Computational molecular engineering by massively-parallel molecular simulation

Martin Horsch, Wolfgang Eckhardt, Colin Glass, Christoph Niethammer, Gábor Rutkai, Jadran Vrabec, and Hans Hasse

TU Kaiserslautern, Engineering Thermodynamics (LTD)
TU München, Scientific Computing in Computer Science (SCCS)
High Performance Computing Centre Stuttgart (HLRS)
University of Paderborn, Thermodynamics and Energy Technology (ThEt)

Daresbury, Cheshire, 11th September 2014
CECAM Workshop
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
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
Molecular models of real fluids

Geometry
Bond lengths and angles

Electrostatics
Point polarities (charge, dipole, quadrupole): Position and magnitude

Dispersion and repulsion
Lennard-Jones potential: Size and energy parameters
Molecular dynamics with *ls1 mardyn*

**large systems 1: molecular dynamics**
Scalable data structures in *ls1 mardyn*

Linked-cell data structure suitable for spatial domain decomposition:

(non-blocking, overlapping MPI send/receive operations)
Scalable data structures in *ls1 mardyn*

Linked-cell data structure suitable for spatial domain decomposition:

Methods for heterogeneous or fluctuating particle distributions:
Long-range correction at planar interfaces

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):

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

For arbitrary geometries, FMM is implemented in a version of *ls1 mardyn*. 

Two-centre LJ fluid (2CLJ)

- Full correction term
- Centre-of-mass term
- Truncated potential

\[ \frac{\gamma}{\epsilon \sigma^{-2}} \]

\[ r_c / \sigma \]

\[ 2.5 \ 3 \ 3.5 \ 4 \ 4.5 \ 5 \]
Scalability of *ls1 mardyn* on *hermit* (HLRS)

**Strong scaling (Amdahl)**
- **Computing time per step / s**
- **Number of processes**
- **Molecules**: $2^{18}$, $2^{26}$
- **States**: bulk, droplet

**Weak scaling (Gustafson)**
- **Computing time per step / s**
- **Number of processes**
- **Molecules / process**: 1024
- **States**: linear scaling, bulk, liquid slab, droplet
MD world record on *SuperMUC* (LRZ)

Up to \( \mathcal{N} = 4 \cdot 10^{12} \) molecules on *SuperMUC*

weak scaling with 31.5 million molecules per core

![Graph showing weak scaling with 31.5 million molecules per core](image-url)
Free release of the *ls1 mardyn* program

Download *ls1 mardyn* on the [www.ls1-mardyn.de](http://www.ls1-mardyn.de) website.
Simulation of bulk properties with \textit{ms2}

\textbf{Second virial coefficient}

\textbf{Thermal conductivity}

\textbf{Self-diffusion coefficient}

\textbf{Shear viscosity}

\textit{ms2} is freely available for academic use: register at \url{www.ms-2.de}

\textbf{Vapour-liquid equilibria: Saturated densities and vapour pressures}
Grand equilibrium simulation

**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 $y$
Grand equilibrium simulation

- Temperature
- Liquid composition
- Partial molar volumes
- Chemical potentials
- Pressure
- Vapour composition
Parallel sampling of multiple Markov chains

- Initial configuration
- Equilibration
- Internal averaging over multiple MC runs

Strong scaling of ms2 for MC simulation

- 5488 molecules
- 2744 molecules
- 1372 molecules

Runtime per MC loop / s vs. number of parallel processes
Fluctuations and thermodynamics

From highly performant molecular simulations, not only ensemble averages, but also higher-order fluctuations are accurately determined.

**Massieu potential** \( \Phi = \frac{A}{T} = -\ln Z_{NVT} \)

**Higher-order derivatives** \( \Phi_{mn} = \left( \frac{\partial^{m+n} \Phi}{\partial \beta^m \partial \rho^n} \right) = \Phi_{mn}^{id} + \Phi_{mn}^{conf} \)

**Energy fluctuations** \( \Phi_{30}^{conf} = \frac{1}{NT^3} \left( \langle U_{pot}^3 \rangle - 3 \langle U_{pot}^2 \rangle \langle U_{pot} \rangle + 2 \langle U_{pot} \rangle^2 \right) \)

The derivatives of the Massieu potential can be applied for:

- Extrapolating simulation results (on the basis of less simulations)
- Parameterizing equations of state (further improving extrapolation)
Quantitatively reliable molecular modelling

ethylene oxide model by Eckl et al. (2008)

- sat. liquid density
- sat. vapour density
- second virial coefficient
- vapour pressure
- enthalpy of vapourization
- normal boiling temperature
- critical density
- critical temperature
- sat. liquid isobaric heat capac.
- sat. vapour isobaric heat capac.
- sat. liquid isothermal compress.
- sat. vapour isothermal compress.
- surface tension
- sat. liquid shear viscosity
- sat. vapour shear viscosity
- sat. liquid thermal conductivity
- sat. vapour thermal conductivity

deviation from reference / %
Molecular models of quadrupolar fluids

2CLJQ models:
• 2 LJ centres
• Quadrupole

Fit of parameters $\sigma$, $\varepsilon$, $L$, $Q$ to VLE data of 29 fluids by Stoll et al.

Deviation:
• $\delta \rho' \approx 1 \%$
• $\delta P^{\text{sat}} \approx 5 \%$

No interfacial properties were considered for the parameterization.
Surface tension of real fluids

2CLJQ models:
- 2 LJ centres
- Quadrupole

Fit of parameters $\sigma$, $\varepsilon$, $L$, $Q$ to VLE data of 29 fluids by Stoll et al.

Deviation:
- $\delta \rho' \approx 1 \%$
- $\delta P_{\text{sat}} \approx 5 \%$
Modelling by multi-criteria optimization

Surface tension: Critical scaling $\gamma = A(1 - T/T_c)^{1.24}$ with two parameters.
Modelling by multi-criteria optimization

Multi-criteria optimization requires massively-parallel molecular modelling.
MD simulation of fluids at interfaces

- Adsorption (fluid-fluid and fluid-solid)
- Vapour-liquid surface tension
- Curved vapour-liquid interfaces
- Contact angle and contact line pinning

\[ T = 0.8 \varepsilon \]
\[ \theta_{pl} = 90^\circ \]
Thermodynamics of curved interfaces

- Droplet + metastable vapour
- Bubble + metastable liquid

Planar limit: The curvature changes its sign, and the radius diverges.

Large length and time scales required.
Transport at interfaces in nanofluidics

The accelerating force is only applied to the fluid molecules within a specified control volume.

It overcompensates the pressure drop, so that (equivalent) density, pressure, and chemical potential gradients are actually present.
From nanofluidics to microfluidics

Methane in graphite: \( T = 166 \) K; values of \( \eta \) and \( \xi \) from Wang et al.

![Graph showing slip velocity and flow velocity vs. channel width](image)

Methane flow in graphite: \( T = 166 \) K; values of \( \eta \) and \( \xi \) from Wang et al.

![Graph showing Darcy's law](image)
MD simulation of nucleation

Yasuoka-Matsumoto method:

- Canonical MD simulation
- Limited time interval for nucleation
- Conditions change over time
NEMD 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.
NEMD simulation of nucleation
Nucleation rates from NEMD simulation

Bridging large length and time scales is crucial for capturing rare events.

- Bridging large length and time scales is crucial for capturing rare events.

- Nucleation rates from NEMD simulation

- Chemical potential supersaturation

- Pressure supersaturation

- Classical theory (CNT)

- Present simulations

- Van Meel et al. (FFS)
Conclusion

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

- Performant and scalable molecular simulation codes were presented: *ls1 mardyn* for large heterogeneous systems, *ms2* for bulk properties.

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

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

- The transition from nano- to microsystems for the length and time scale can now be accomplished by highly performant MD simulation.