Molecular simulation of dispersed fluid phases and H bonding fluids

Martin Horsch, Steffen Reiser, Stephan Werth, and Hans Hasse

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Dispersed fluid phases in equilibrium

- Droplet + metastable vapour
Dispersed fluid phases in equilibrium

- Droplet + metastable vapour

Spinodal limit: For the external phase, metastability breaks down.
Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets

Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).
Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets

Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

At the spinodal, the results suggest that $R_\gamma = 2\gamma / \Delta p \to 0$.

This implies

$$\lim_{R_\gamma \to 0} \gamma = 0,$$

as conjectured by Tolman (1949) …
Surface tension from molecular simulation

Integral over the pressure tensor

Test area method:
Small deformations of the volume

Mutually contradicting simulation results!

(Source: Sampayo et al., 2010)

LJSTS fluid ($T = 0.8 \epsilon$)

$N_{\text{liq}}$
Analysis of radial density profiles

The thermodynamic approach of Tolman (1949) relies on effective radii:

- Equimolar radius $R_\rho$ (obtained from the density profile) with
  \[
  \Gamma = \int_0^{R_\rho} dR \ R^2 [\rho(R) - \rho'] + \int_{R_\rho}^{\infty} dR \ R^2 [\rho(R) - \rho''] = 0
  \]
- Laplace radius $R_\gamma = 2\gamma/\Delta \rho$ (defined in terms of the surface tension $\gamma$)

Since $\gamma$ and $R_\gamma$ are under dispute, this set of variables is inconvenient here.
Analysis of radial density profiles

Various formal droplet radii can be considered within Tolman’s approach:

- Equimolar radius $R_\rho$ (obtained from the density profile)
- Capillarity radius $R_\kappa = 2\gamma_\infty/\Delta p$ (defined by the planar surface tension $\gamma_\infty$)
- Laplace radius $R_\gamma = 2\gamma/\Delta p$ (defined by the curved surface tension $\gamma$)

The capillarity radius can be obtained reliably from molecular simulation.

Approach: Use $\gamma/R_\gamma = \Delta p/2$ instead of $1/R_\gamma$, use $R_\kappa = 2\gamma_0/\Delta p$ instead of $R_\gamma$. 

LJTS fluid $T = 0.75 \varepsilon$
Extrapolation to the planar limit

Radial parity plot

- The magnitude of the excess equimolar radius is consistently found to be smaller than $\sigma / 2$.

- This suggests that the curvature dependence of $\gamma$ is weak, i.e. that the deviation from $\gamma_\infty$ is smaller than 10% for radii larger than 5 $\sigma$.

- This contradicts the results from the virial route and confirms the grand canonical and test area simulations.
Gas bubbles in equilibrium

- 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 $R_y$ diverges.
Interpolation to the planar limit

- **Convention**: Negative curvature (bubbles), positive curvature (droplets).

- Properties of the planar interface, such as its Tolman length, can be obtained by interpolation to zero curvature.

- A positive slope of $\Delta p/2R_\rho$ over $1/R_\rho$ in the Nijmeijer diagram corresponds to a *negative* $\delta$, on the order of $-0.1 \sigma$ here, conforming that $\delta$ is small.

- However, $R \to 0$ for droplets in the spinodal limit for the surrounding vapour (Napari et al.) implies $\gamma \to 0$. 

\[ \left( \frac{\Delta p}{2R_\rho} \right) / \varepsilon \sigma^{-2} \]
Finite size effects for planar liquid slabs

By simulating small liquid slabs, curvature-independent size effects can be considered.

As expected, the density in the centre of nanoscopic liquid slabs deviates significantly from that of the bulk liquid at saturation.
Curvature-independent size effect on $\gamma$

Surface tension for thin slabs:

Relation with $\gamma(R)$ for droplets?

Correlation: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$
Curvature-independent size effect on $\gamma$

Surface tension for thin slabs:

Relation with $\gamma(R)$ for droplets?

$\delta_0$ is small and probably negative

Malijevský & Jackson (2012):

$\delta_0 = -0.07$

“an additional curvature dependence of the $1/R^3$ form is required ...”

Correlation:

$$\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$$
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.”
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“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

O — H

simple approach

O — H

polarizable models

internal degrees of freedom

Oxygen: LJ concentric with negative charge

Hydrogen: Positive partial charge (no LJ)
Molecular modelling approaches for H···O

- short-range square well
- simple “beak” approach
- polarizable models
- internal degrees of freedom

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.

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

Liquid ethanol ($p = 100$ kPa)

This approach is also valid for methanol and mixtures of H bonding fluids.
Hydrogen bonding in molecular simulation

equimolar mixture of methanol and carbon dioxide
Hydrogen bonding in molecular simulation

equimolar mixture of methanol and carbon dioxide

350 K
100 kPa
Zoom in: Point charge models of H bonding

The Stockmayer dipole is decomposed into two separate point charges:

- **beak fluid (asymmetric)**
  - Reflects OH group structure
  - Dipole $\mu = dq$
  - $\sigma$ and $d$ are involved

- **symmetric charges**
  - Negative and positive sites are equal

LJ
Potential energy surface

Electrostatic contribution to the dimer bond energy:

H — H repulsion

electronegative site repulsion

electropositive site repulsion

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.

\[
T = 0.7 \; T_c \\
\rho = \rho'(T)
\]

\[
\mu^2 = 2.6 \\
\mu^2 = 3.2 \\
\mu^2 = 4 \\
\mu^2 = 4.9 \\
\mu^2 = 6
\]
As desired, both the dipole strength $\mu^2$ (→ polarity) and the elongation $d$ (→ intensity of H bonding) influence the VLE behaviour.
The symmetric model does not capture the thermodynamics of hydrogen bonding: Phase behaviour is controlled by polarity only.
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)

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 $p_c$.

(However, comparably poor for the liquid density at low temperatures …)
Modelling aqueous electrolyte solutions

Molecular models:
- Ions: 1 CLJ, 1 point charge
- Water: 1 CLJ, 3 partial charges

Literature models:
- Scattering of model parameters

Reference property:
- Density $\rho$

→ Large deviation from experimental data!

Parameters for Na$^+$:

\[
1.9 < \sigma_{\text{Na}^+} < 4.1
\]
\[
0.06 < \varepsilon_{\text{Na}^+} < 1068.8
\]
Parameter optimization for alkali halides

Adjustable parameters:
- Ions: 1 CLJ with 1 point charge (±1e): 2 parameters

Target:
- Reduced density for varying salinity at $T = 293\, \text{K}$, $p = 1\, \text{bar}$

\[
\rho^\text{%o} = \frac{\rho_{\text{solution}}}{\rho_{\text{pure solvent}}} = \rho^\text{%o} \left( \sigma_{\text{cat}}, \sigma_{\text{an}}, \epsilon_{\text{cat}}, \epsilon_{\text{an}}, x \right)
\]

Simulation conditions:
- Monte Carlo simulations
- SPC/E water model
- Simulation code: extended version of ms2
Reduced density over salt concentration

Reduced density of NaCl solutions ($T = 298$ K, $p = 1$ bar)

Sensitivity study:
- $\sigma_{\text{ion}}$ dominant
- $\epsilon_{\text{ion}}$ negligible

$$\rho^{\circ} = \rho^{\circ}(\sigma_{\text{cat}}, \sigma_{\text{an}}, x)$$

Adjustment:
$$m = \frac{d\rho^{\circ}}{dx} = \frac{d\rho^{\circ}}{dx}(\sigma_{\text{cat}}, \sigma_{\text{an}})$$
Aqueous electrolyte solutions: Overview

Reduced density \( (T = 293 \, \text{K}, \, p = 1 \, \text{bar}) \)

\[ \sigma_{\text{Li}} = 1.88 \, \text{Å} \]
\[ \sigma_{\text{Na}} = 1.89 \, \text{Å} \]
\[ \sigma_{\text{K}} = 2.77 \, \text{Å} \]
\[ \sigma_{\text{Rb}} = 3.26 \, \text{Å} \]
\[ \sigma_{\text{Cs}} = 3.58 \, \text{Å} \]

Anions

\[ \sigma_{\text{F}} = 3.66 \, \text{Å} \]
\[ \sigma_{\text{Cl}} = 4.41 \, \text{Å} \]
\[ \sigma_{\text{Br}} = 4.54 \, \text{Å} \]
\[ \sigma_{\text{I}} = 4.78 \, \text{Å} \]
Fine tuning of the molecular models

Adjustment of the LJ energy parameters $\epsilon_{\text{ion}}$ to the self-diffusion coefficient in solution ($T = 298$ K, $p = 1$ bar)

- Reasonable parameter range:
  $200$ K $\leq \epsilon_{\text{Br}^-} \leq 400$ K
- Similar dependence of $D_i$ on $\epsilon_i$ for all alkali and halide ions

(water model: SPC/E)
Fine tuning of the molecular models

Adjustment of the LJ energy parameters $\varepsilon_{\text{ion}}$ to the first peak in the radial distribution function ($T = 293$ K, $p = 1$ bar)

- Reasonable match: $\varepsilon_{\text{Br}^-} = 200$ K
- Final compromise: $\varepsilon_{\text{cat}} = \varepsilon_{\text{an}} = 200$ K

(water model: SPC/E)
Temperature dependence of the density
Predictions for aqueous solution \((T = 333 \text{ K}, p = 1 \text{ bar})\)

- Experimental data (this work)
- Simulation
Temperature dependence of the density

Predictions for aqueous solution ($T = 333\ K$, $p = 1\ bar$)

Graphs showing the temperature dependence of the density for various substances.
Non-aqueous electrolyte solutions (CH$_3$OH)

Molecular models:

- Ions
  - 1 CLJ
  - 1 point charge

- Methanol
  - 2 CLJ
  - 3 partial charges

Reference property:
- Reduced density
  $$\rho^\% = \frac{\rho_{\text{solution}}}{\rho_{\text{pure solvent}}}$$

Simulation:
- MC simulations at $T = 298$ K, $p = 1$ bar
Methanolic electrolyte solutions

Predictions ($T = 298\,\text{K}$, $p = 1\,\text{bar}$)

- Experimental data (this work)
- Simulation
Conclusion

• Mechanical and thermodynamic routes lead to contradicting results for the curvature dependence of the surface tension. Present results for the excess equimolar radius confirm the thermodynamic route.

• The surface tension of the dispersed liquid phase is reduced due to a curvature-independent effect which is present in planar slabs as well as spherical droplets.

• By simulating the beak fluid, i.e. the OH group without a rest, it is shown that point charge models can adequately cover polarity and hydrogen bonding as related, but distinct effects.

• Molecular models were developed for alkali and halide ions, which were fitted to aqueous electrolyte solution properties and correctly predict properties of non-aqueous solutions as well.