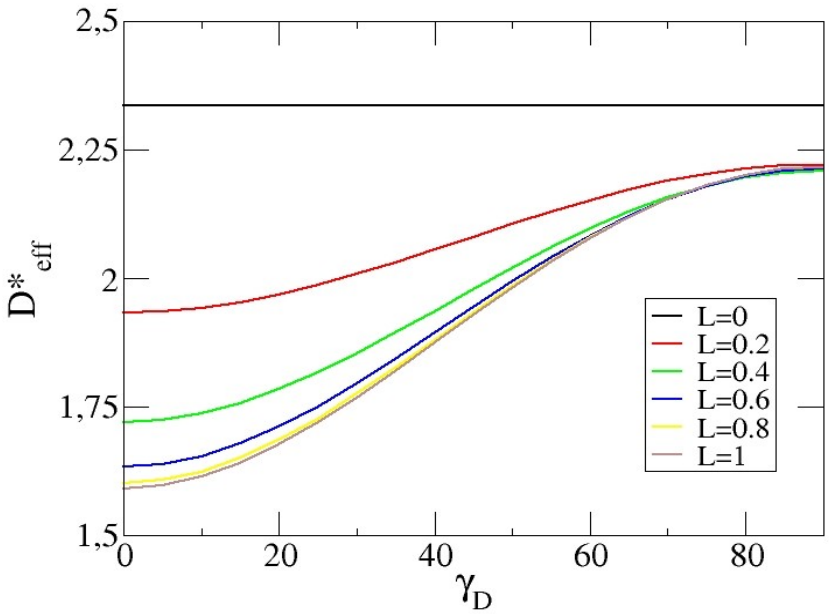


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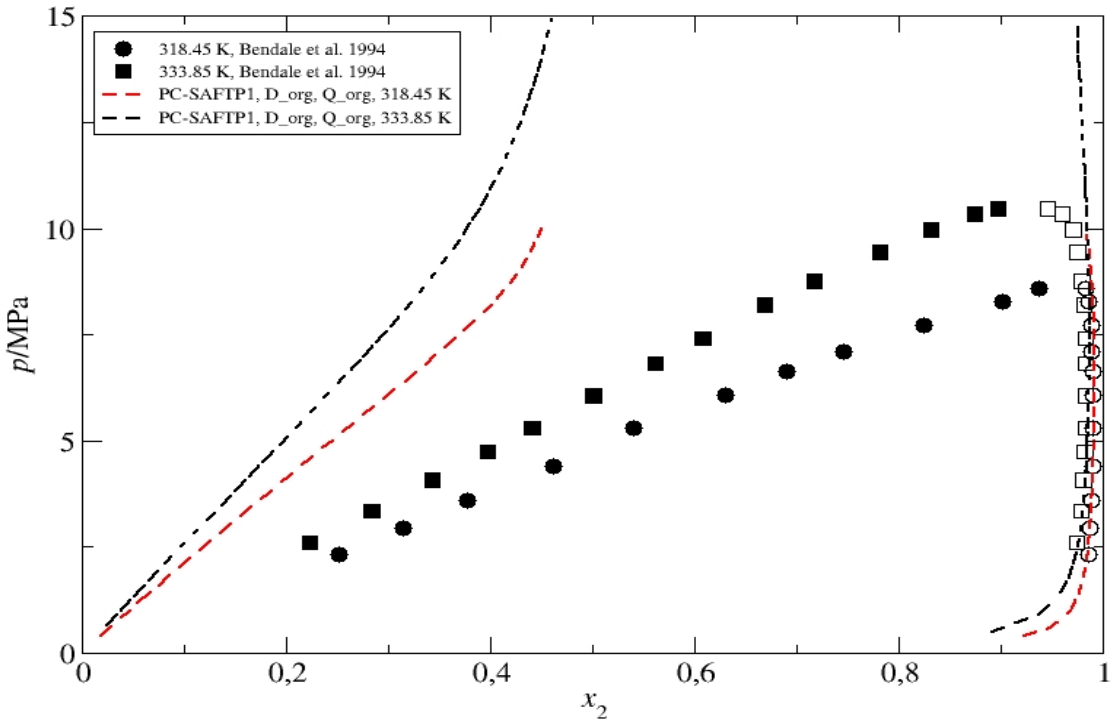


$CO_2$ + acetonitrile:
P1
London mixing rule (no mixing parameter).

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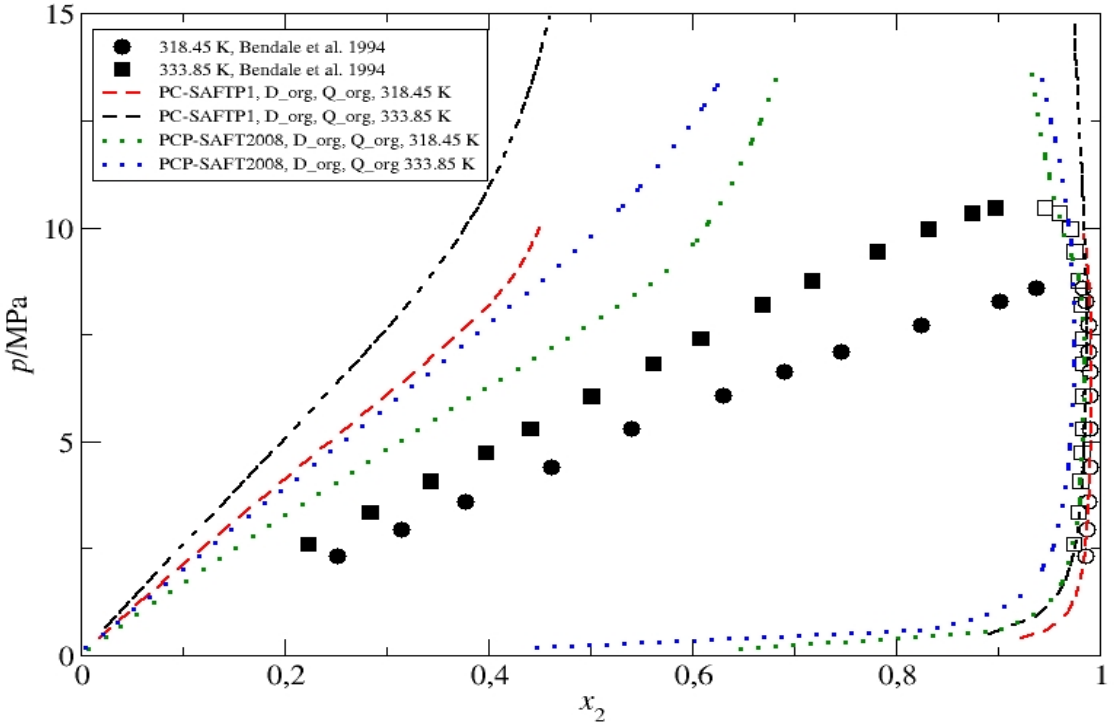


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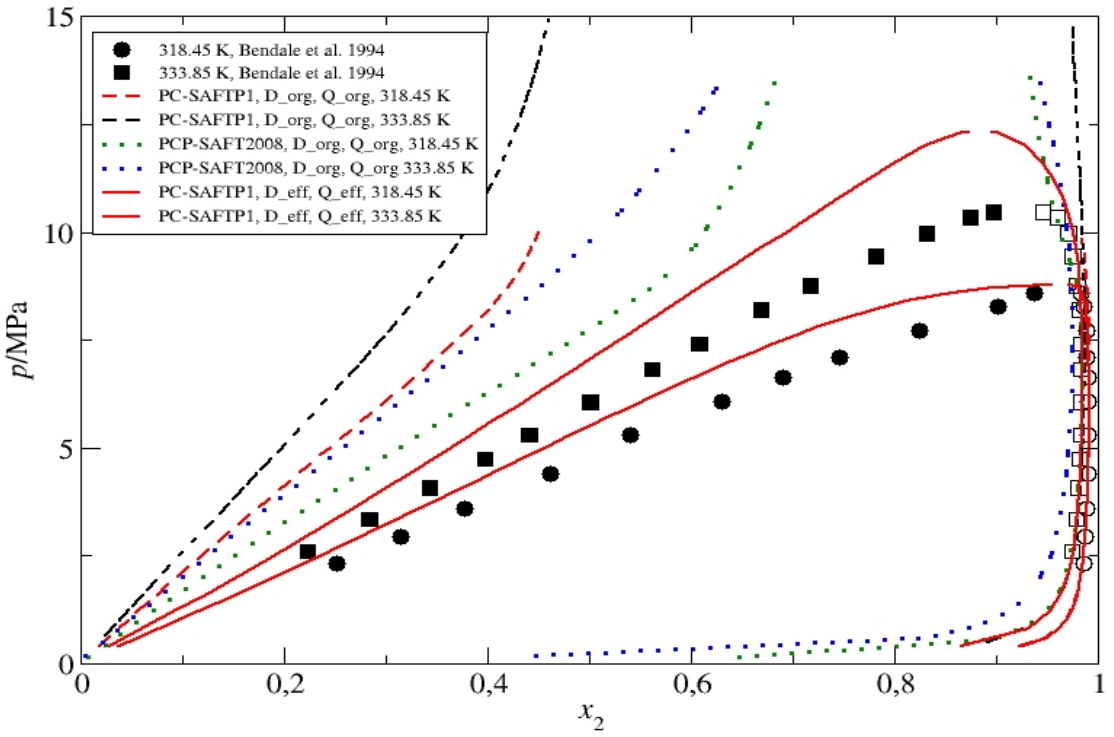


$CO_2$ + acetonitrile

P1 + PCP + P1 for $Q_{eff}$ fittet for single components

London mixing rule, no mixing parameter

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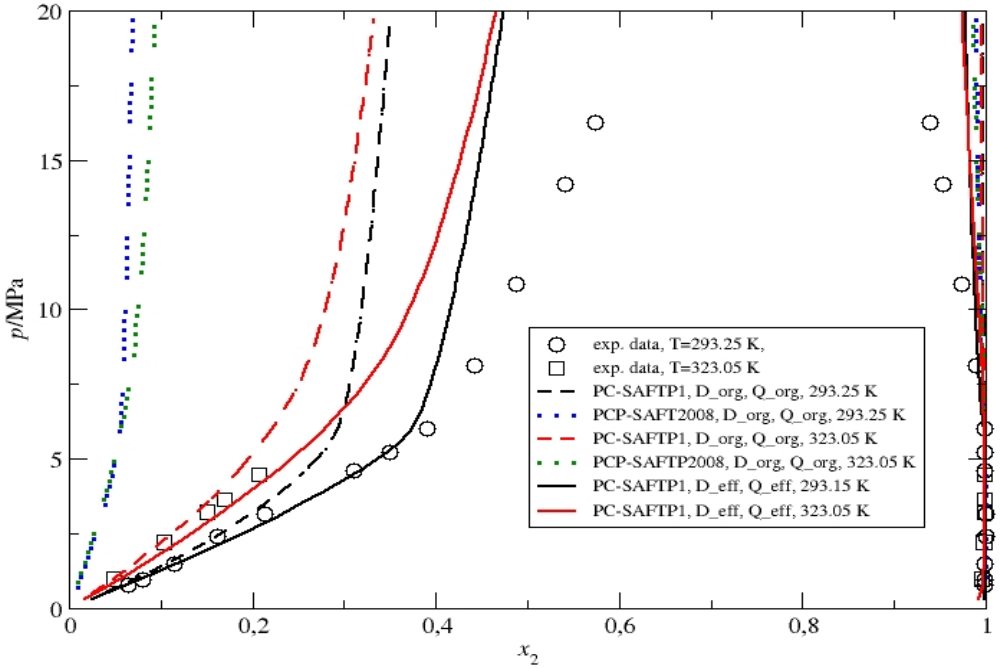


ethene + dimethylformamid
comparing P1, PCP, P1 + $D_{eff}$ , $Q_{eff}$
London mixing rule, no mixing parameter

# Conclusions and Outlook

- SAFT overestimates dielectric energy
- $D_{eff}, Q_{eff}$ : functions of *L (*or *m* in case of PCP*)*
- Mopac: rescaling of classical multipoles
- no new parameters !

work in progress:

- adjusting $\sigma$ as function of $D_{mopac}, Q_{mopac}$