Computational molecular engineering by large-scale molecular dynamics simulation

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Agra, India, 22nd February 2015
Indo-German Frontiers of Engineering
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

Bottom up ➔

Top down ←
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

Bottom up ➔

Top down

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Molecular modelling of fluids

Geometry
Bond lengths and angles

Dispersion and repulsion
Lennard-Jones potential:
Size and energy parameters
Molecular modelling of fluids

Geometry
Bond lengths and angles

Dispersion and repulsion
Lennard-Jones potential:
Size and energy parameters

Electrostatics
Point polarities
(charge, dipole, quadrupole):
Position and magnitude
Quantitatively reliable molecular models

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 capacitance
- sat. vapour isobaric heat capacitance
- sat. liquid isothermal compressibility
- sat. vapour isothermal compressibility
- surface tension
- sat. liquid shear viscosity
- sat. vapour shear viscosity
- sat. liquid thermal conductivity
- sat. vapour thermal conductivity

deviation from reference / %

uncertainty of reference
molecular model
Molecular models: Parameterization

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.
Molecular models: Prediction and validation

2CLJQ models:
- 2 LJ centres
- Quadrupole

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

Deviation:
- $\delta\rho' \approx 1\%$
- $\delta P_{\text{sat}} \approx 5\%$
Molecular models: Multicriteria optimization

Pareto optimality criterion

Pareto set for carbon dioxide

Multicriteria optimization requires massively-parallel molecular modelling.
Separation of length scales for simulation

For planar interfaces:

Long-range correction from the density profile, following Janeček.

Long range (correction)

Angle-averaging expression for multi-site models, following Lustig.

Angle-averaging

Full evaluation of all pairwise interactions is too expensive ...

... instead, short-range interactions are evaluated for neighbours.
Separation of length scales for simulation

For planar interfaces:

**Long-range correction** from the density profile, following Janeček.

![Two-centre LJ fluid (2CLJ)](image)

**Angle-averaging** expression for multi-site models, following Lustig.

For arbitrary geometries, e.g. the fast multipole method can be employed.
Scalable data structures for large systems

Linked-cell data structure suitable for spatial domain decomposition:

Methods for heterogeneous or fluctuating particle distributions:

(non-blocking, overlapping MPI send/receive operations)
Large systems in molecular dynamics

Download ls1 mardyn on the www.ls1-mardyn.de website.

released as free software (BSD license)
Scaling on *hermit* at HLRS, Stuttgart

**Strong scaling (Amdahl)**

- Linear scaling
- Computing time per step vs. number of processes

**Weak scaling (Gustafson)**

- Linear scaling
- Computing time per step vs. number of processes

- 1024 molecules / process
- Liquid slab
- Droplet
Scaling on SuperMUC at LRZ, Garching

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

weak scaling with 31.5 million molecules per core
Non-equilibrium molecular dynamics
Non-equilibrium molecular dynamics

Non-equilibrium MD (NEMD): Process is simulated in a steady state.

Requires the intervention of a regulatory mechanism (daemon)

Example: Grand canonical MD simulation with McDonald's daemon
Challenge: Realistic fluid-solid contact

- Adsorption and wetting
- Contact angle and line pinning
- Lubrication and heat transfer
- Modelling of cutting liquids
- Tribological effects
Challenge: Realistic fluid-solid contact

Wetting and contact line pinning

\[ T = 0.8 \varepsilon \]
\[ \theta^\text{pl} = 90^\circ \]

Ratio between droplet and pedestal radius vs. contact angle

CRC 926 MICOS Component Surfaces
Computational Molecular Engineering

Simulation
- ls1 mardyn
- Scale-bridging MD simulation
- Heterogeneous systems

Processes
- Non-equilibrium MD
- Phase transitions
- Nanofluidics

Interfaces
- Long-range correction
- Interfacial tension
- Adsorption

Quantitatively reliable molecular modeling