Molecular simulation of real fluids in nanofiltration membranes

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Nanoporous membranes: Molecular model

Optimized potential parameters for graphite:

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Structure</th>
<th>$T_g$ (°C)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrimid® 5218</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>323</td>
<td>1.22</td>
</tr>
<tr>
<td>P84</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>315</td>
<td>1.31</td>
</tr>
</tbody>
</table>


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<table>
<thead>
<tr>
<th>Cutoff</th>
<th>Attraction</th>
<th>Repulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = 2.0$ Å (1.8 Å)</td>
<td>$\mu = 2.275$ Å$^{-1}$ (2.2119 Å$^{-1}$)</td>
<td>$\lambda = 3.587$ Å$^{-1}$ (3.4879 Å$^{-1}$)</td>
</tr>
<tr>
<td>$S = 2.35$ Å (2.1 Å)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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RDF
rescaled
Tersoff

Interatomic distance / Å

1.35 1.40 1.45 1.50
Dispersive fluid-wall interaction

Both fluid-fluid and fluid-wall dispersion is modelled by the Lennard-Jones potential … two effective interaction parameters:

\[ \sigma_{fw} = \eta \cdot \sigma \]
\[ \varepsilon_{fw} = \xi \cdot \varepsilon \]

graphite / methane

\[ \xi = 0.075; \eta = 1 \]
\[ \xi = 0.160; \eta = 1 \]
\[ \xi = 0.353; \eta = 0.947 \]
\[ \xi = 0.497; \eta = 0.957 \]

\( T = 166.3 \, \text{K} \)
Vapour-liquid interfaces under confinement

Tolman equation (cylindrical)

\[ \frac{\gamma_0}{\gamma} = 1 + \frac{\delta}{R} + O(\delta^2 R^{-2}) \]

Young-Tolman equation

\[ \frac{1}{\cos \theta} = \frac{\gamma_0}{\Delta \gamma_s} + \frac{2\delta}{h} + O(\delta^2 h^{-2}) \]
Grand canonical MD simulation

- Specification of $\mu$, $V$, and $T$

- Test insertions and deletions of single particles in alternation with MD steps:

$$P_{\text{ins}} = \min \left[ 1, \exp \left( \frac{\mu - \Delta U_{\text{pot}}}{T} \right) \frac{V}{\Lambda^3 (N + 1)} \right]$$

$$P_{\text{del}} = \min \left[ 1, \exp \left( \frac{-\mu - \Delta U_{\text{pot}}}{T} \right) \frac{1}{\Lambda^3 \rho} \right]$$

Application: Chemical potential gradient induced Poiseuille flow

Graphite + argon (LJTS), $T = 0.85 \varepsilon/k$, $\mu = \mu_s(T)$

$h = 24 \sigma$

saturated bulk
Explicit compensation of the pressure drop

Opposite forces act on fluid molecules and wall atoms in the entire system.

Non-equilibrium molecular dynamics (NEMD) of a stationary flow.

Periodic boundary condition: No actual gradients. Friction and force cancel out exactly.
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.
Viscous and diffusive mass transfer

Following the approach of Travis and Gubbins, the transport diffusion coefficient $D_t$ consists of contributions from two different mechanisms:

$$J_i = -D_t \nabla \rho_i = -L_s \nabla \left( \frac{\mu_i}{T} \right) - D'_t \nabla \rho$$

**Diffusive transport**: Self-diffusivity $D_s$, expressed above in terms of the Onsager type coefficient $L_s$, caused by the random thermal movement of individual molecules.

**Viscous transport**: Ordered collective motion of the molecules due to a pressure gradient, which can be understood in terms of a fluid continuum.

In principle, equilibrium MD computes $D_s$, whereas NEMD yields $D_t$. 
Avendaño’s dæmon

The self-diffusivity can be determined by NEMD if a gradient in $\mu$ (→ diffusive transport) is present without a pressure gradient (→ viscous transport).

Actually identical fluid molecules are assigned different labels (blue or green “colour”) and accelerated in opposite directions by Avendaño’s dæmon.
Entrance effects

By comparison between the flow in

- an infinite (i.e. periodic) channel
- an “open” system including a bulk section ...

... the influence of the channel entrance and exit regions on the overall effective diffusivity can be isolated.
Velocity profile and boundary slip

Methane in graphite

$T = 166$ K
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](chart1.png)

![Graph showing $-\frac{dp}{dz} v_z^{-1}$ vs. channel width](chart2.png)

Darcy's law

$\eta$ and $\xi$ from Wang et al.
Nanopore with a patterned surface

14.5 \sigma

12 \sigma

11 \sigma

rigid wall atoms

coupling region

56 \sigma

64.5 \sigma

fluid particles
Rotation inside the cavity

... induced by Poiseuille flow:

\[
\langle J \rangle = \frac{1}{N} \sum_i r_i \times p_i
\]

2D
\[
\nu = 0.8 \\
C = 0.5
\]
Oliver et al. (2006)

3D
\[
\nu = 0.82 \\
C = 0.5
\]
Hsiang et al. (present)
Massively parallel molecular dynamics

weak and strong scaling of the *ls1 mardyn* program

homogeneous truncated-shifted LJ system

HLRS nehalem cluster Baku/Laki

methane + graphite

2,000, 4,000, 8,000, and 16,000 particles per process

number of processes

computing time in units of s

speedup

50 100 150 processes
Conclusion

⇒ The relation between the fluid-wall dispersive energy and the contact angle in a slit pore was established using a Lennard-Jones model.

⇒ Planar Poiseuille flow can be investigated by non-equilibrium MD simulation, e.g. by DCV-GCMD, dp compensation, and DG-NESSMD.

⇒ Darcy’s law was found to hold down to the molecular length scale. Significant boundary slip was present for diameters below 100 nm.

⇒ Avendaño’s dæmon makes self-diffusion accessible to NEMD for confined systems, for which the Green-Kubo formalism is less suitable.

⇒ Massively parallel MD (e.g. with ls1 mardyn) promises to make a molecular analysis of microfluidics feasible within the present decade.