Interfacial properties of fluids by computational molecular engineering

Martin Horsch, Stefan Becker, Stephan Werth, and Hans Hasse
Technische Universität Kaiserslautern

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Computational molecular engineering

From Physics (qualitative accuracy)
- Physically realistic modelling of intermolecular interactions
- Separate contributions due to repulsive and dispersive as well as electrostatic interactions

To Engineering (quantitative reliability)
- No blind fitting, but parameters of effective pair potentials are adjusted to experimental data
- Physical realism facilitates reliable interpolation and extrapolation
Vapour-liquid equilibria: Grand Equilibrium

**Given:** Temperature $T$, liquid composition $x$

**First step:** $NpT$ simulation of the liquid phase

An estimate, which may deviate from $p^{\text{sat}}(T)$, is used for $p$ in this simulation. The chemical potential and its first and second derivatives with respect to pressure are determined.

**Second step:** Pseudo-$\mu VT$ vapour simulation

Grand-canonical simulation where the value of $\mu$ is determined on the fly from the pressure.

**Obtained:** Pressure $p$, vapour composition $y$
Vapour-liquid equilibria: Grand Equilibrium

- temperature
- liquid composition

- partial molar volumes
- chemical potentials

- pressure
- vapour composition
Simulation of bulk properties with ms2

Second virial coefficient

Thermal conductivity

Self-diffusion coefficient

Shear viscosity

ms2 is freely available for academic use – register at http://www.ms-2.de/

ms2par

ms2chart

ms2molecules
Scalable MD simulation with *ls1 mardyn*

Linked-cell data structure suitable for spatial domain decomposition:

Methods for heterogeneous or fluctuating particle distributions:

- adaptive cells
- *k*-d decomposition

(non-blocking, overlapping MPI send/receive operations)
Long-range correction: Planar geometry

Correction from the **density profile**, following Janeček (2006):

$$\Delta U_i = 2\pi \int_0^L dy \rho(y) \int_R^\infty dr \ u(r) r$$

with $R = \max(r_c, \Delta y)$

**Angle-averaging** expression for multi-site models (Lustig, 1988):

For complex geometries, a version of \textit{ls1} applies the fast multipole method.
MD simulation of nucleation

Yasuoka-Matsumoto method:
-Canonical MD simulation
-Limited time interval for nucleation
-Conditions change over time

Alternative approach:
-Grand-canonical MD simulation

Thermodynamic conditions of the supersaturated state are maintained.
Intervention rate and nucleation rate

Not all of the removed clusters would have grown to macroscopic size

\[ J = J_\theta q(\theta). \]

The probability for a droplet to grow from size \( \theta \) to infinity is

\[ q(\theta) = \frac{\int_1^\theta dn \exp\left(\frac{2F}{T}\right)}{\int_1^\infty dn \exp\left(\frac{2F}{T}\right)}, \]

and for the critical nucleus it is approximately \( q(n^*) \approx 1/2 \).
Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets

- Vrabec et al. (2006)
- Horsch et al. (2008)
- Napari et al. (2009)
- Capillarity, i.e. CNT

Down to 100 molecules: agreement with CNT ($y = y_0$).

At the spinodal, the results suggest that $R_y = 2y / \Delta \rho \to 0$. This implies

$$\lim_{R_y \to 0} y = 0,$$

as conjectured by Tolman (1949) ...
Tolman length in the planar limit

Radial parity plot

- The deviation between the equimolar radius and the capillarity radius is consistently found to be smaller than $\sigma / 2$.

- The curvature dependence of $\gamma$ is weak: The deviation from the planar surface tension is smaller than 10% for radii larger than 5 $\sigma$.

$\delta_0 = \lim_{\Delta \rho \to 0} \left( R_\kappa - R_\rho \right)$
Nanoscopic 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 $R_γ$ diverges.
A curvature-independent size effect

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: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$
Modelling hydrogen bonding fluids

Model parameters are adjusted to VLE data

vapour-liquid equilibrium

Source: Guevara Carrión et al. (2008)
Modelling hydrogen bonding fluids

- Simple "beak" approach

Oxygen: LJ with negative charge
Hydrogen: Positive charge (no LJ)

Graph: self-diffusivity vs. temperature for liquid ethanol ($\rho = 100$ kPa)

+ experiment
● Schnabel et al. model

Source: Guevara Carrión et al. (2008)

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Polarity and hydrogen bonding

\[ \text{temperature} / \varepsilon \]

\[ \text{fluid density} / \sigma^{-3} \]

\[ \mu^2 = 6 \quad \mu^2 = 4.84 \quad \mu^2 = 4 \]

vapour \quad liquid

\[ \nabla d = 0.3 \quad d = 0.4 \quad \Delta d = 0.5 \]
Surface tension of quadrupolar fluids

2CLJQ models:
- 2 LJ centres
- Quadrupole

Fit of parameters $\sigma$, $\varepsilon$, $L$, $Q$ to VLE data of 20 fluids by Stoll et al.

Deviation:
- $\delta \rho' \approx 1\%$
- $\delta P^{\text{sat}} \approx 5\%$
Multi-criteria model optimization

Two-centre LJ + quadrupole

Pareto front for carbon dioxide

$\gamma = A(1 - \frac{T}{T_c})^{1.24}$ with two parameters.
Adsorption at real component surfaces

**Titanium components**

- Covered by oxide layer
- Possibly rough and/or intentionally patterned surface
- Surface may be contaminated with organic matter

First step: Reliable molecular simulation of water adsorbed on a clean and planar surface.

CRC 926 MICOS Component Surfaces
Quantum mechanical simulation

Computation of the electrostatic potential:

-125 kJ/mol

Dry rutile surface

-33 kJ/mol

Physisorbed water

Chemisorbed water

VASP simulation parameters (structure optimization with PBE functional):

Plane-wave cutoff at 282 eV, k-point spacing 0.5 Å⁻¹, O s pseudopotential.
Influence of the water model

Available water models do not capture all properties equally well.

“In Olympic medalists” from benchmark of Vega and Abascal (2011)

|$T = 298$ K

In the present case, the choice of the water model is relatively insignificant.
Patterned surfaces: Wenzel state

According to Wenzel, the roughness factor

\[ f^{ro} = \frac{\text{actual surface area}}{\text{projected planar surface area}} \]

characterizes wetting of structured surfaces if the rough sites are entirely filled with liquid.

Wenzel's "law" assumes

\[ \cos \theta^{ro} = \frac{\gamma_{vs}^{ro} - \gamma_{ls}^{ro}}{\gamma_{vl}} = f^{ro} \cos \theta^{pl} \]

\[ = f^{ro} \left( \frac{\gamma_{vs}^{pl} - \gamma_{ls}^{pl}}{\gamma_{vl}} \right) = f^{ro} \cos \theta^{pl}. \]
Patterned surfaces: Contact line pinning

Epitaxial Cassie state

$LJTS$

$T = 0.8 \varepsilon$

$\theta_{pl} = 90^\circ$

Graph showing relationship between contact angle and ratio between droplet and pedestal radius.
Conclusion

• Computational molecular engineering combines massively-parallel molecular simulation with quantitatively reliable molecular modelling.

• Non-equilibrium MD simulation of large systems, employing Maxwellian daemons, yields insights on processes at interfaces, e.g. nucleation.

• For nanoscopic systems with interfaces, the size dependence of the surface tension is relevant. Beside Tolman's law for the influence of curvature, a curvature-independent size effect has to be considered.

• 2CLJ models from previous work predict the surface tension well, with $\delta \gamma \approx 20\%$. Multi-criteria optimization can further improve them.

• Phenomena at real component surfaces, such as contact line pinning and characterizing adsorbed organic matter, remain challenging.