Molecular simulation of real fluids in nanofiltration membranes

Bundesministerium für Bildung und Forschung
DAAD Deutscher Akademischer Austausch-Dienst German Academic Exchange Service
Computational Molecular Engineering

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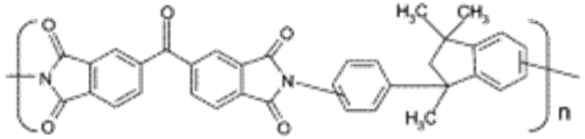
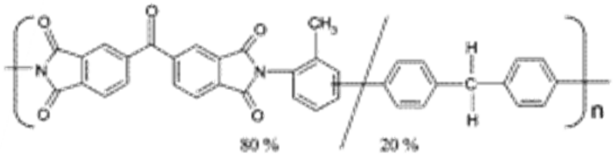
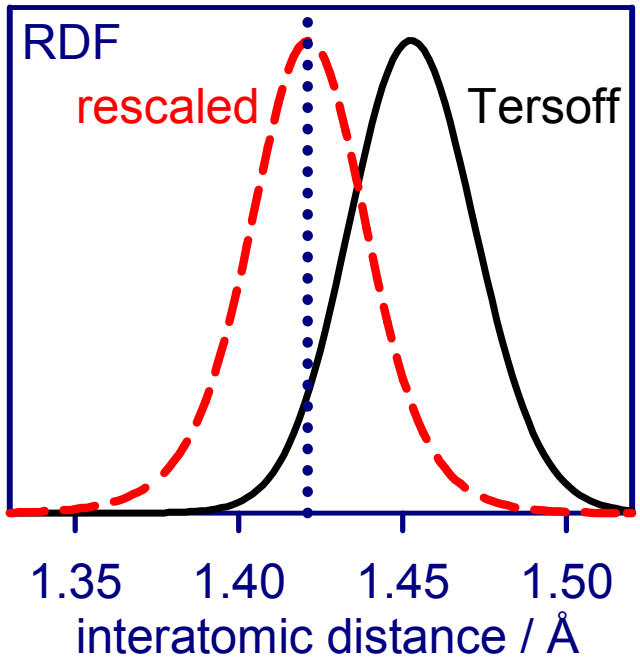
Nanoporous membranes: Molecular model

Material	Chemical Structure	T_g (°C)	Density (g/cm³)
Matrimid® 5218		323	1.22
P84		315	1.31

Tin *et al.* (2004), Ind. Eng. Chem. Res. **43**: 6467.



Optimized potential parameters for graphite:

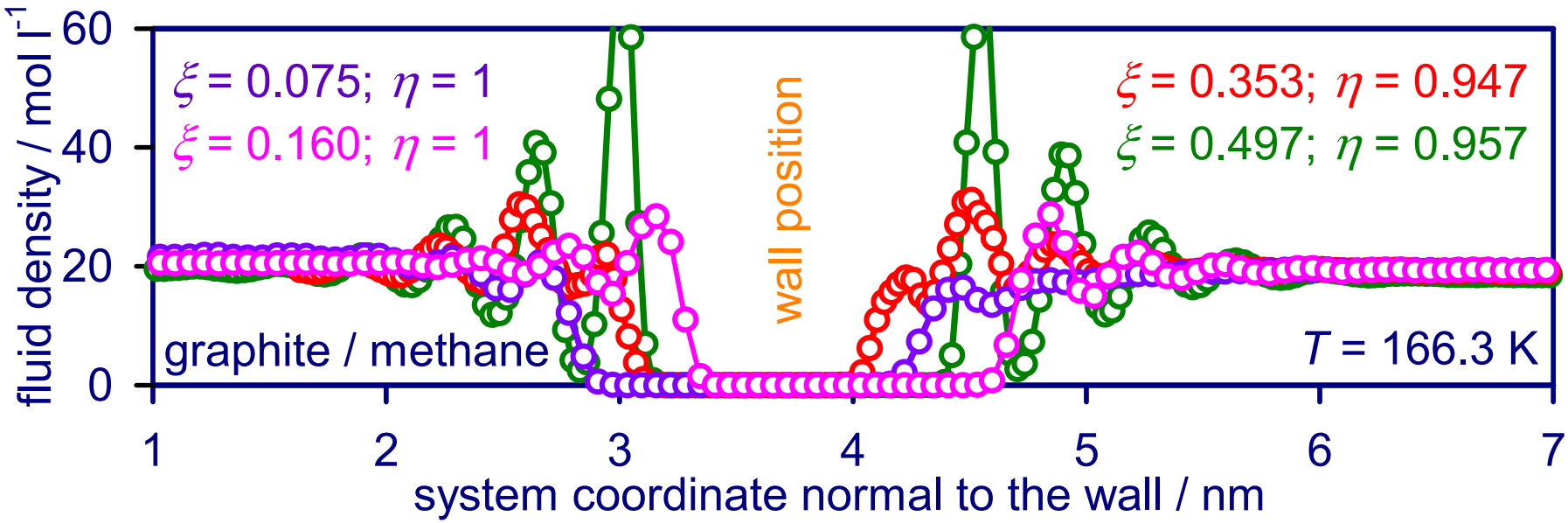
Cutoff	Attraction	Repulsion
R = 2.0 Å (1.8 Å) S = 2.35 Å (2.1 Å)	μ = 2.275 Å^{-1} (2.2119 Å^{-1})	λ = 3.587 Å^{-1} (3.4879 Å^{-1})

Dispersive fluid-wall interaction

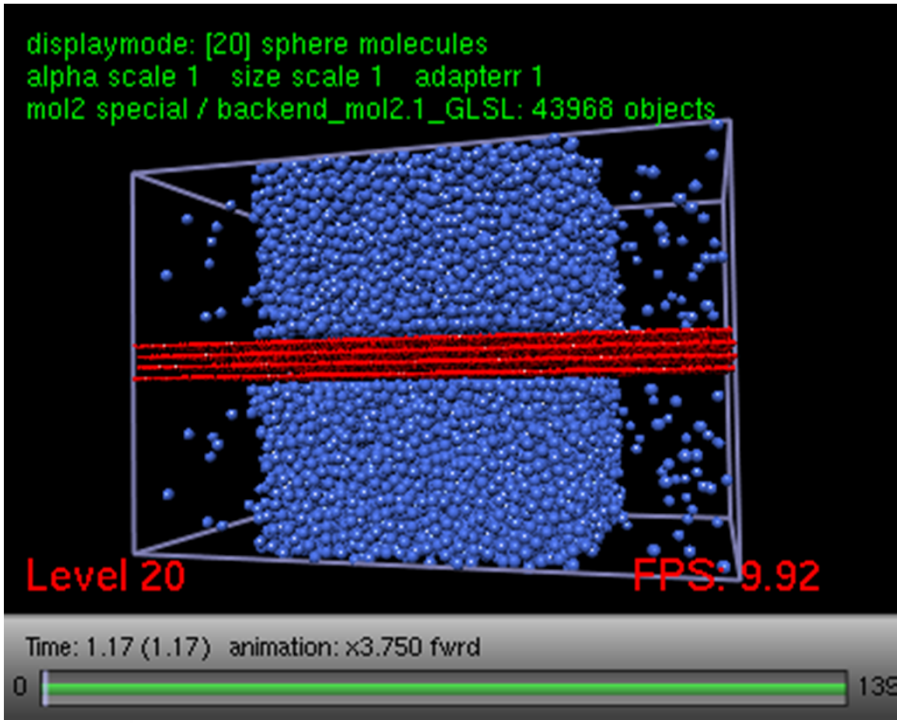
Both fluid-fluid and fluid-wall dispersion is modelled by the Lennard-Jones potential … two effective interaction parameters:

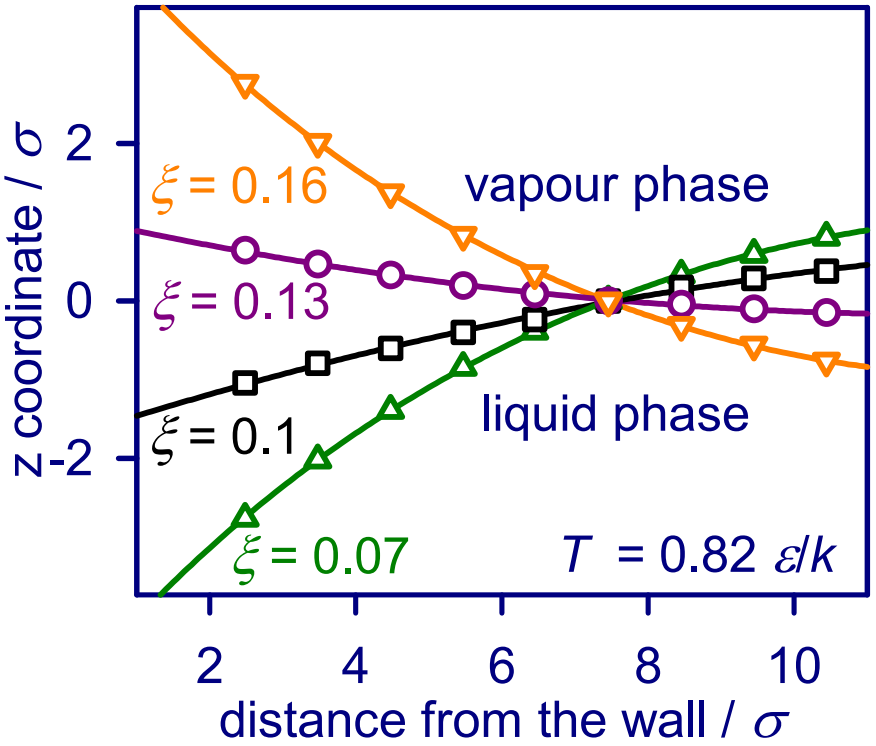
unlike LJ size parameter $\sigma_{fw} = \eta \cdot \sigma$

unlike LJ energy parameter $\varepsilon_{fw} = \xi \cdot \varepsilon$



Vapour-liquid interfaces under confinement





Tolman equation (cylindrical)

$$\frac{\gamma_0}{\gamma} = 1 + \frac{\delta}{R} + O\left(\delta^2 R^{-2}\right)$$

Young- Tolman equation

$$\frac{1}{\cos\theta} = \frac{\gamma_0}{\Delta\gamma_s} + \frac{2\delta}{h} + O\left(\delta^2 h^{-2}\right)$$

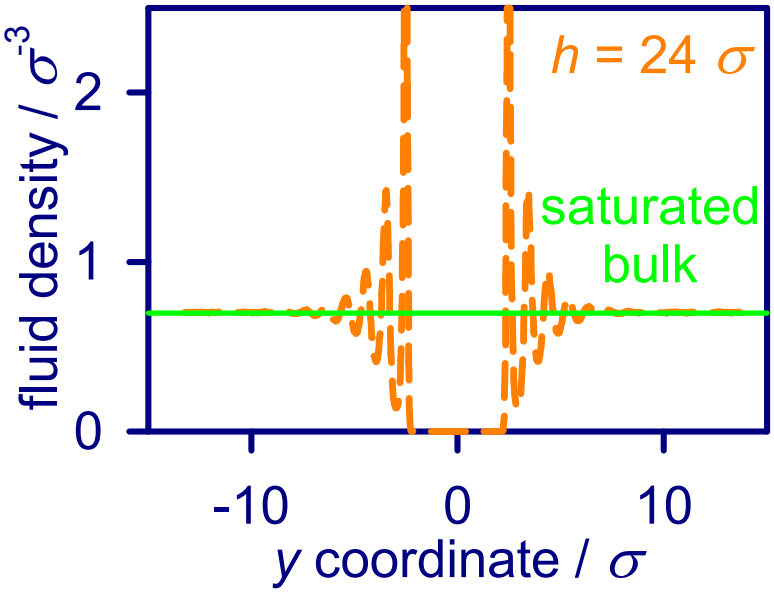
Grand canonical MD simulation

- Specification of μ, V, and T
- Test insertions and deletions of single particles in alternation with MD steps:

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

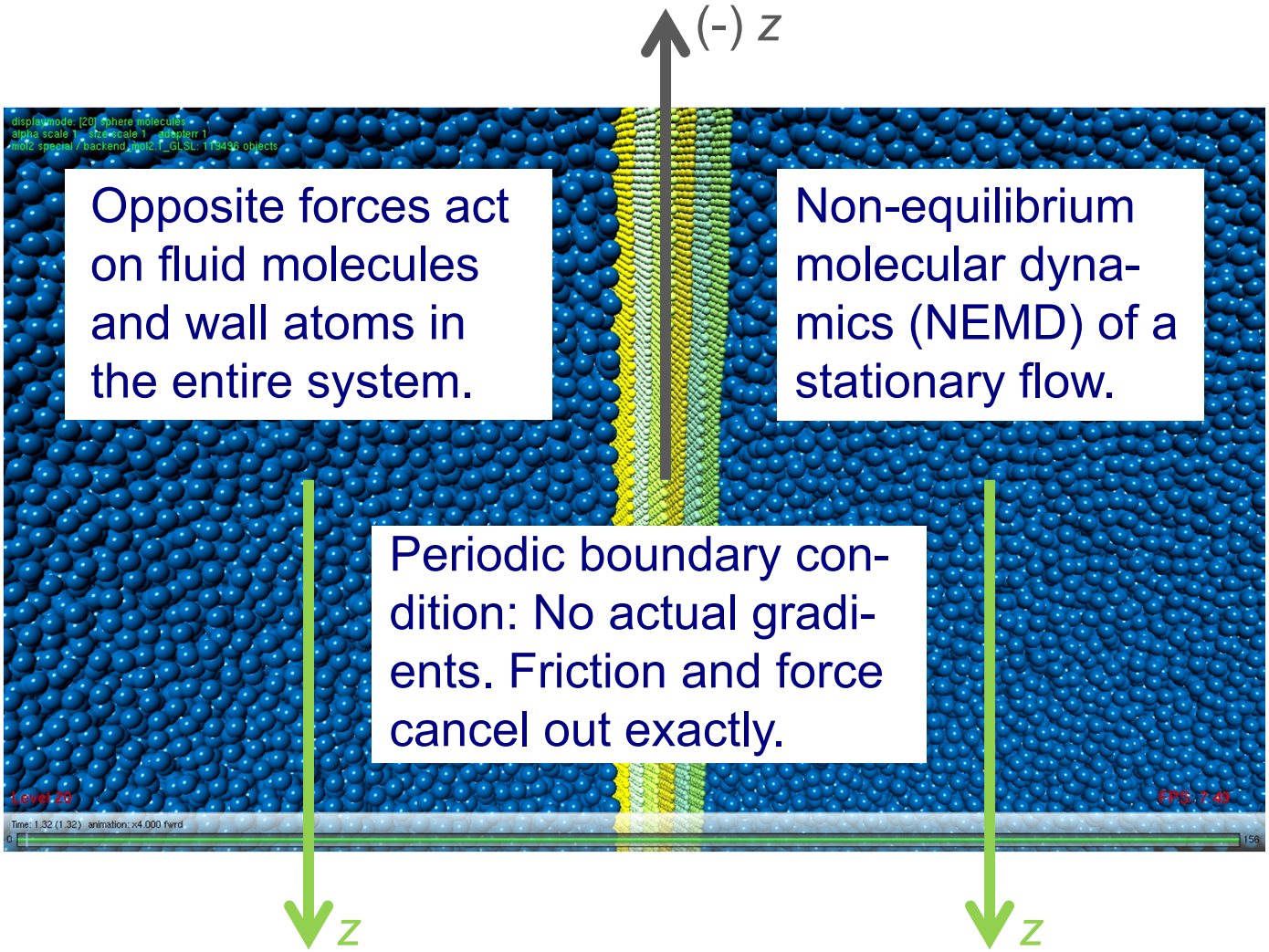
$$P_{\text{del}} = \min\left[1, \exp\left(\frac{-\mu - \Delta U_{\text{pot}}}{T}\right)\frac{1}{\Lambda^3 \rho}\right]$$

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

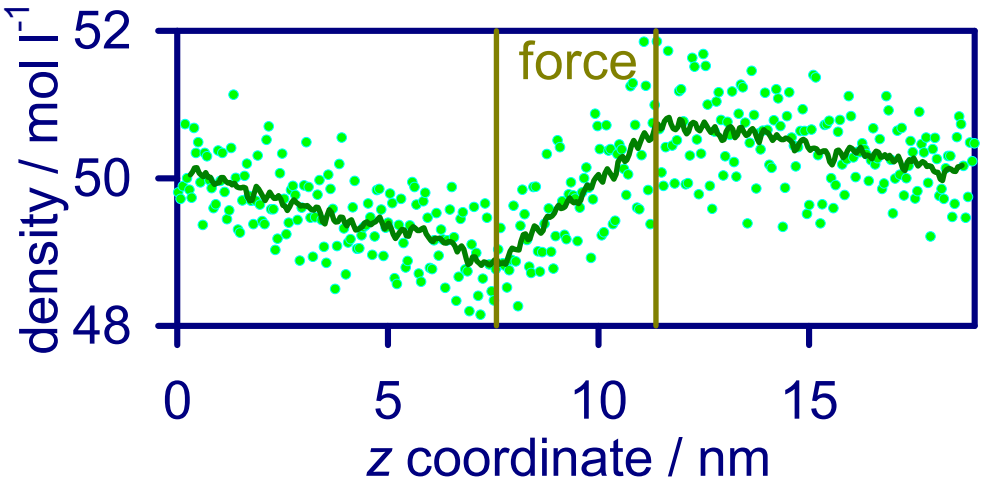


Application: Chemical potential gradient induced Poiseuille flow

Explicit compensation of the pressure drop

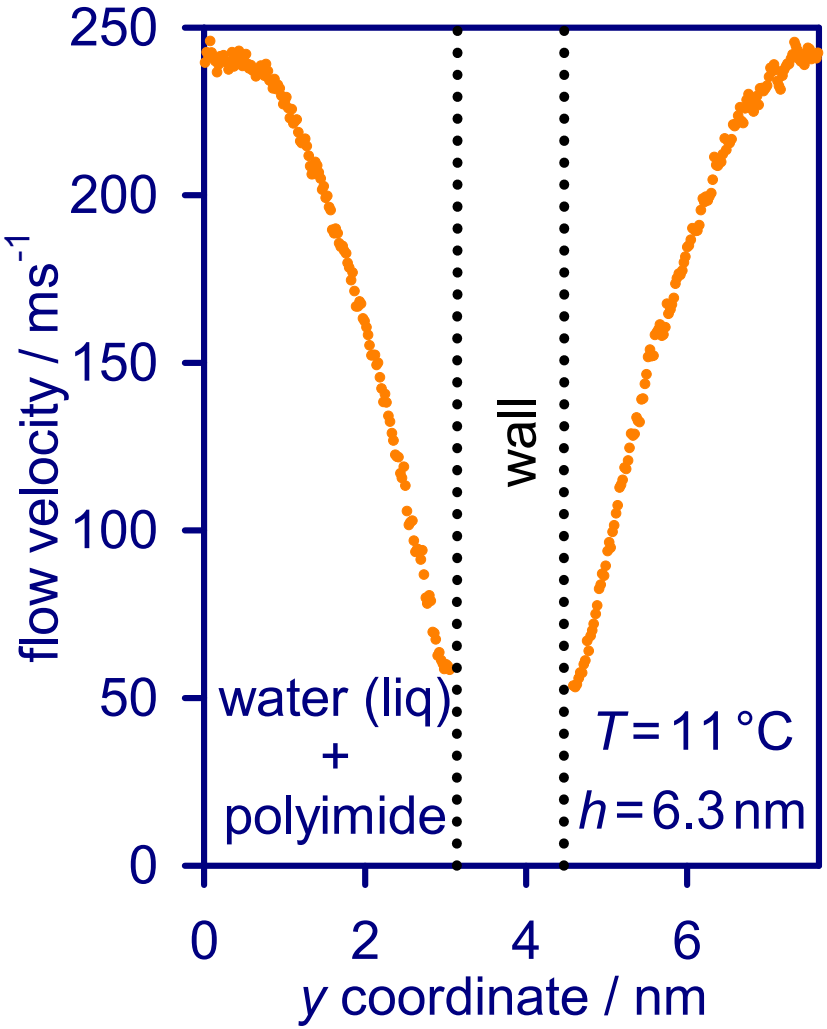


Density-gradient NE steady-state MD



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:

$$J_i = -D_t \nabla \rho_i = -L_s \nabla \left(\mu_i / T \right) - D_t' \nabla p$$

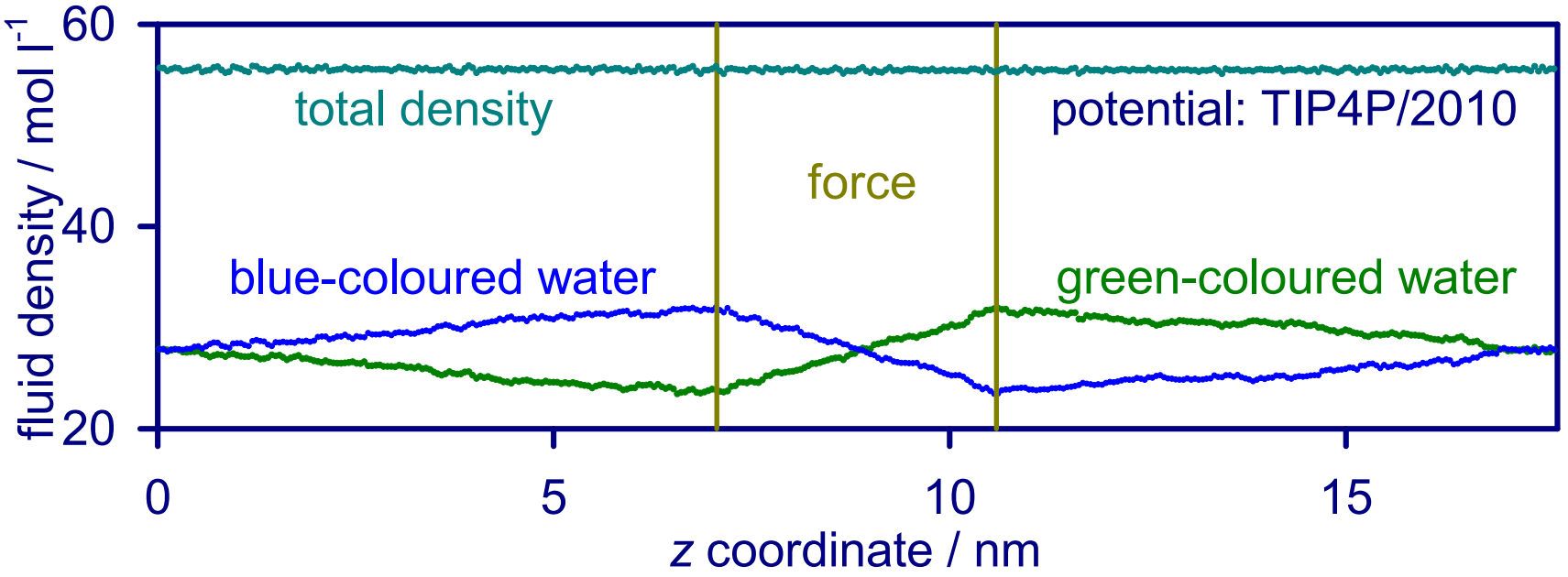
Diffusive transport: Self-diffusivity D_s, expressed above in terms of the Onsager type coefficient L_s, caused by the random thermal movement of individual molecules.

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.

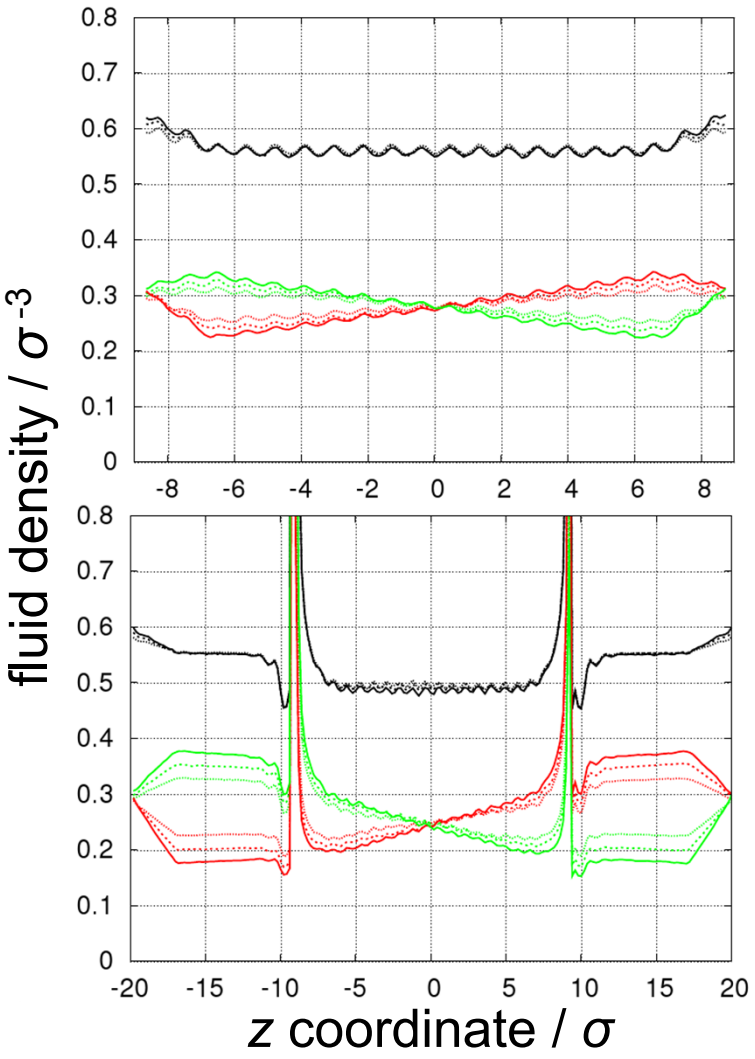
Avendaño's dæmon

The self-diffusivity can be determined by NEMD if a gradient in μ (→ 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.

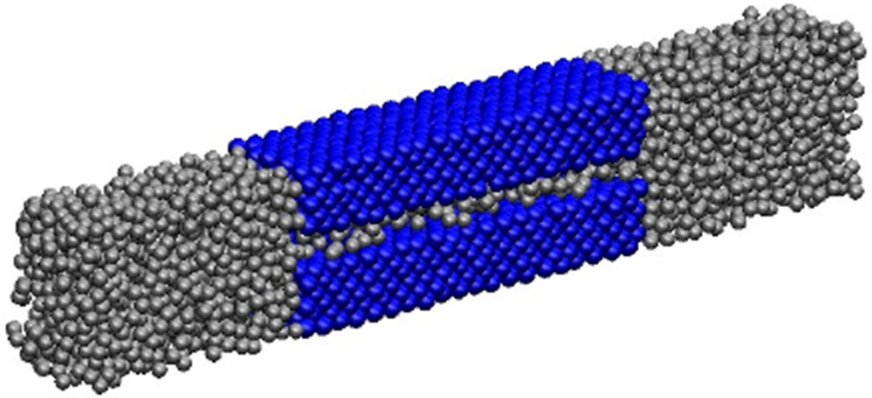
Entrance effects



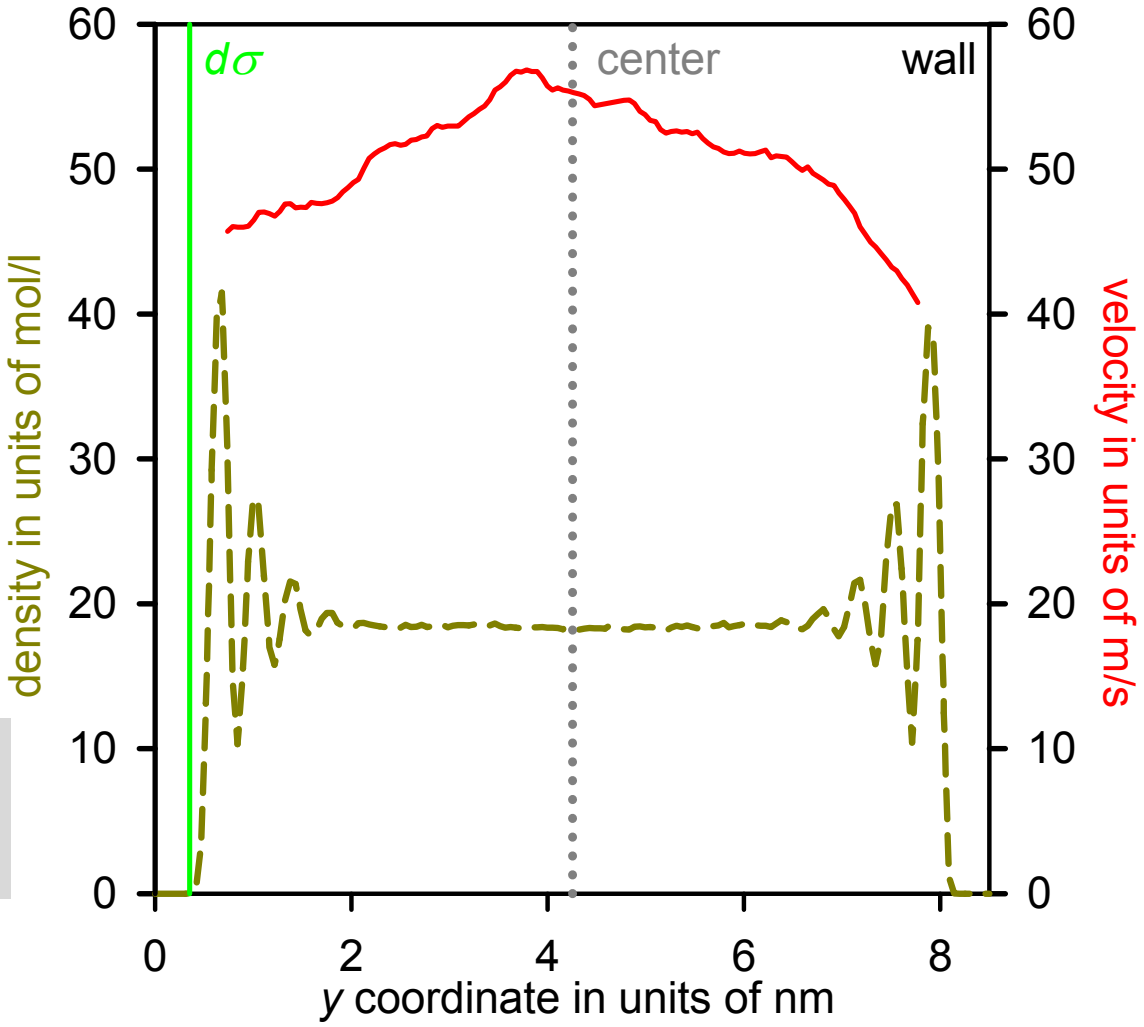
By comparison between the flow in

- 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

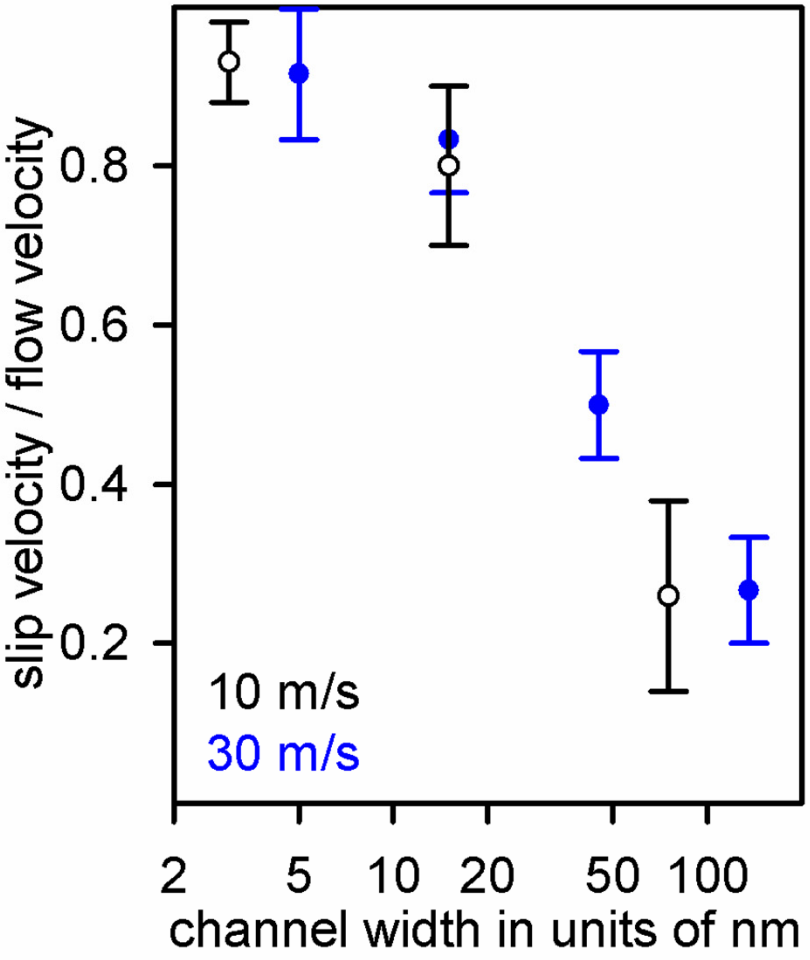


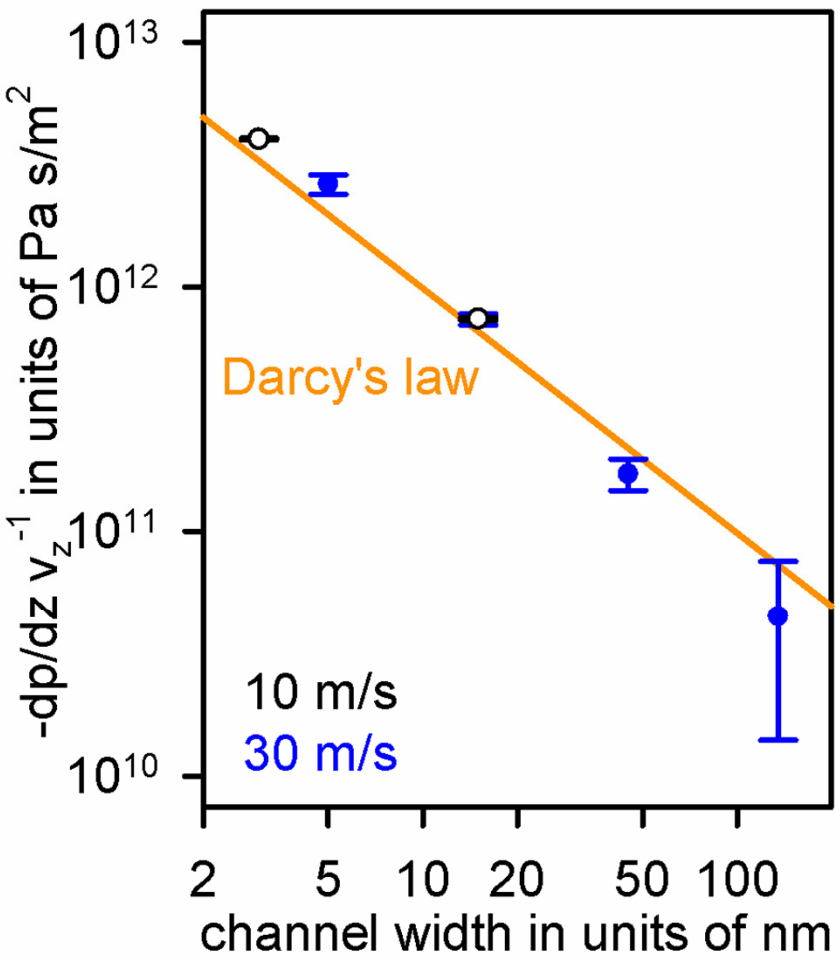
Methane in graphite

T = 166 K

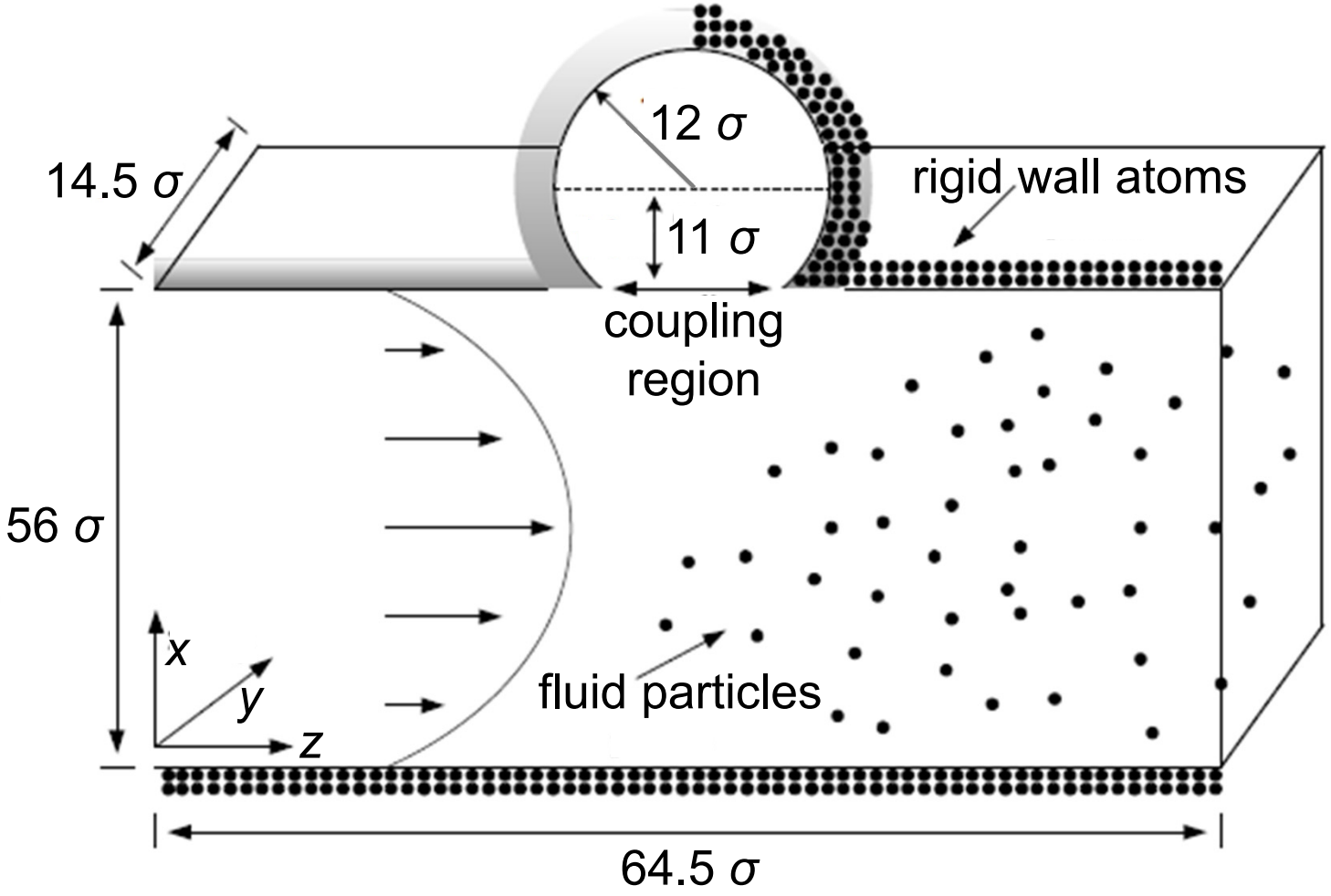
From nanofluidics to microfluidics

Methane in graphite: T = 166 K; values of η and ξ from Wang *et al.*





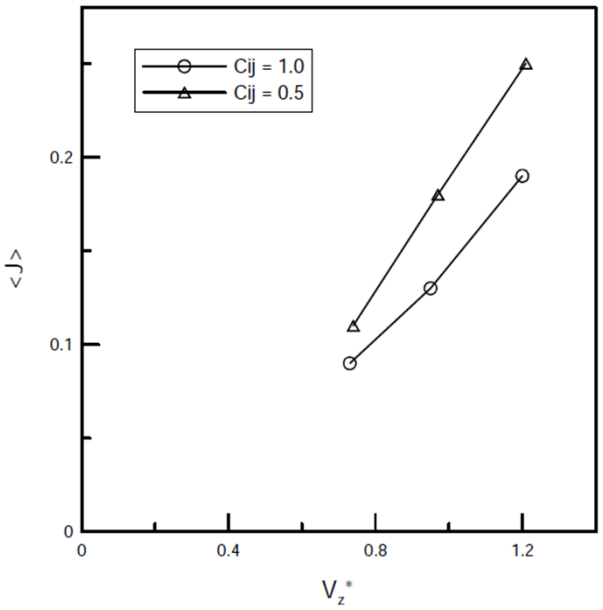
Nanopore with a patterned surface

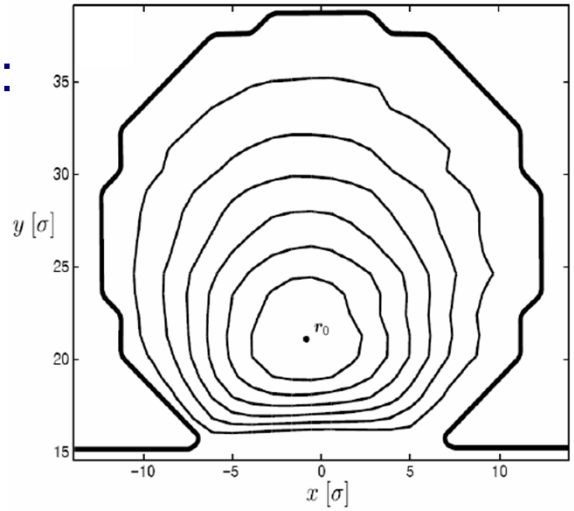


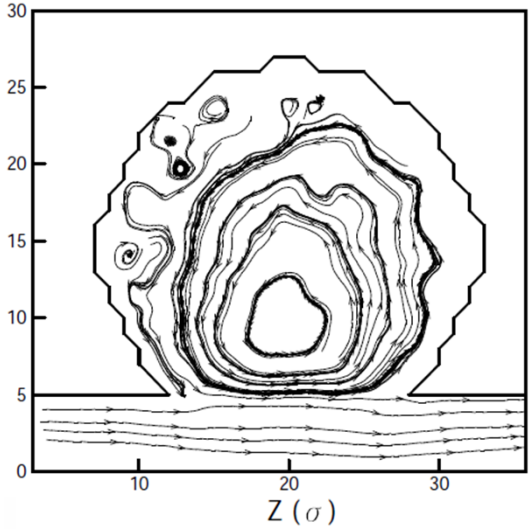
Rotation inside the cavity

… induced by Poiseuille flow:

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







2D

v = 0.8
C = 0.5

Oliver *et al.* (2006)

3D

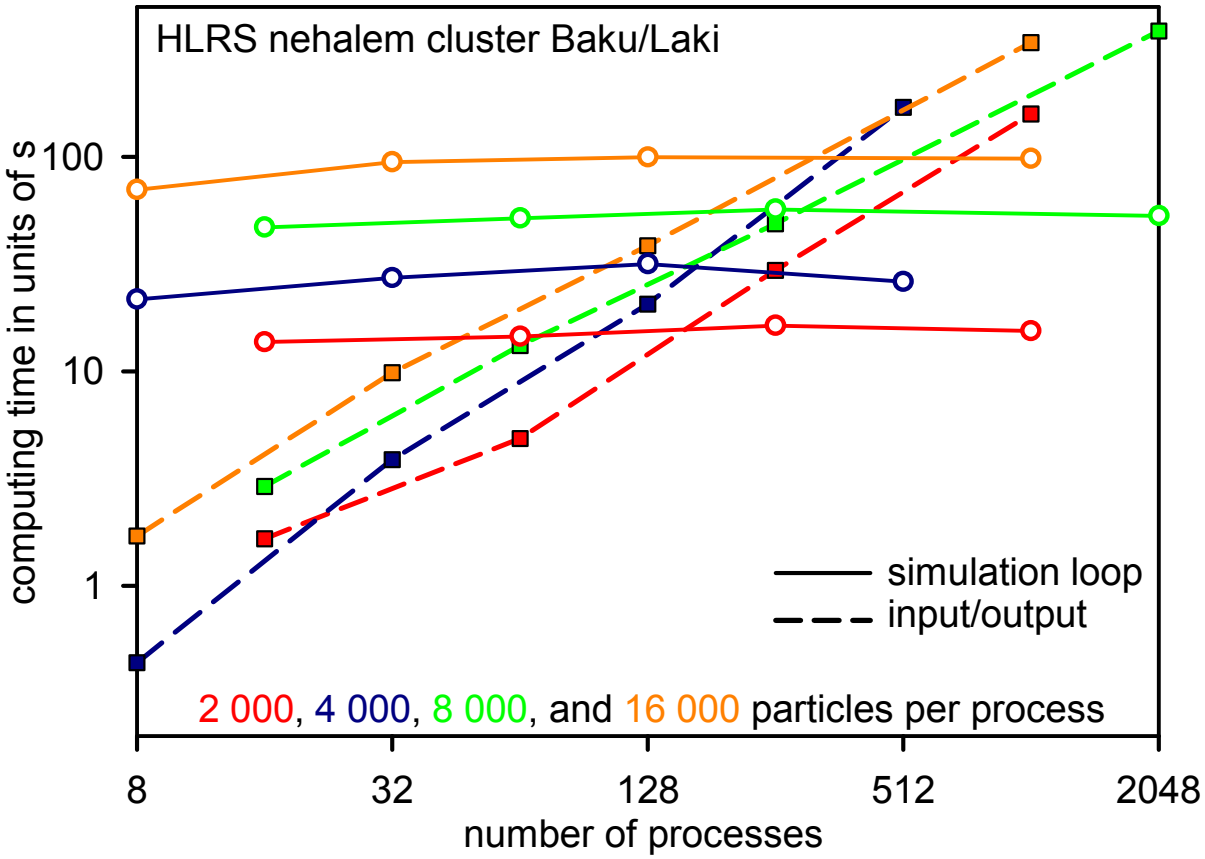
v = 0.82
C = 0.5

Hsiang *et al.* (present)

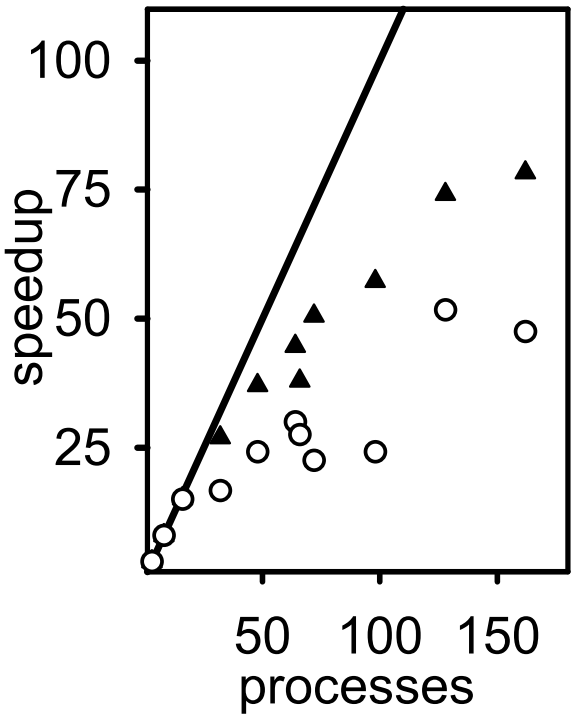
Massively parallel molecular dynamics

weak and strong scaling of the *ls1 mardyn* program

homogeneous truncated-shifted LJ system



methane + graphite



○ uniform subdomains
▲ static load balancing

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.