Molecular modelling and simulation of hydrogen bonding fluids

Martin Horsch, Alptekin Celik and Hans Hasse

Lehrstuhl für Thermodynamik (LTD)
Technische Universität Kaiserslautern

Computational Molecular Engineering

Rostock, 27th March 13

Second Symposium
Thermophysical Properties for Technical Thermodynamics

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 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):

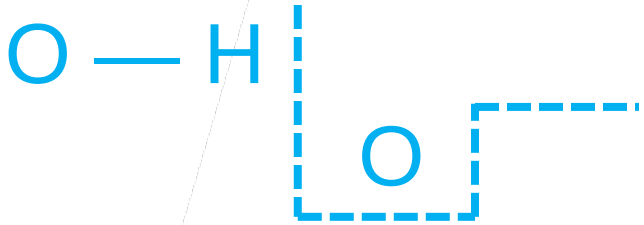
“The hydrogen bond is an attractive interaction … from a molecule … X—H in which X is more electronegative than H, and … in which there is evidence for bond formation.”

“The forces involved … include

- those of an electrostatic origin,
- those arising from … partial covalent bond formation …,
- and those originating from dispersion.”

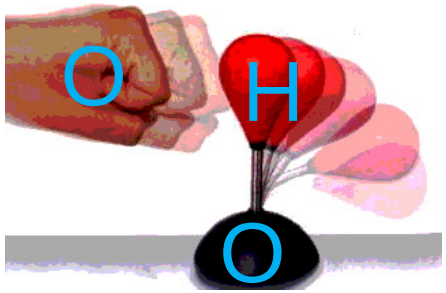
Molecular modelling approaches for H···O

short-range square well

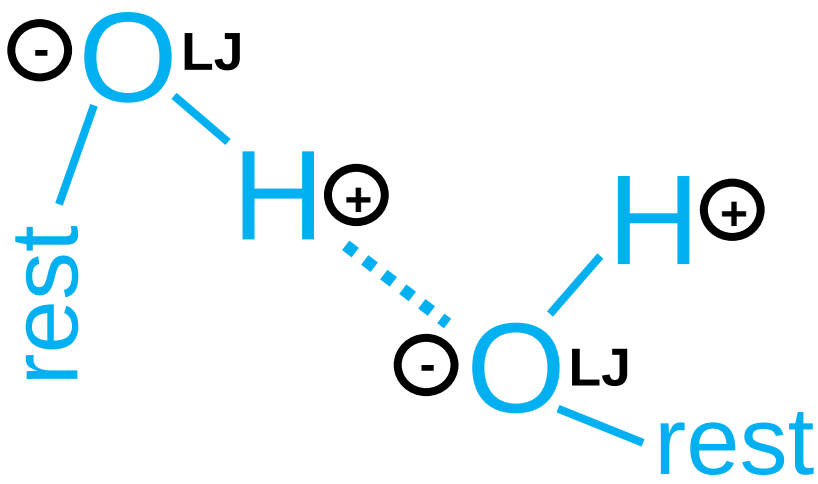


polarizable models

internal degrees of freedom



simple approach

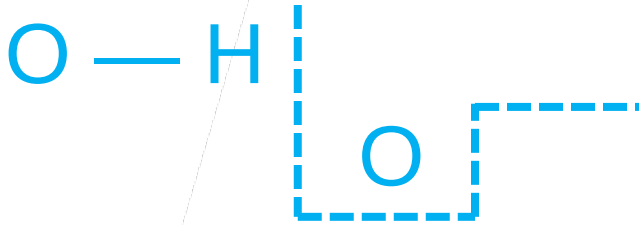


Oxygen: LJ concentric with negative charge

Hydrogen: Positive partial charge (no LJ)

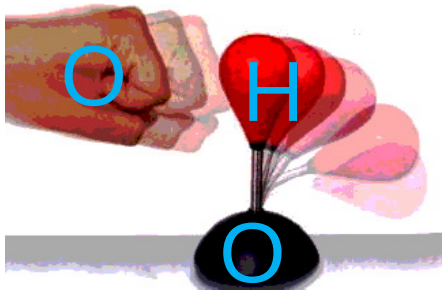
Molecular modelling approaches for H···O

short-range square well

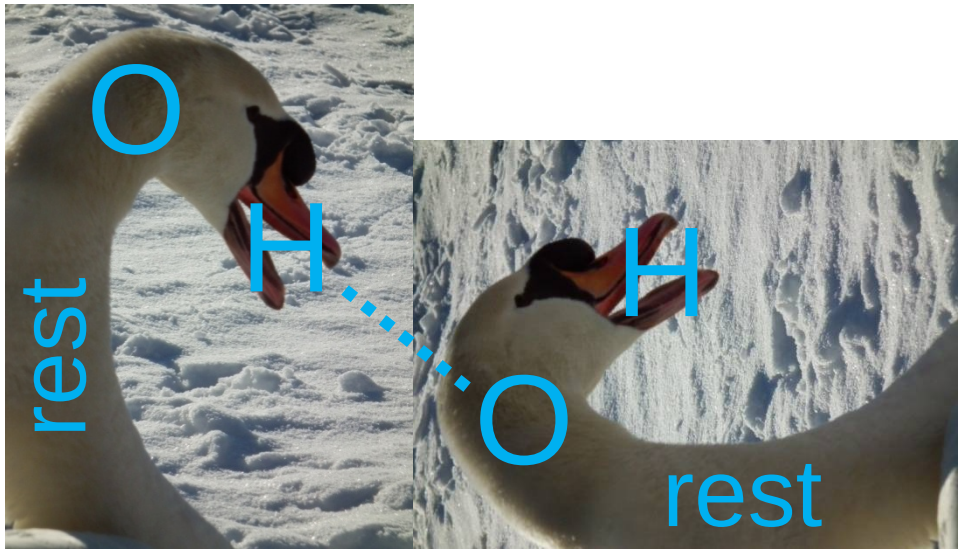


polarizable models

internal degrees of freedom



simple “beak” approach



Oxygen: LJ concentric with negative charge

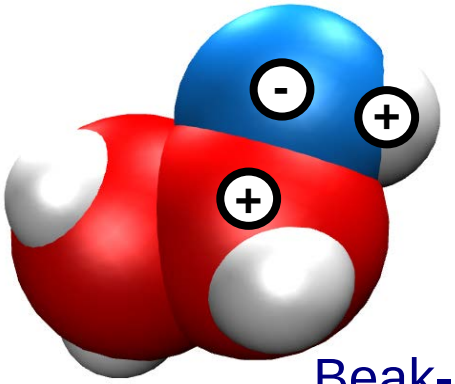
Hydrogen: Positive partial charge (no LJ)

Simple beak-shaped hydroxyl group model

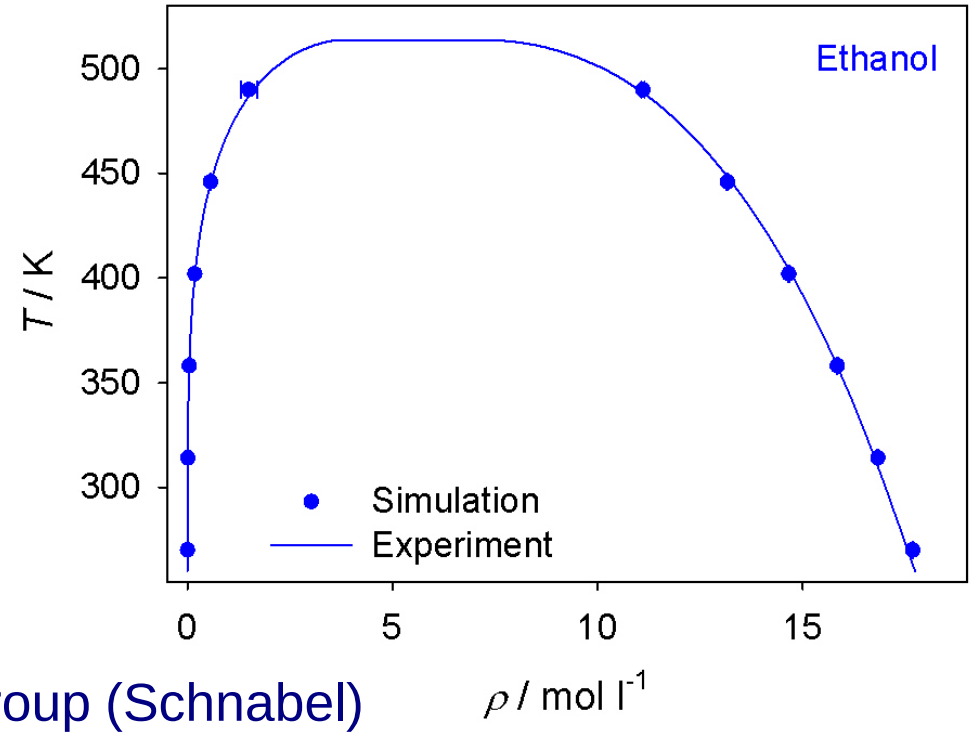
Ethanol:

- three LJ interaction sites
- three point charges

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



Beak-like OH group (Schnabel)

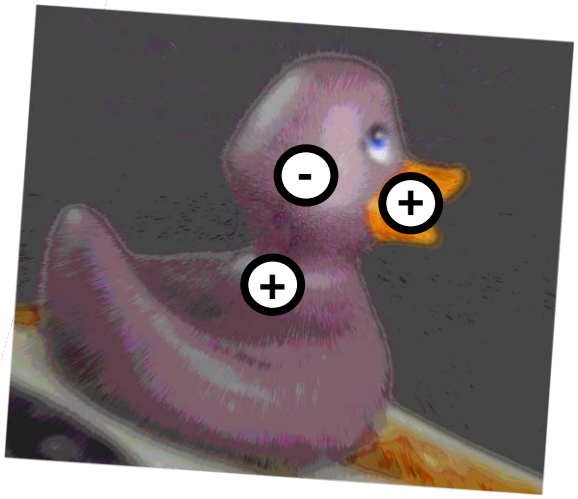


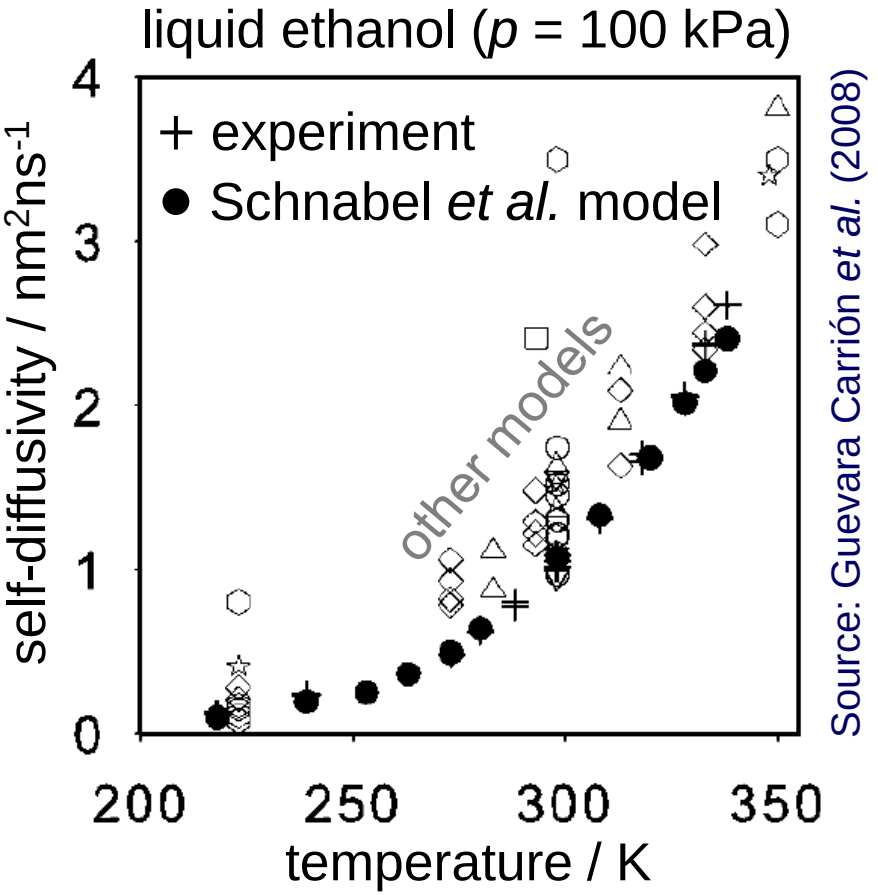
This approach is also valid for methanol and mixtures of H bonding fluids.

Simple beak-shaped hydroxyl group model

Ethanol:

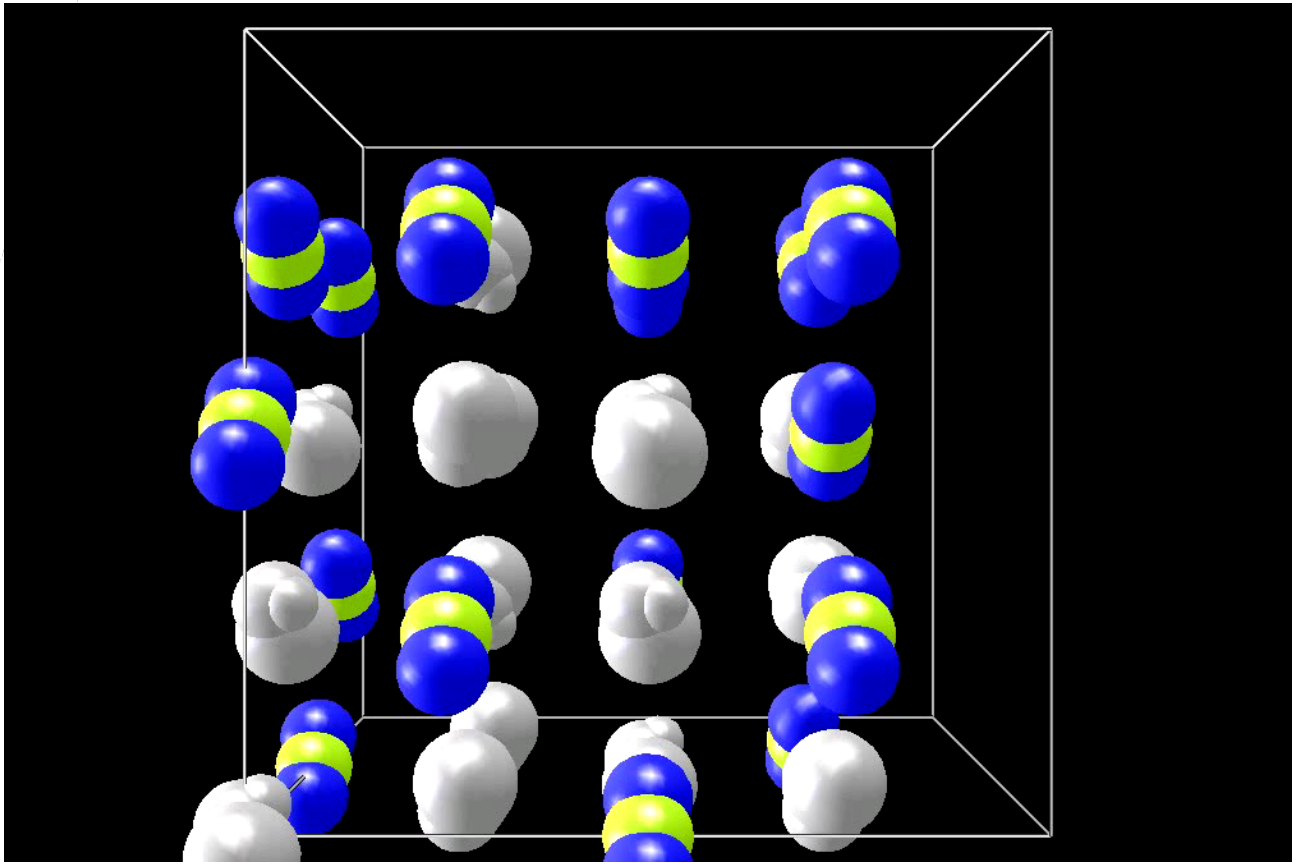
- three LJ interaction sites
- three point charges





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

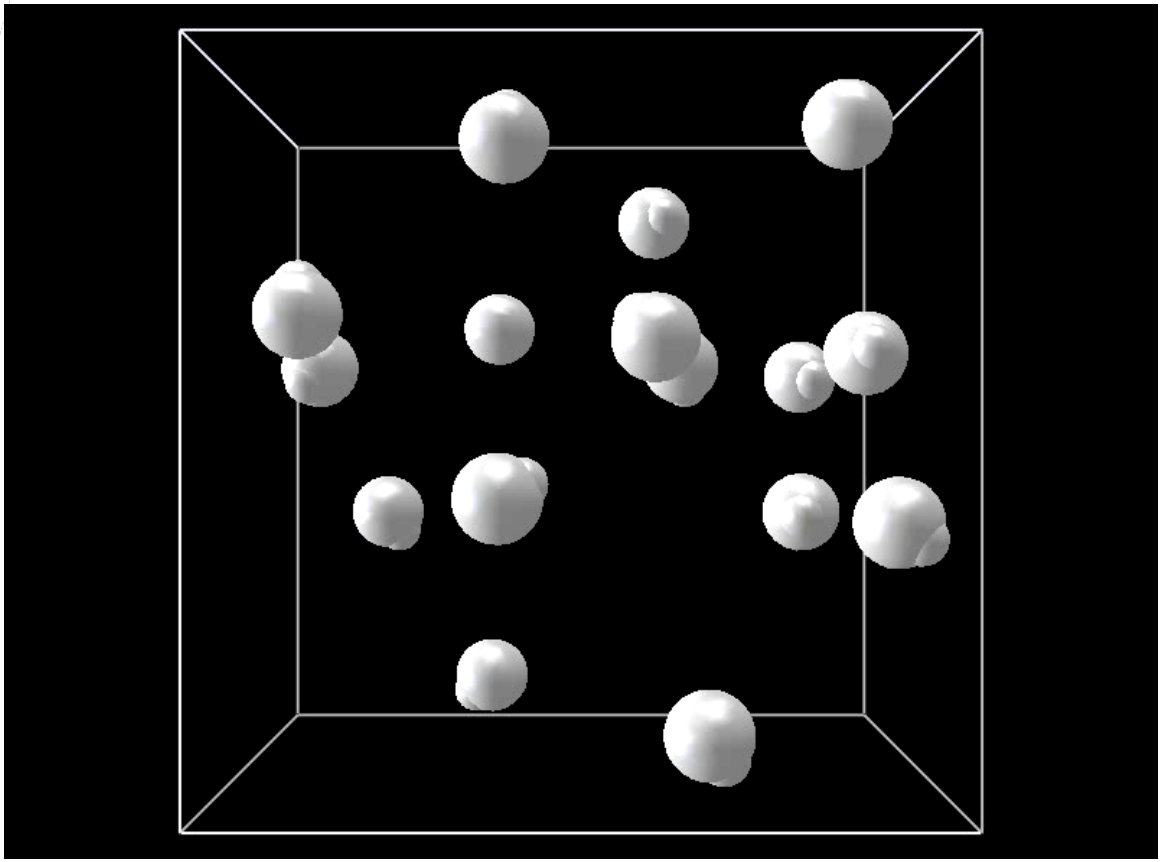
Hydrogen bonding in molecular simulation



350 K
100 kPa

equimolar mixture of methanol and carbon dioxide

Hydrogen bonding in molecular simulation



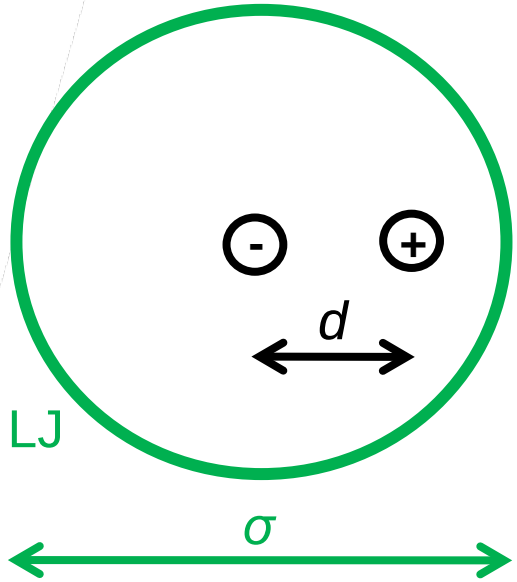
350 K
100 kPa

equimolar mixture of methanol and carbon dioxide

Zoom in: Point charge models of H bonding

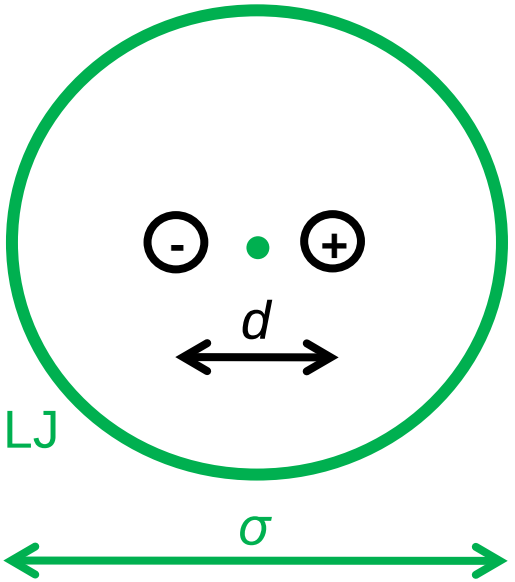
The Stockmayer dipole is decomposed into two separate point charges:

beak fluid



dipole $\mu = dq$

symmetric charges

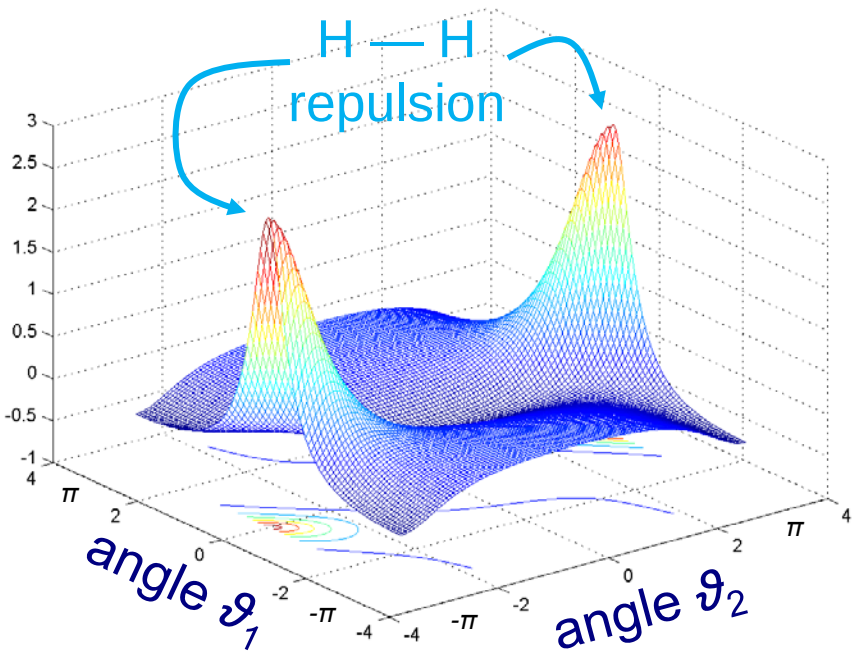


reflects structure of the OH group

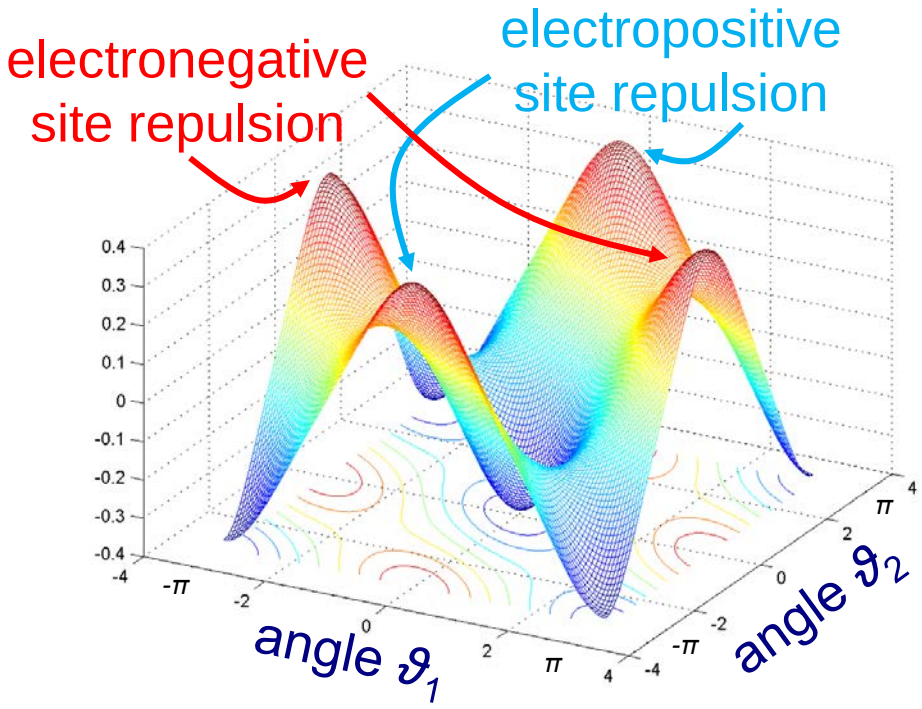
electronegative site resembles proton

Potential energy surface

Electrostatic contribution to the dimer bond energy:

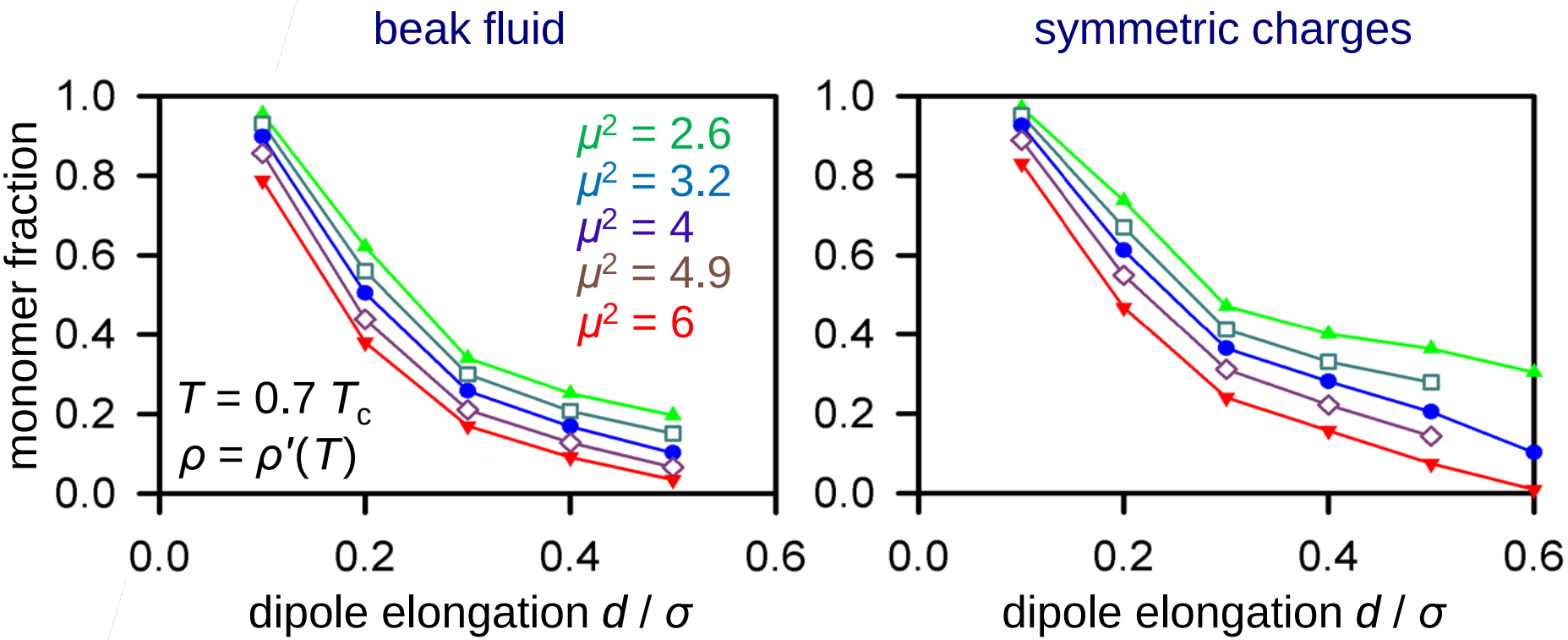


beak fluid



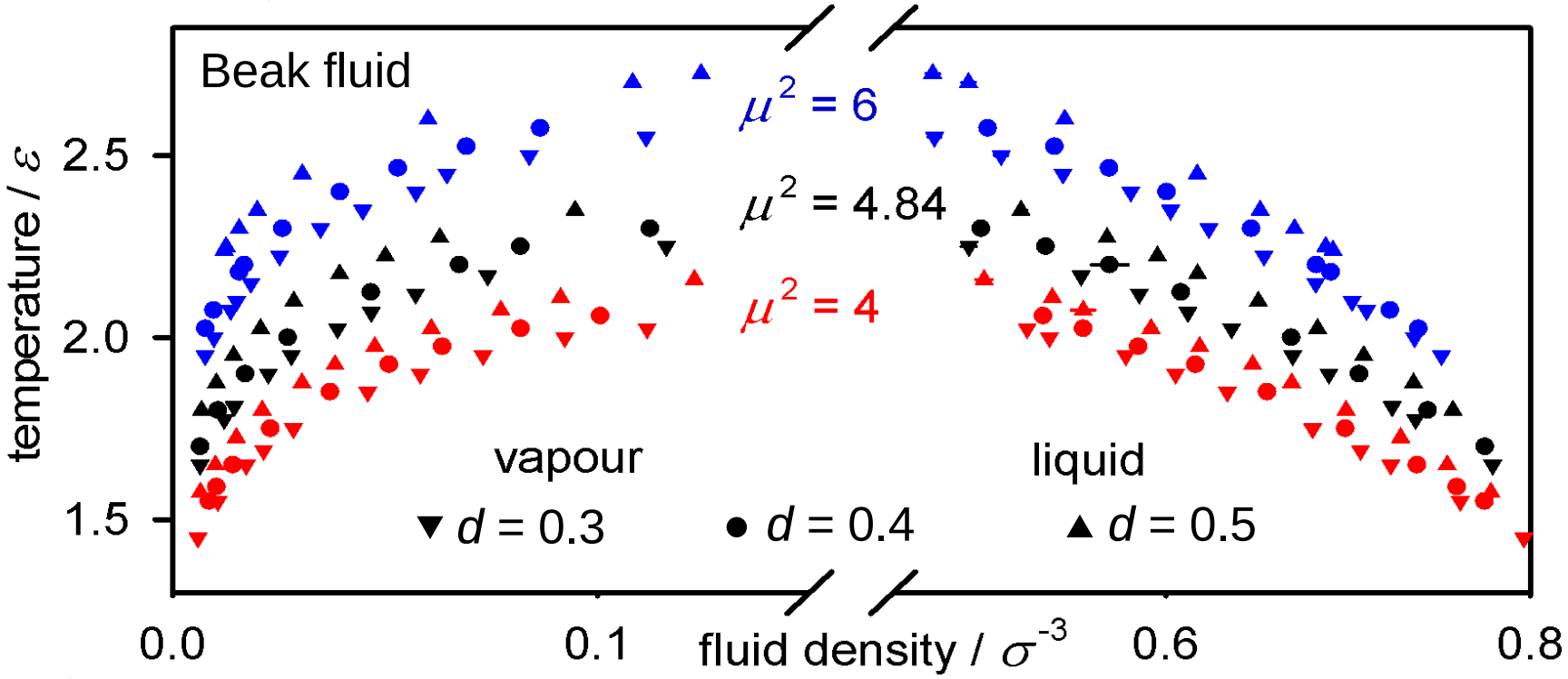
symmetric charges

Hydrogen bonds in the liquid phase



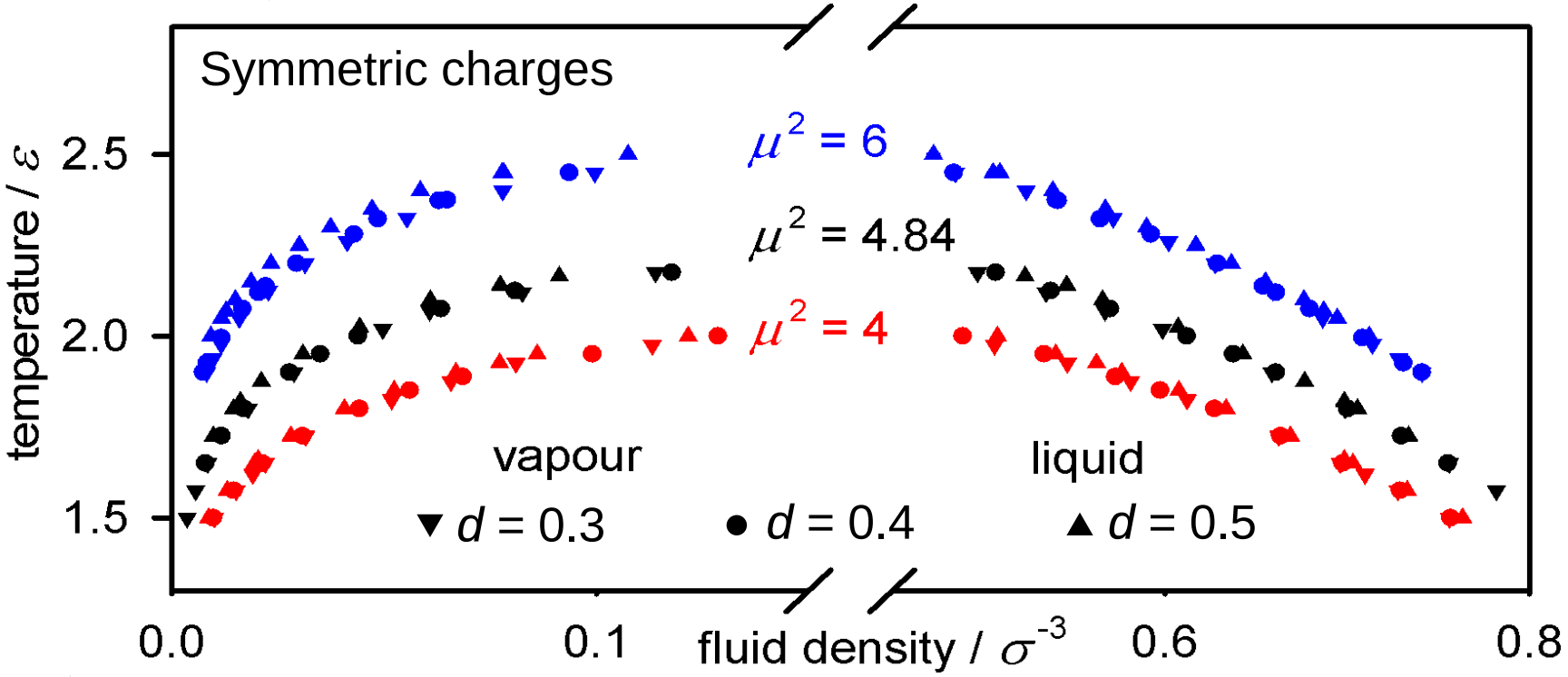
As expected, hydrogen bonding depends significantly on the distance between the partial charges (and on the dipole) for both model classes.

Vapour-liquid equilibria



As desired, both the dipole strength μ^2 (→ polarity) and the elongation d (→ intensity of H bonding) influence the VLE behaviour.

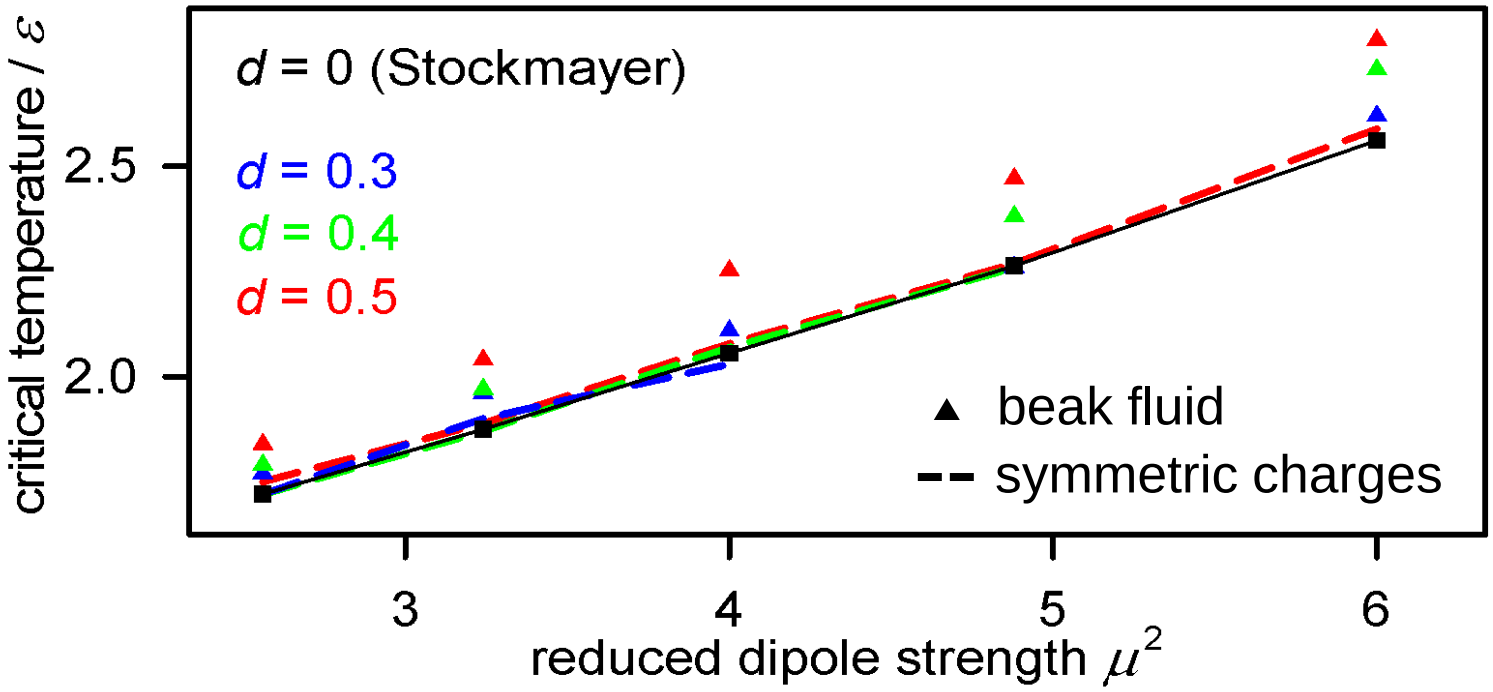
Vapour-liquid equilibria



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

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 (“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 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.