Molecular modelling
of hydrogen bonding fluids

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Computational
Molecular Engineering

The nature of the hydrogen bond

Pauling (1960, "The Nature of the Chemical Bond") on the hydrogen bond:

It "was for some time thought to result from the formation of two covalent bonds," but it "is now understood that the hydrogen bond is largely ionic"

Hope: H bonds can be described by simple electrostatics (point charges).

New **IUPAC** definition (2011):

"The hydrogen bond is an attractive interaction … from a molecule … X—H in which X is more electronegative than H, and … in which there is evidence for bond formation."
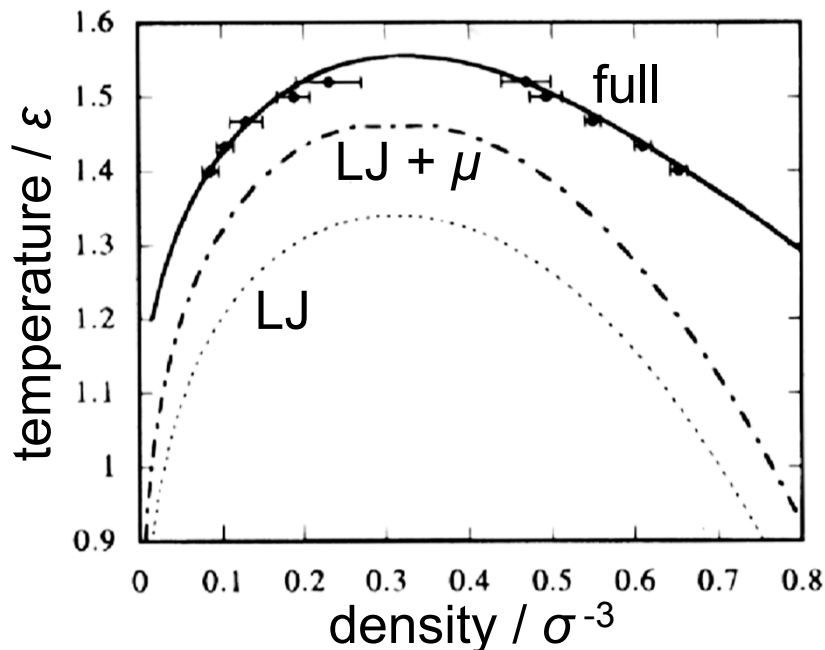
"The forces involved … include
- those of an electrostatic origin,
- those arising from … partial covalent bond formation …,
- and those originating from dispersion."

Thermodynamics of H bonding molecules

SAFT

PC-SAFT

$$A^r = A^r_{LJ} + A^r_\mu + A^r_{HB}$$
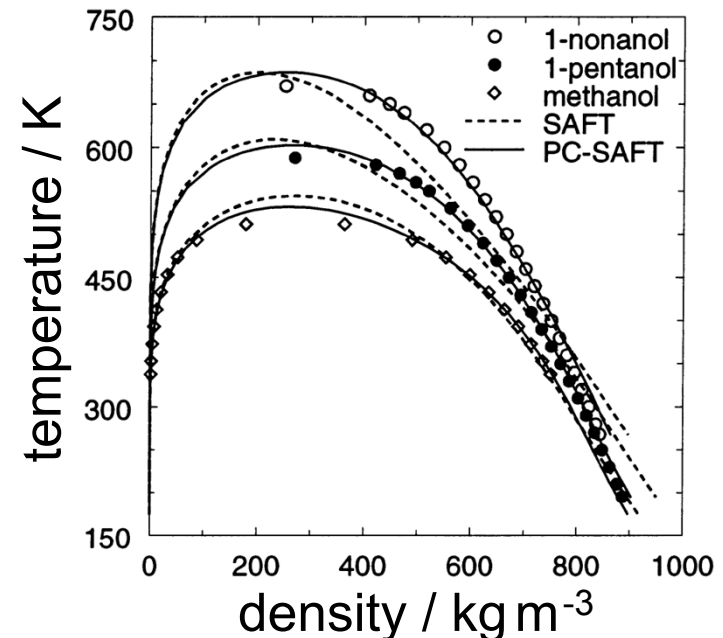
$$Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc}$$

temperature / ε vs density / σ^{-3}: curves labeled full, LJ + μ, LJ

Müller and Gubbins (1995)

temperature / K vs density / kg m^{-3}: 1-nonanol, 1-pentanol, methanol, SAFT, PC-SAFT

Groß and Sadowski (2002)

Separate influence of μ and H bonds

... captured by a single Z^{assoc} term
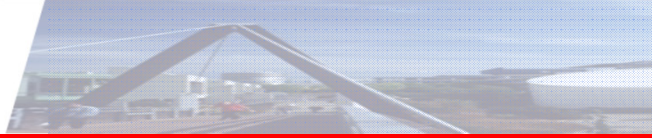
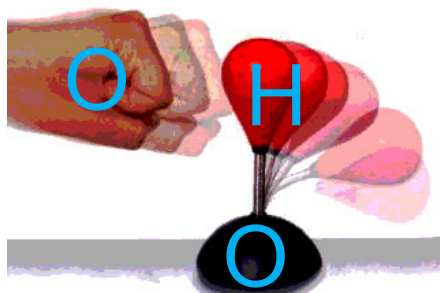# Modelling approaches for O—H ··· O
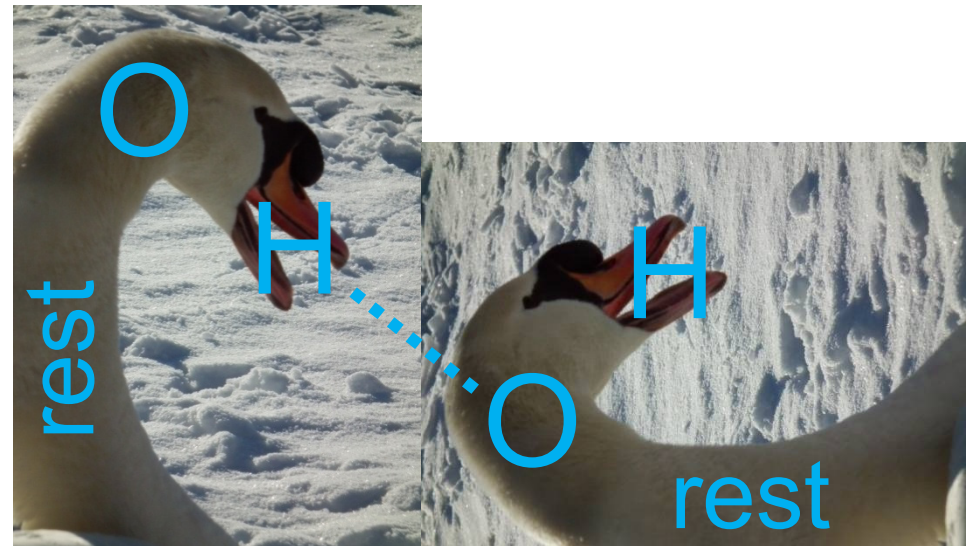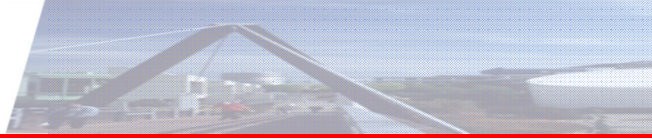
short-range square well

polarizable models

internal degrees of freedom

simple "beak" approach

Oxygen: LJ concentric with negative charge

Hydrogen: Positive partial charge (no LJ)

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Classical molecular models of water

Water models following the simple beak approach (SPC, TIP3P, SPC/E) are quite popular. However, their overall reliability is relatively limited:
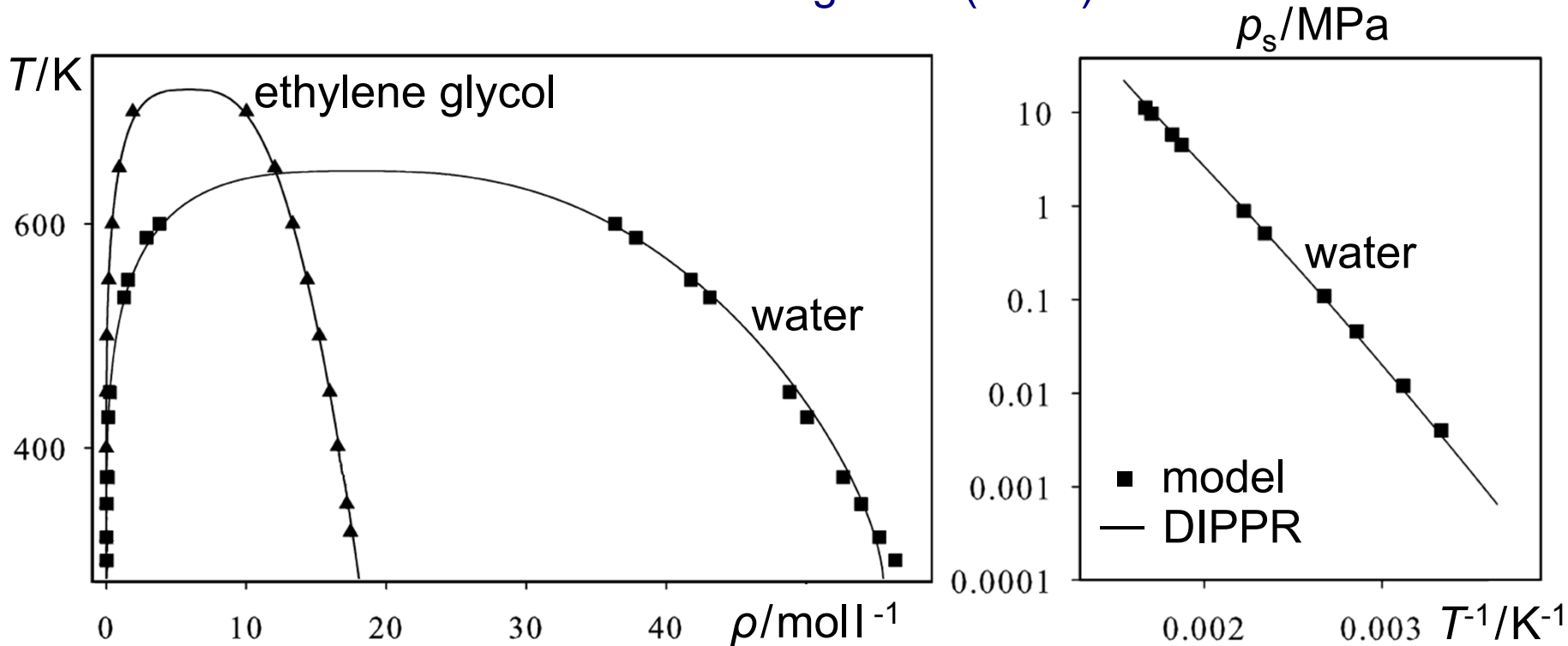

"Olympic medalists" from benchmark of **Vega** and **Abascal** (2011)

?

10

7.2

5.1

TIP4P/2005   SPC/E
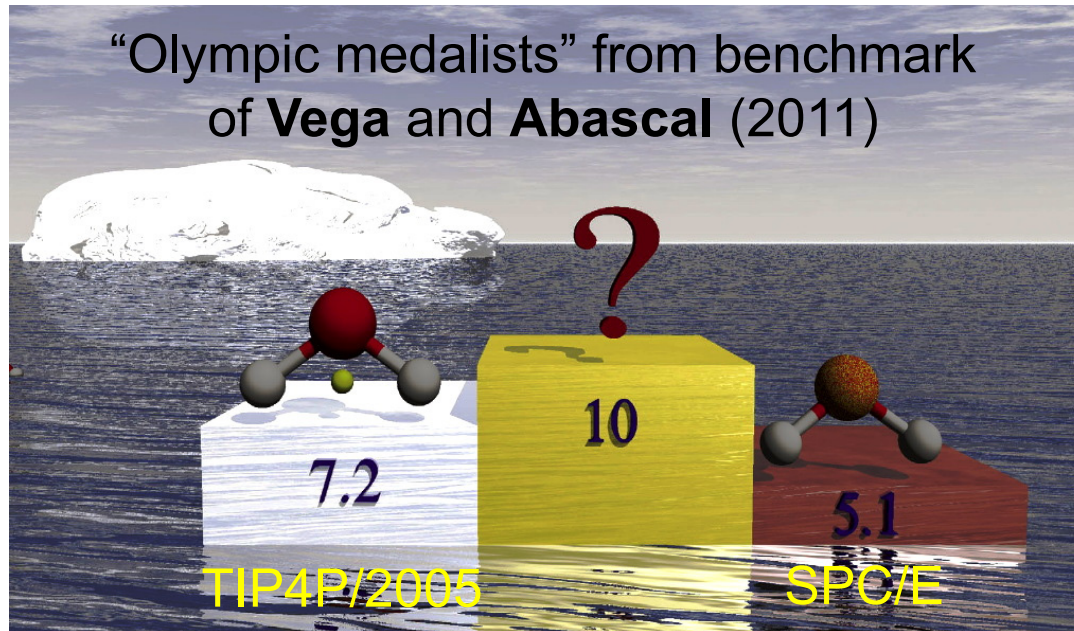
Vega and Abascal: "Neglecting **polarizability** prevents an accurate description of" pressure-related properties like $B(T)$, $p_s(T)$, and p_c.

Recent developments in modelling water

New TIP4P-like four-site model of Huang *et al.* (2012)

Nearly perfect agreement for critical properties, including p_c.

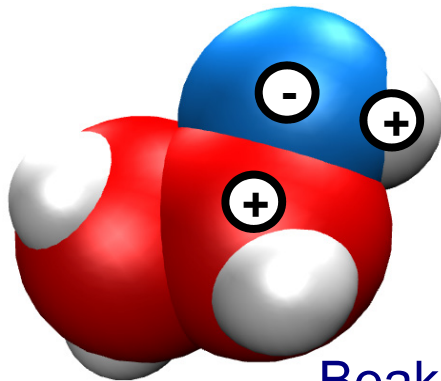Poor model for the liquid density at low temperatures and probably for ice …

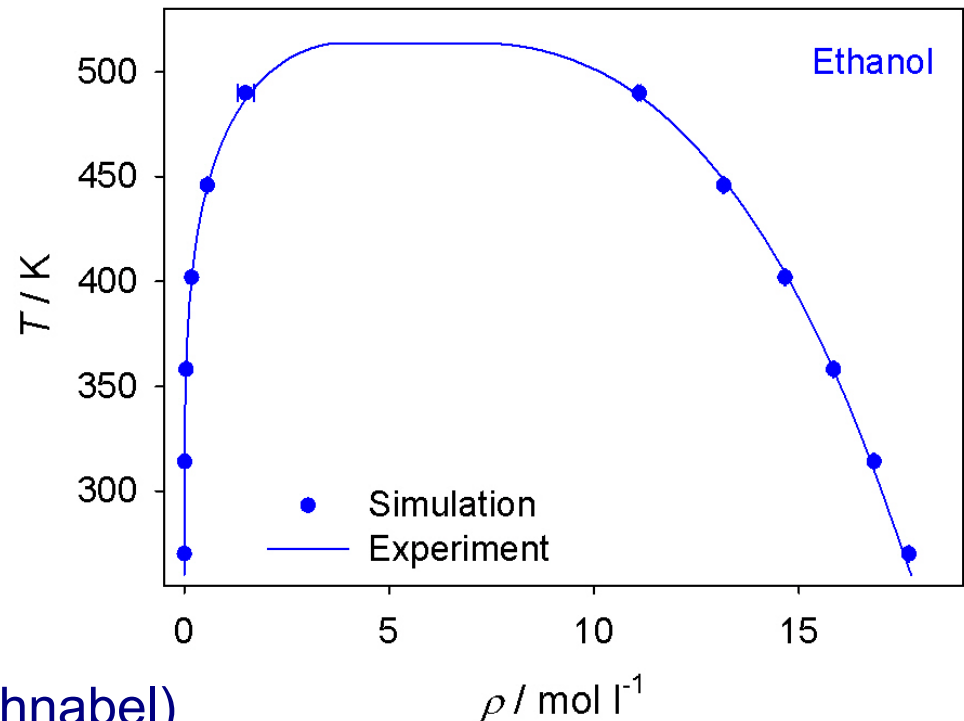# Simple beak-shaped hydroxyl group model

Ethanol:

- three LJ interaction sites
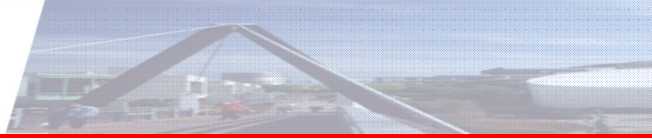- three point charges

Simple electrostatic sites account for **polarity** as well as **H bonding**.
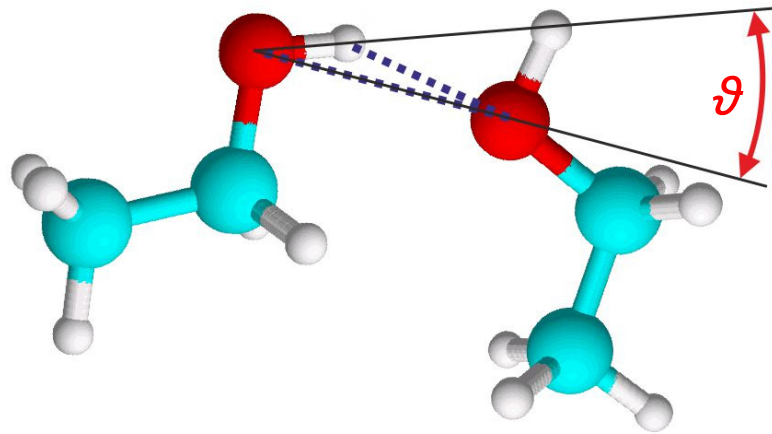

Beak model (Schnabel)

This approach is also valid for methanol and mixtures of H bonding fluids.

Hydrogen bonding in molecular simulation

Bond definition by a geometric criterion:

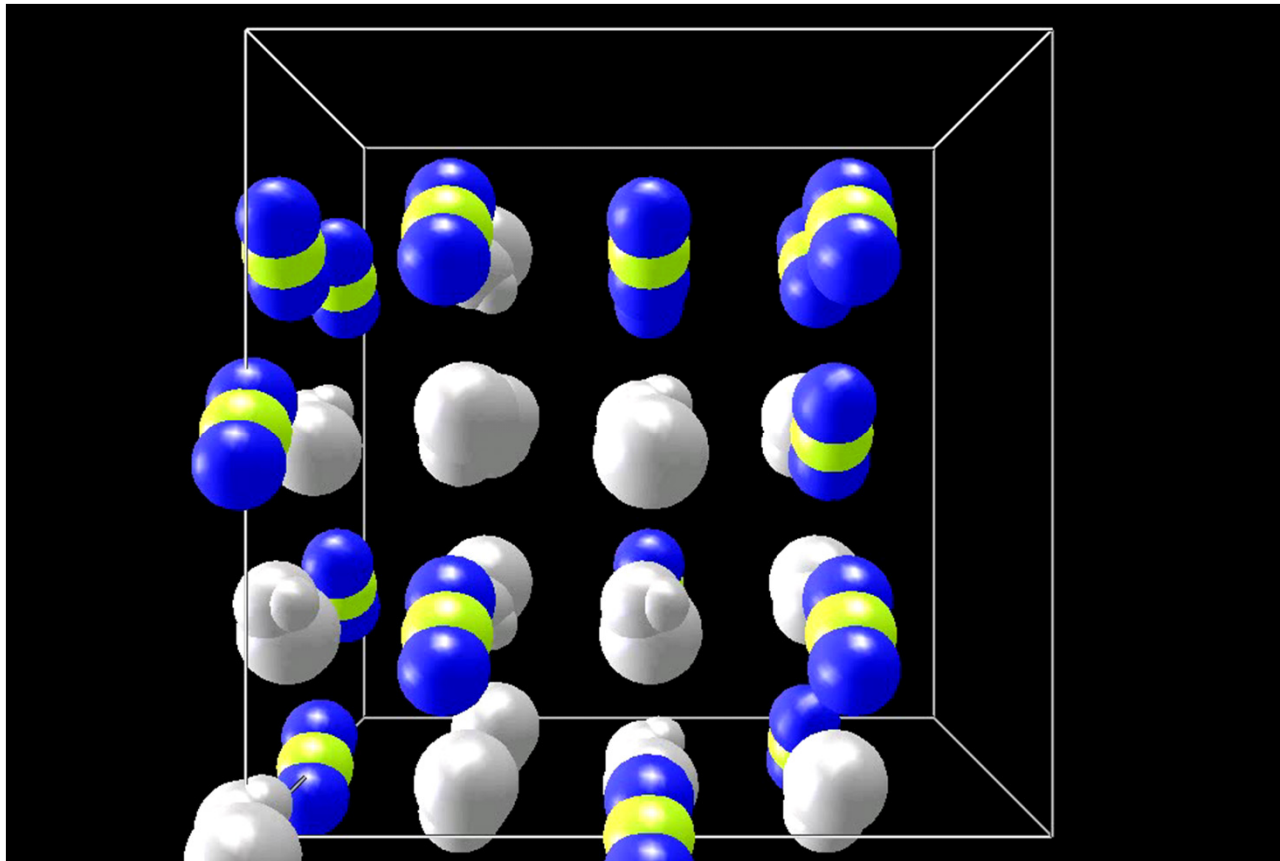- Introduced by Saiz et al. for ethanol:

$r_{HO} \leq 2.6$ Å
$r_{OO} \leq 3.5$ Å
$\vartheta \leq 30°$

- Identical with the criterion of Haughney et al. for methanol

- Validated by agreement between MC results and X-ray scattering

- Applied in reduced units (assuming $\sigma_{LJ} \approx 3$ Å) for the present study
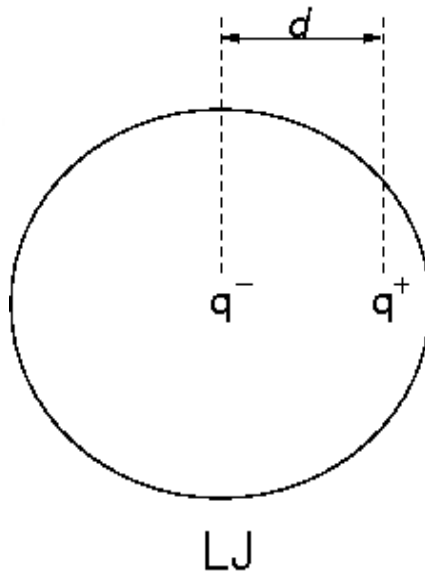
Hydrogen bonding in molecular simulation

equimolar mixture of methanol and carbon dioxide
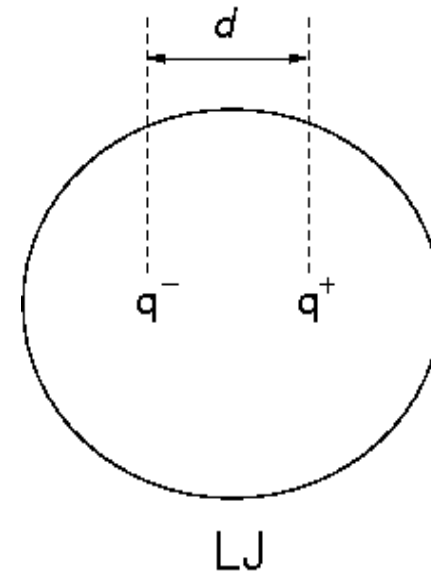
Zoom in: Point charge models of H bonding

The Stockmayer dipole is decomposed into two separate point charges:

"simple beak fluid"
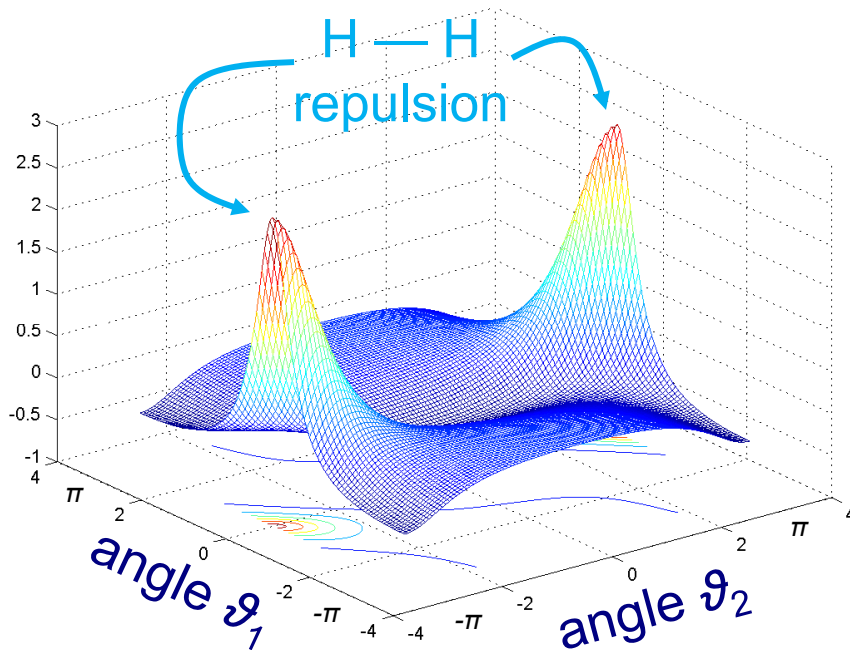
symmetric charges

reflects structure of the OH group

electronegative site resembles proton

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Potential energy surface

Electrostatic contribution to the dimer bond energy:

H — H
repulsion

electronegative
site repulsion

electropositive
site repulsion
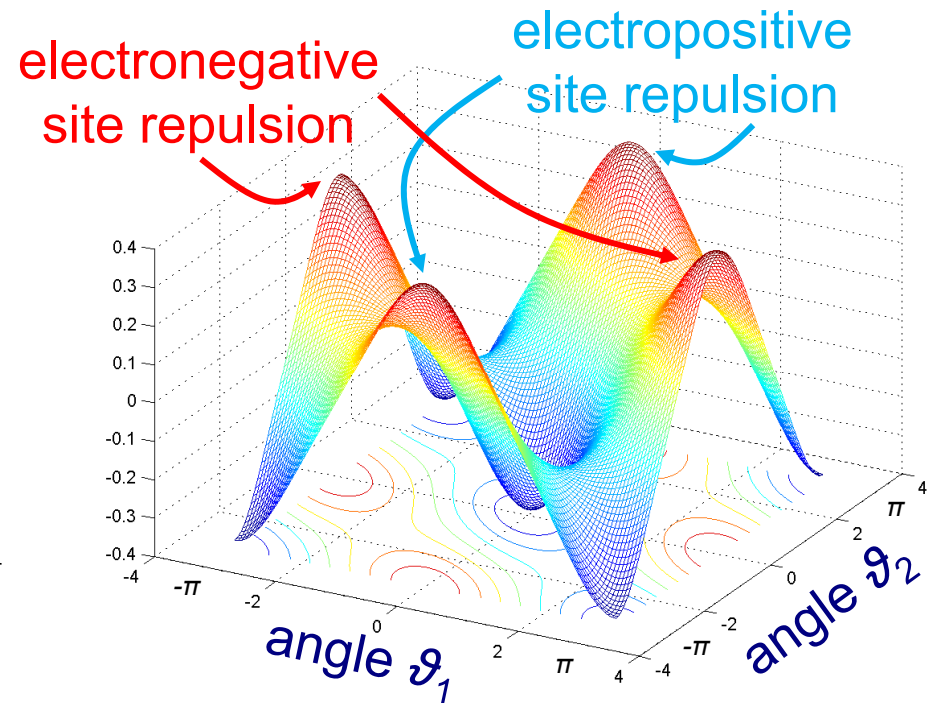
simple beak fluid

symmetric
charge model

Hydrogen bonds in the liquid phase

simple beak fluid

symmetric charges

$T = 0.7\,T_c$
$\rho = \rho'(T)$
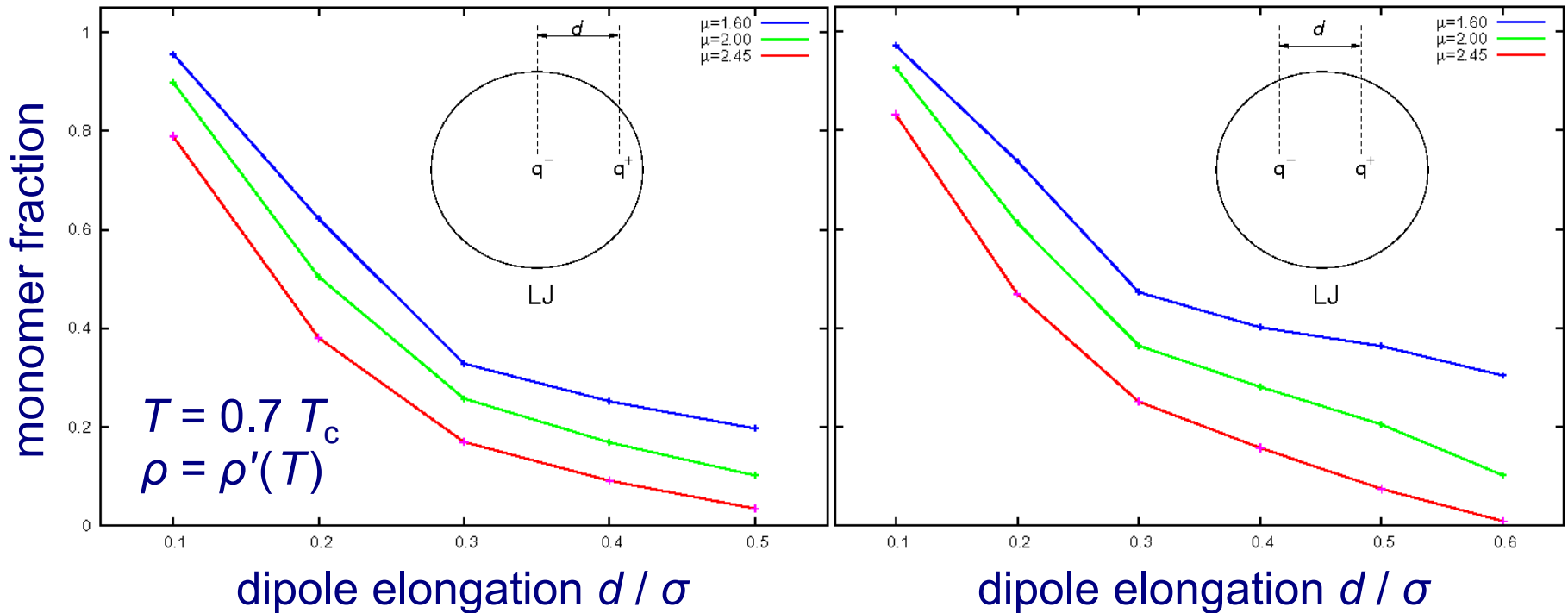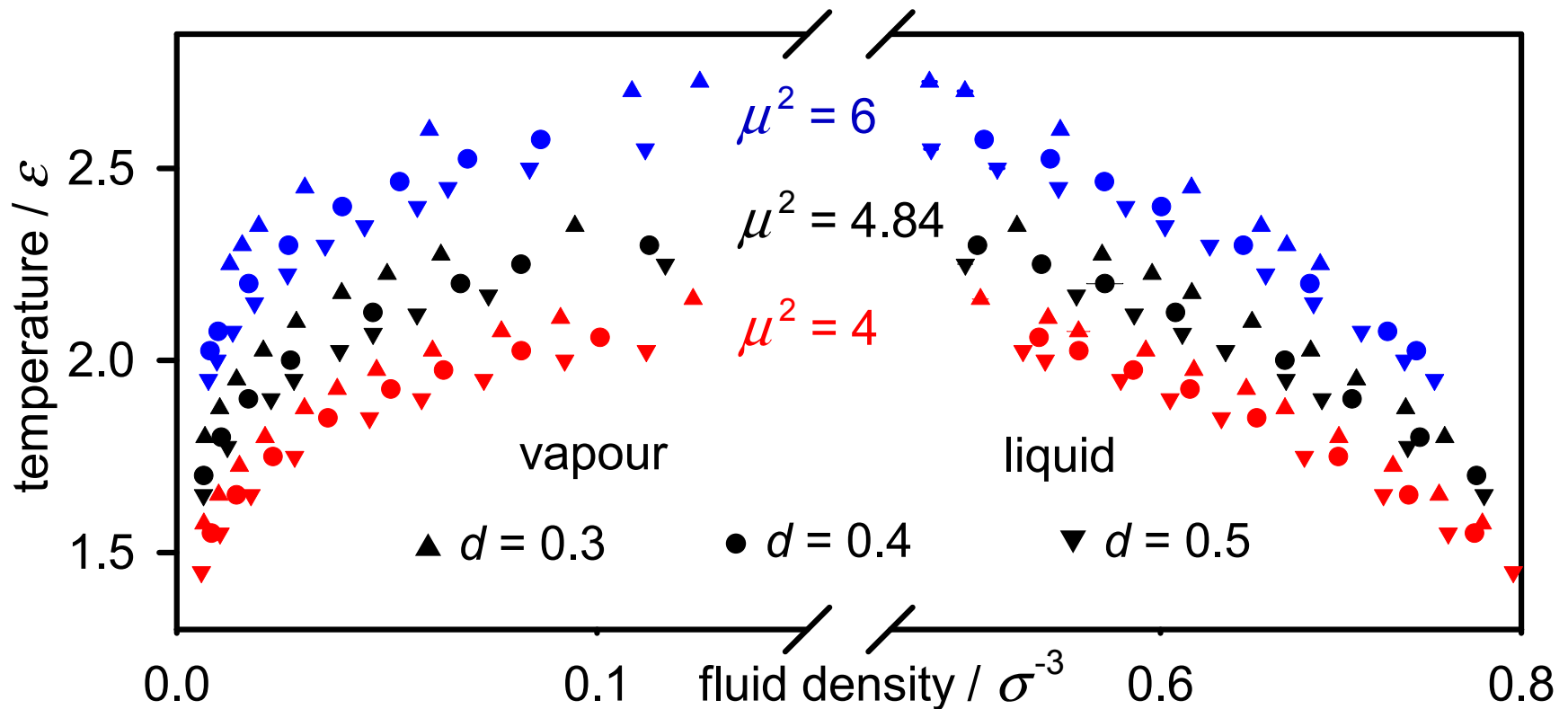
For both model classes, hydrogen bonding depends significantly
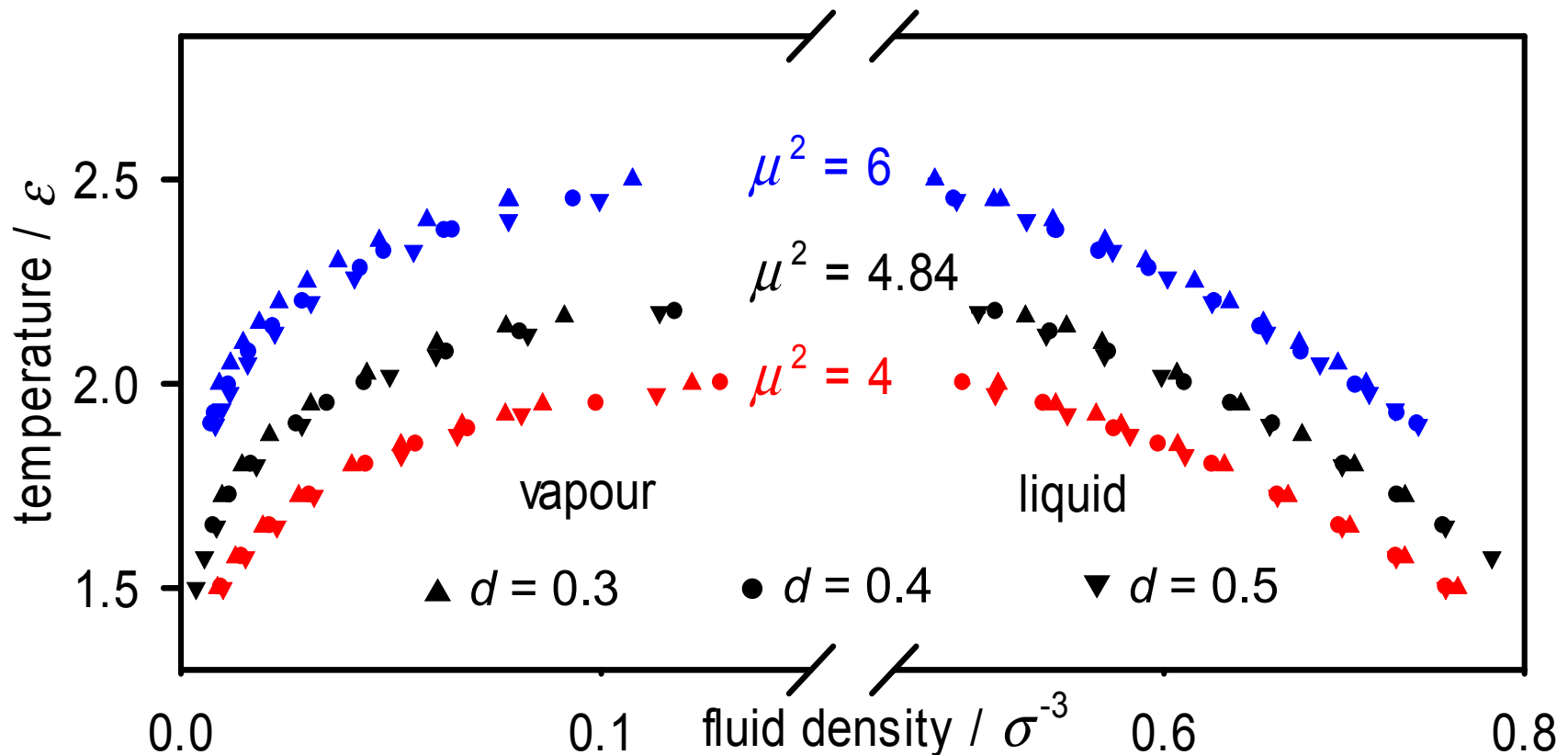on the distance between the partial charges (as expected).

Vapour-liquid equilibria for the simple beak

As desired, both the dipole strength μ^2 ($\rightarrow$ polarity) and the elongation d ($\rightarrow$ intensity of H bonding) influence the VLE behaviour.
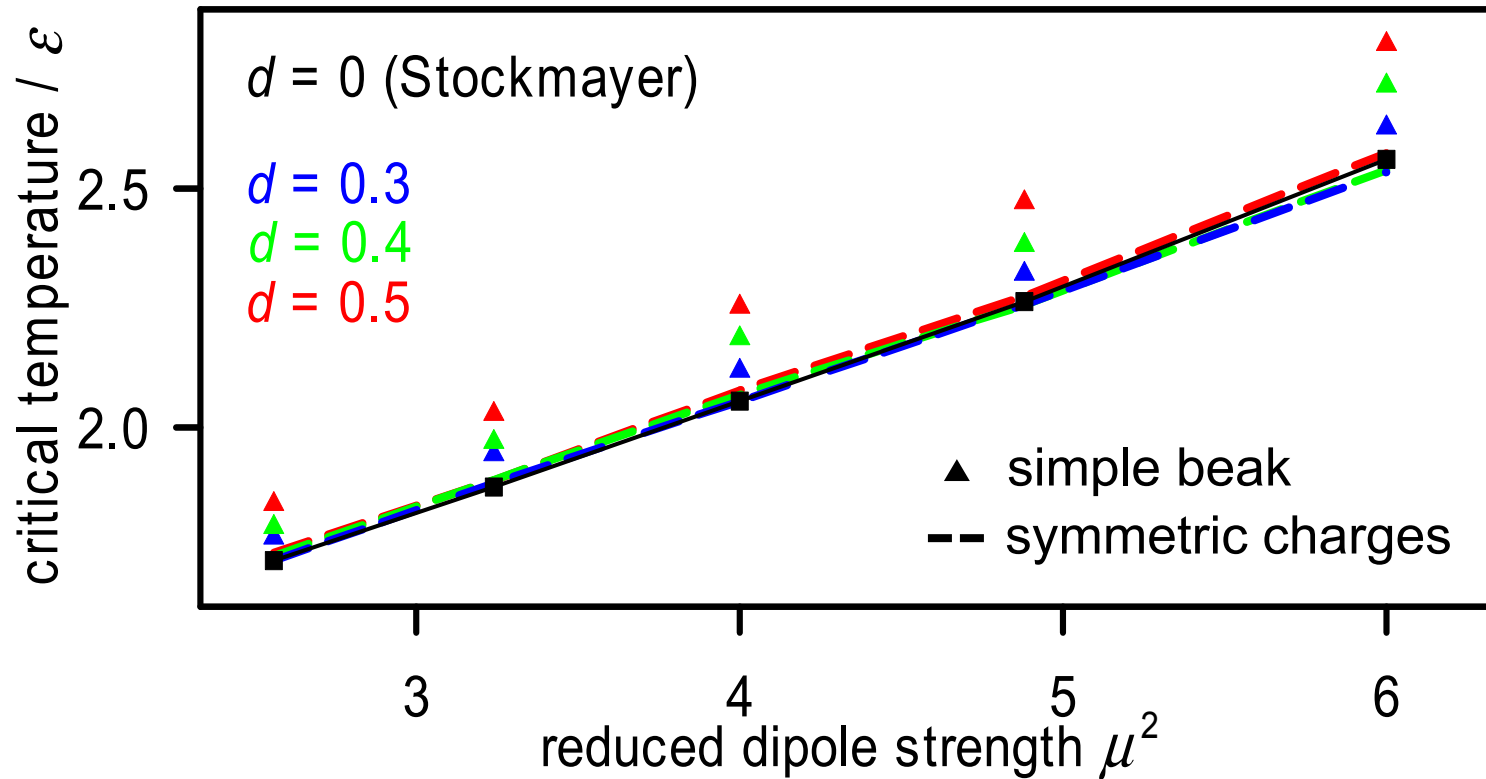
VLE for the model with symmetric charges

The symmetric model does not capture the thermodynamics of the H bond.

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H bonding and the critical temperature

The critical properties were estimated by fitting a Guggenheim type binodal:

Independent μ and HB effects are only present for the simple beak model.

Conclusion

- Polarity and H bonding are distinct phenomena. However, they are sufficiently related to be captured by a single modelling framework.

- Fluid phase equilibria of pure alcohols and mixtures are reliably reproduced using beak-shaped models for the OH group (Schnabel).

- By simulating the OH group (simple beak "fluid") without a rest, it is shown that point charge models can adequatetly cover polarity and hydrogen bonding as related, but distinct effects.

- The geometry of the beak-shaped model makes sense. If it is further simplified such that q^+ and q^- are equidistant from the LJ centre, the H bonding effects become entirely subordinated to those of the dipole.

- Water may be an exception …