Non-equilibrium molecular dynamics simulation of real fluids in nanoporous materials

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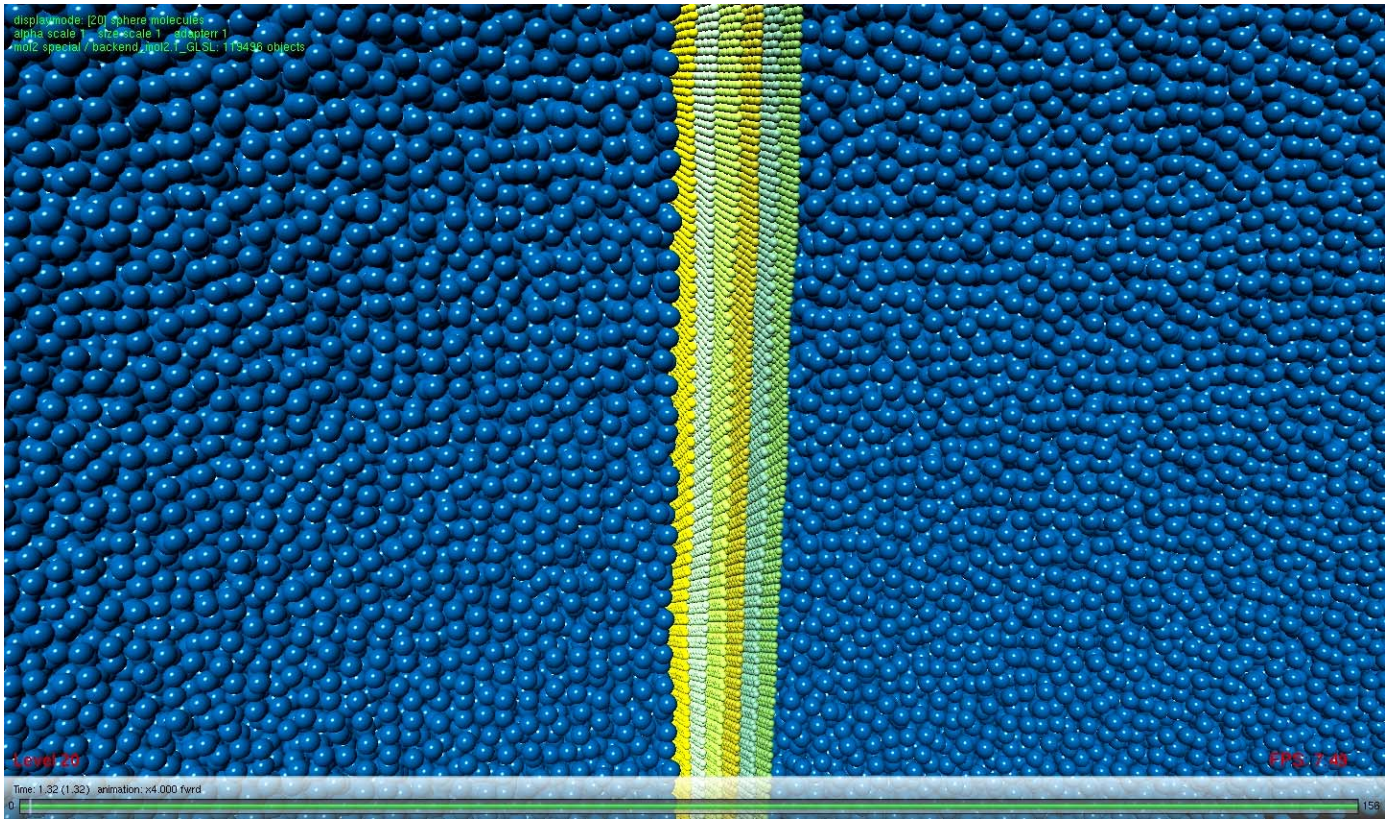
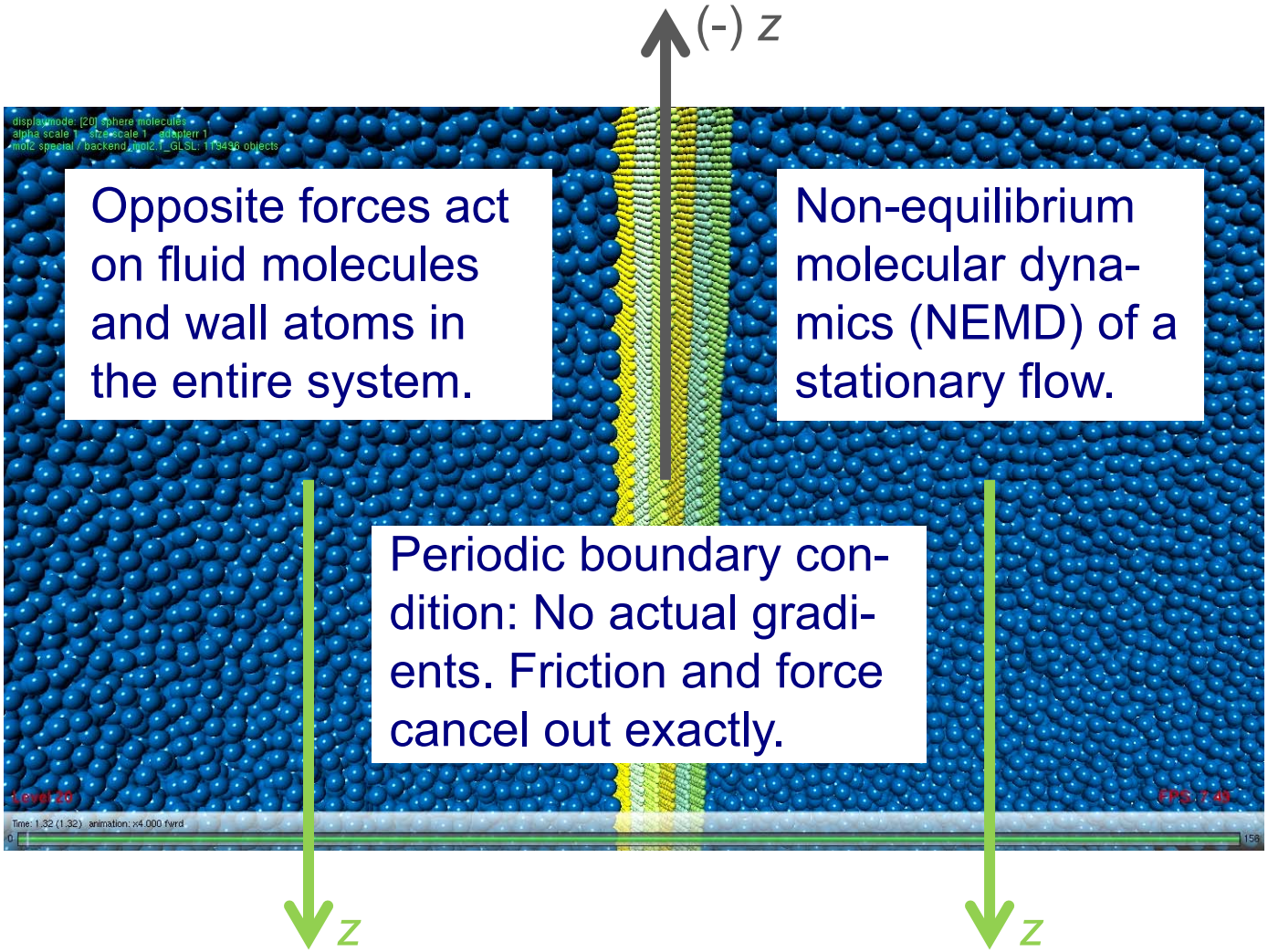
Lyon, 19th March 12

Computational
Molecular Engineering

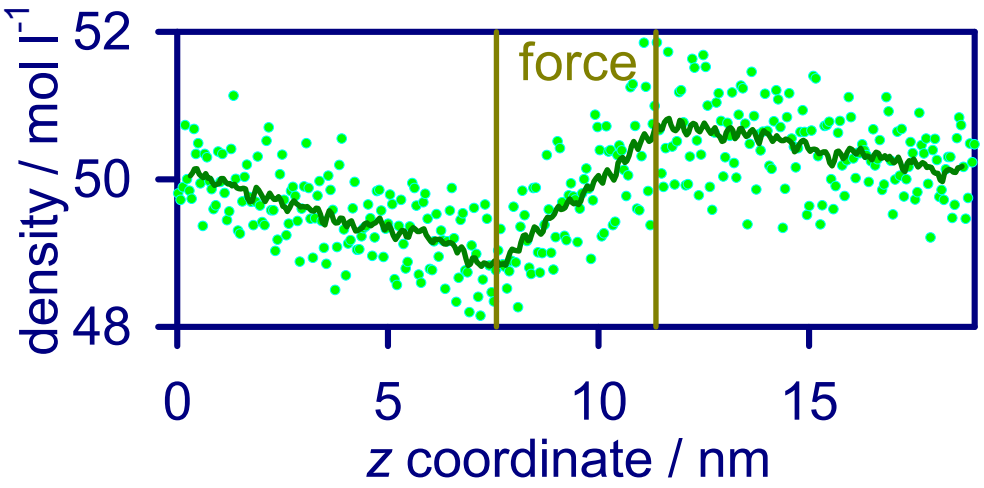
Exact compensation of the pressure drop



Exact compensation of the pressure drop

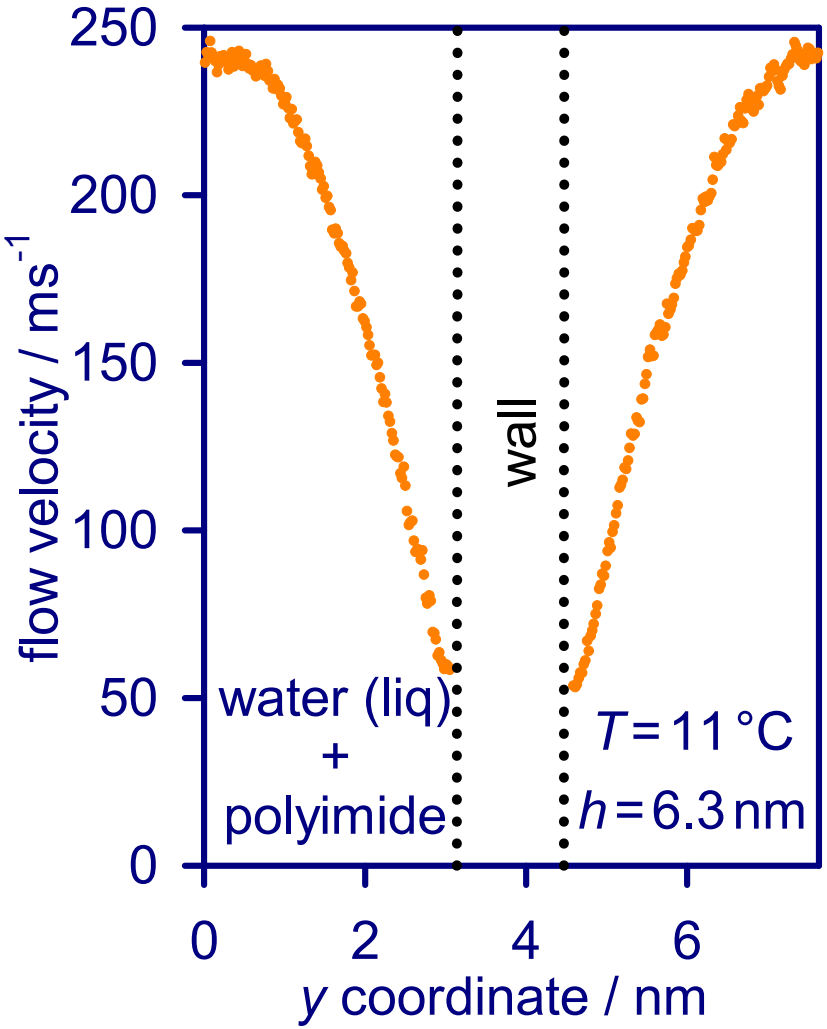


Overcompensation of the pressure drop



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

The transport diffusion coefficient D_t consists of contributions from two different mechanisms:

$$J_i = -D_t \nabla \rho_i = -L_f \nabla (\mu_i / T) - D_t' \nabla p$$

Diffusive transport: Mobility $D_0 = D_s + D_\xi$, expressed above in terms of the Onsager type coefficient L_f, caused by the random thermal movement of individual molecules.

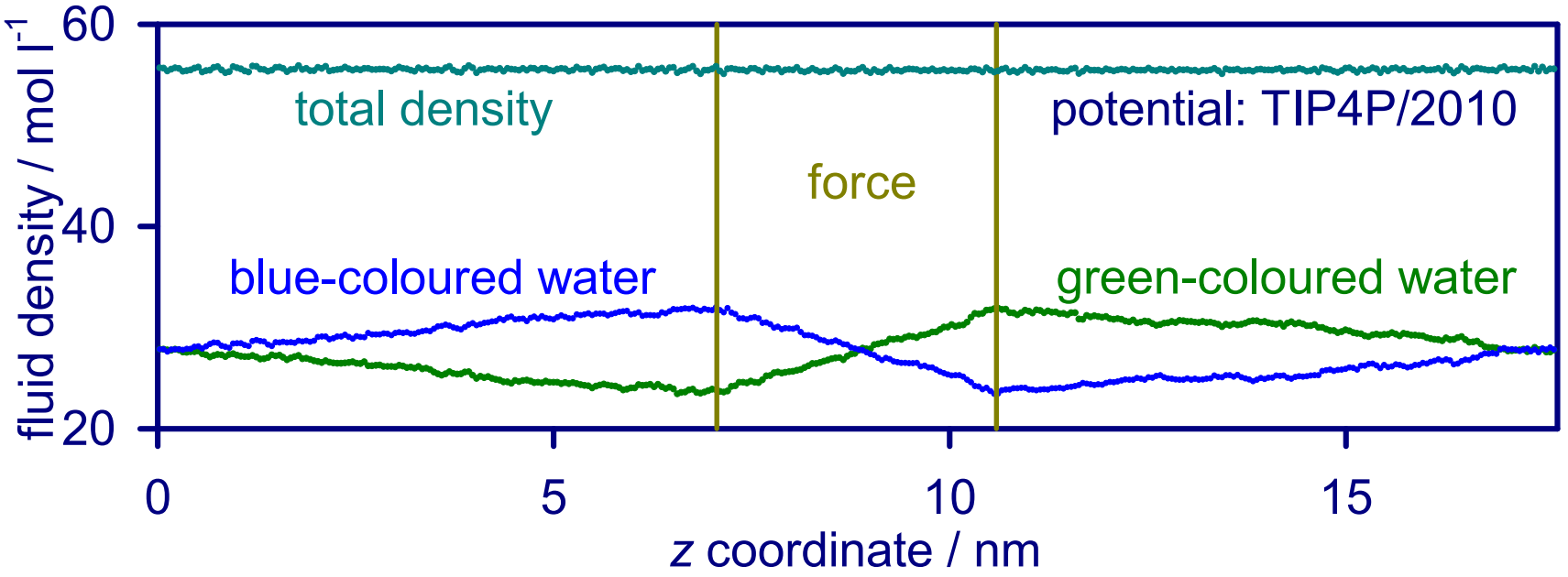
Viscous transport: Ordered collective motion of the molecules due to a pressure gradient, which can be understood in terms of a fluid continuum.

In principle, equilibrium MD computes D_s, whereas NEMD yields D_t.

Note: For a pure substance, μ_i and p cannot be varied independently.

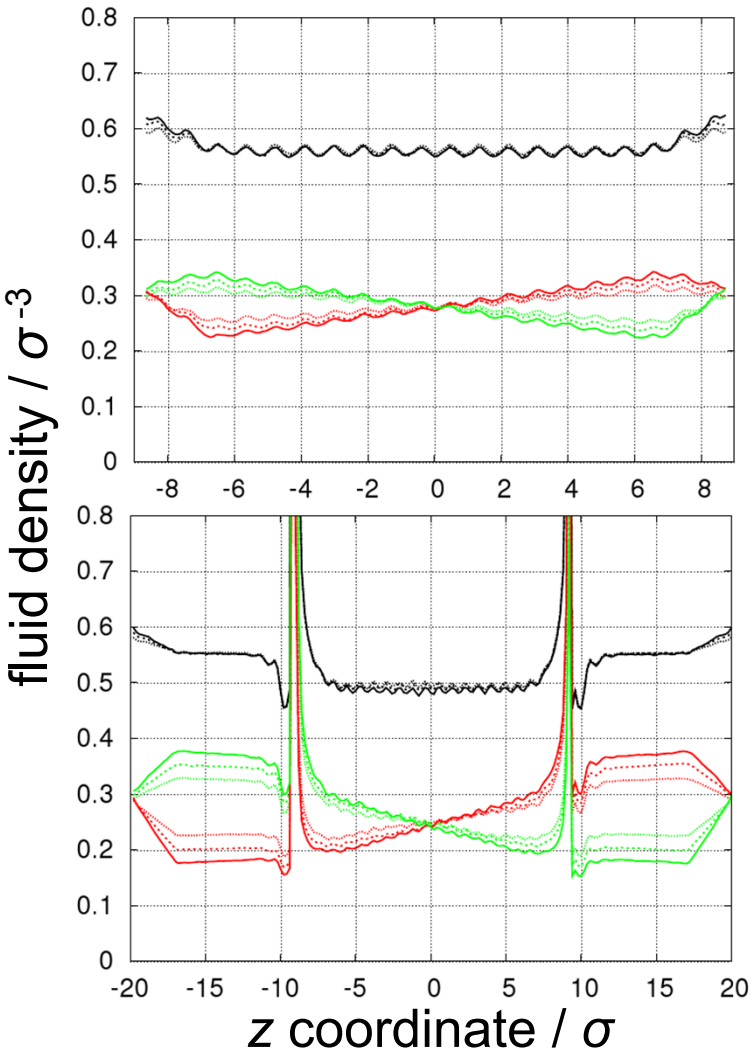
Avendaño's dæmon

The mobility D_0 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.

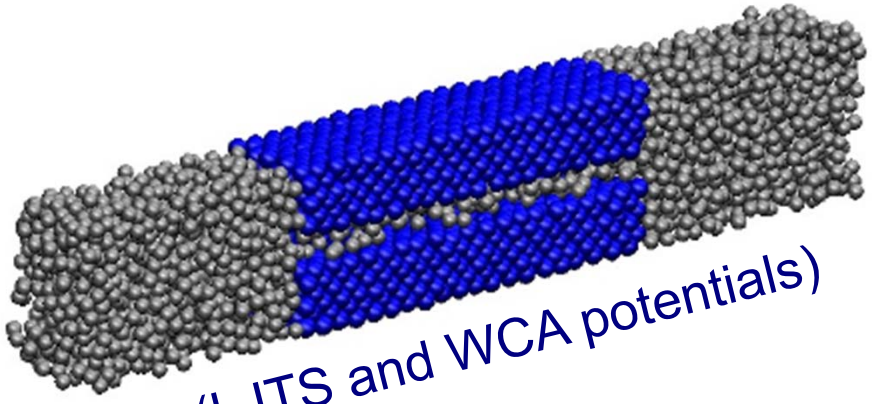
Membrane topology



By comparison between the flow in

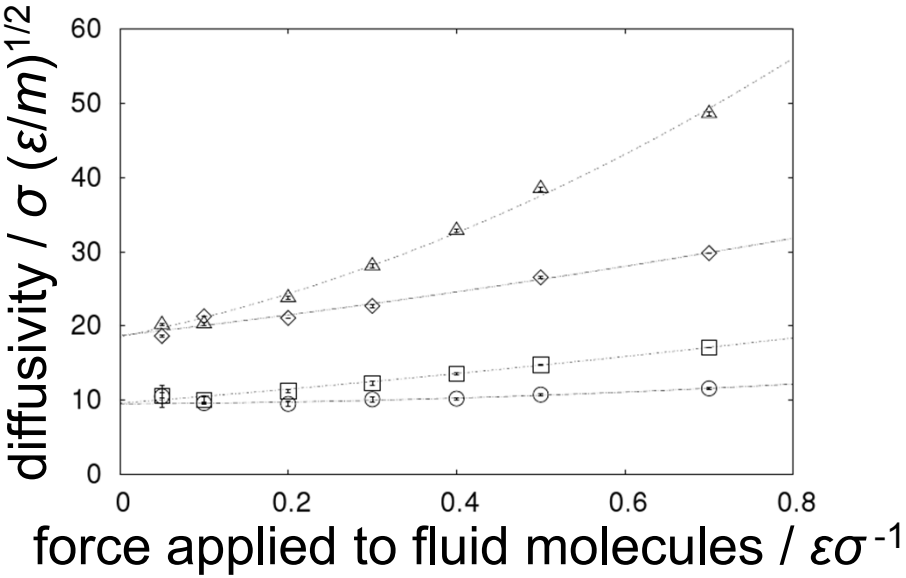
- an infinite (i.e. periodic) channel
- an "open" system including a bulk section …

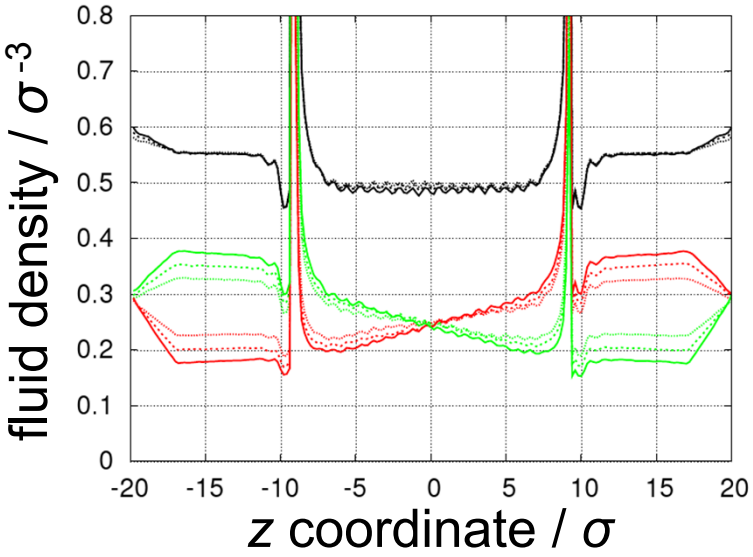
… the influence of the channel entrance and exit regions on the overall effective diffusivity can be isolated.

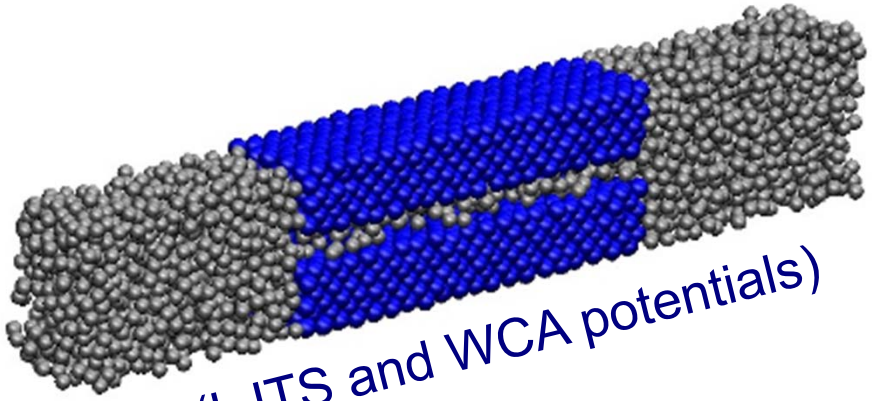


Effective diffusivity

Diffusivities are obtained as linear response coefficients, i.e. in the limit where the accelerating force, which perturbs the equilibrium state of the system, approaches zero

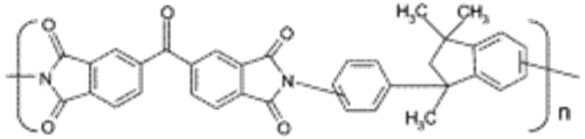
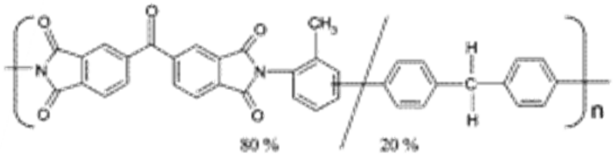




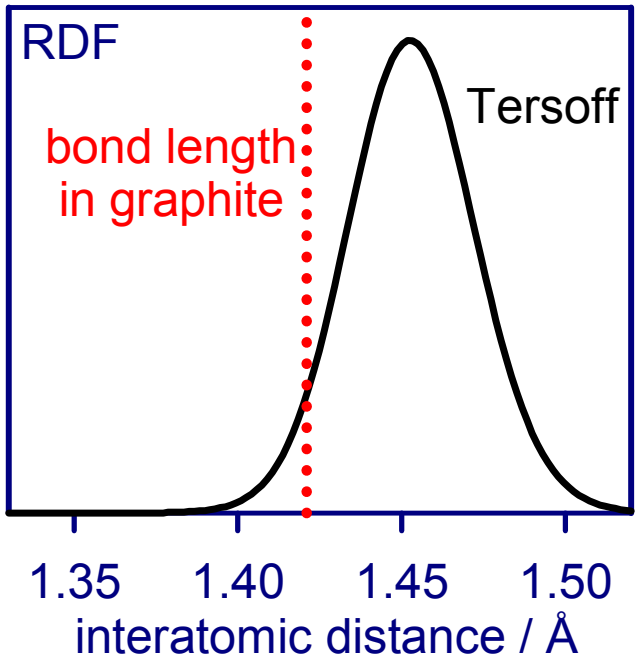


(LJTS and WCA potentials)

Nanofiltration 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.



Length scale of the Tersoff potential for carbon:

Cutoff	Attraction	Repulsion
R = 1.8 Å S = 2.1 Å	μ = 2.2119 Å^{-1}	λ = 3.4879 Å^{-1}

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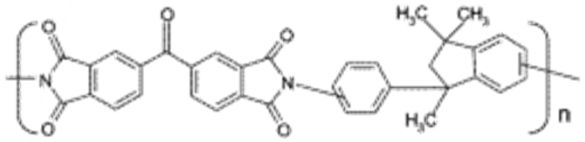
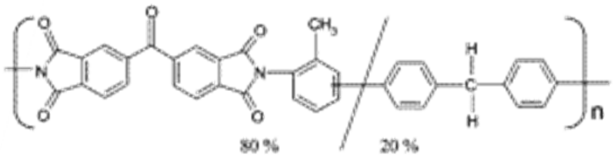
Material	Chemical Structure	T_g (°C)	Density (g/cm³)
Matrimid® 5218		323	1.22
P84		315	1.31

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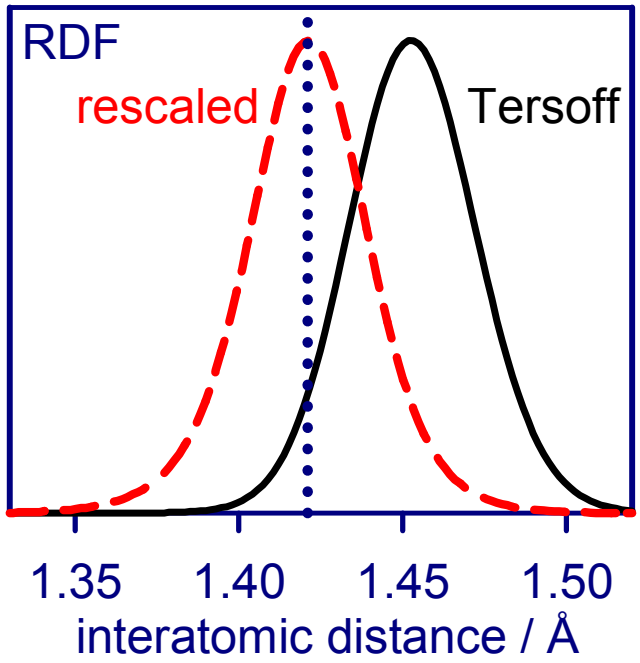
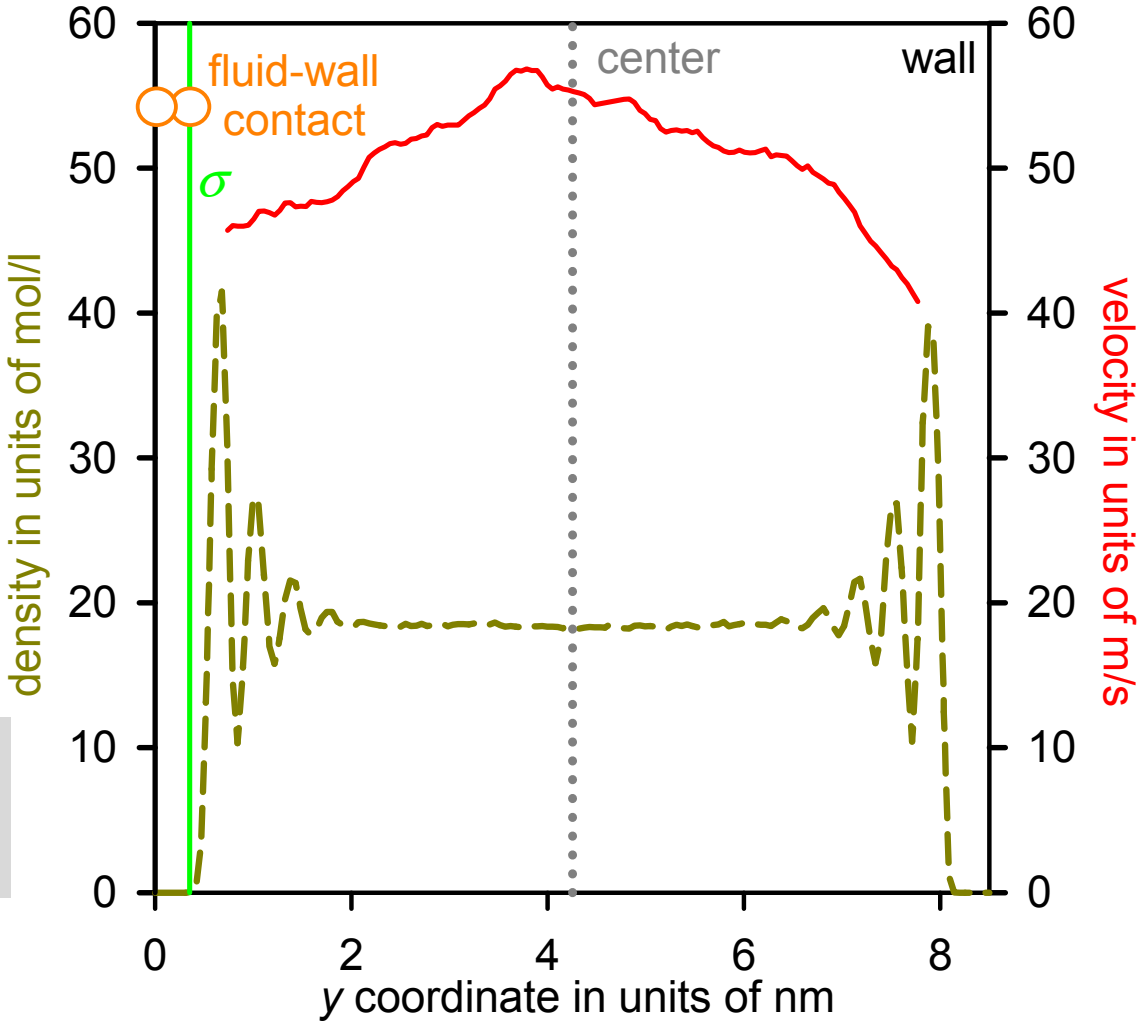


Optimized potential parameters for graphite:

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})

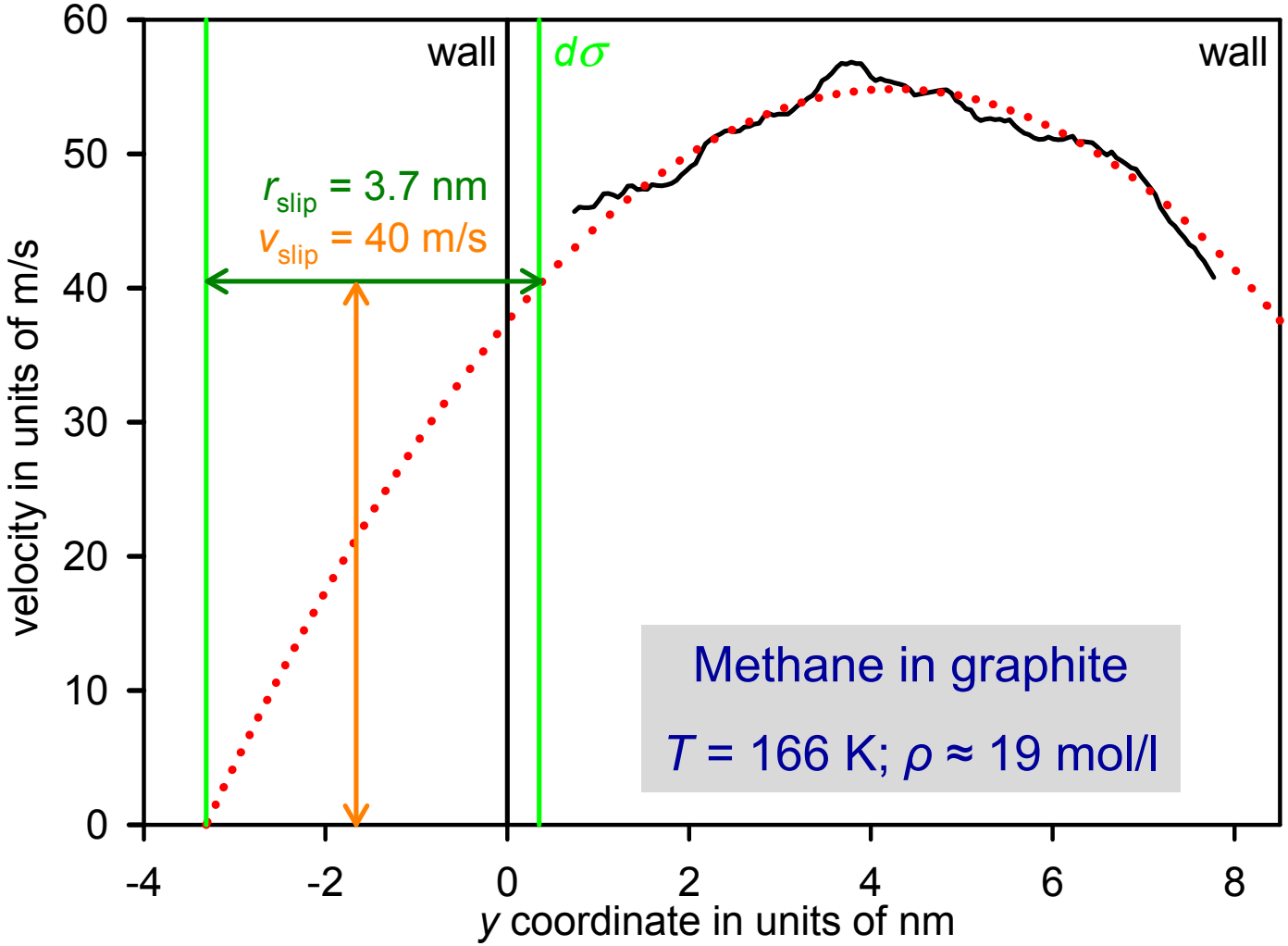
Velocity profile and boundary slip



Methane in graphite

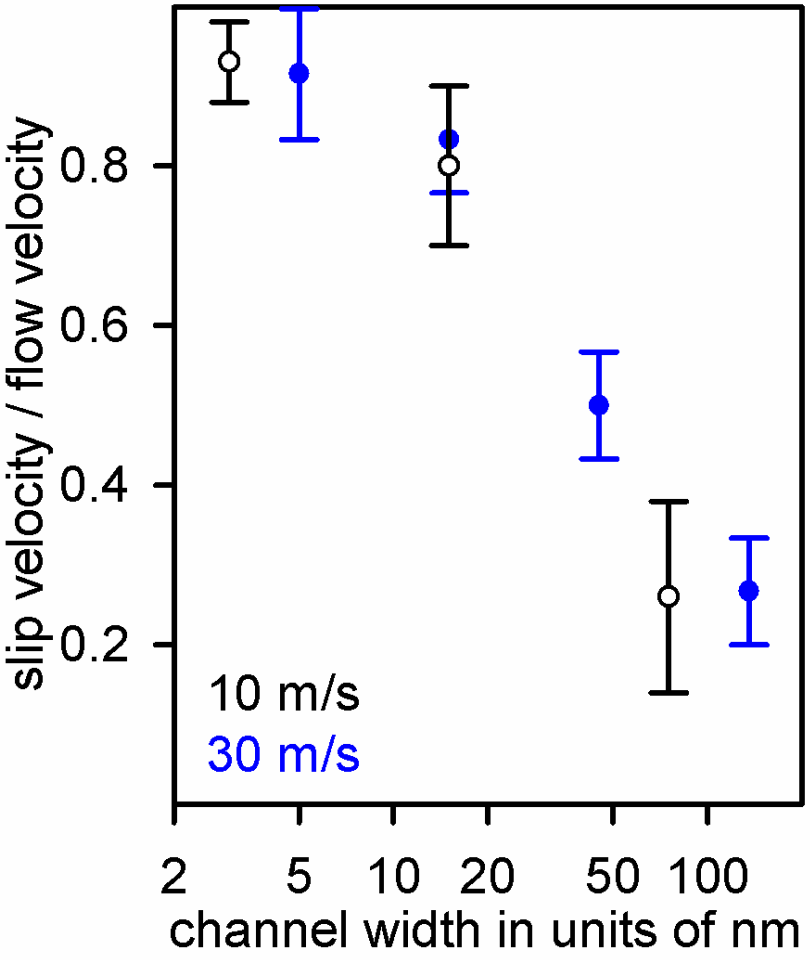
T = 166 K

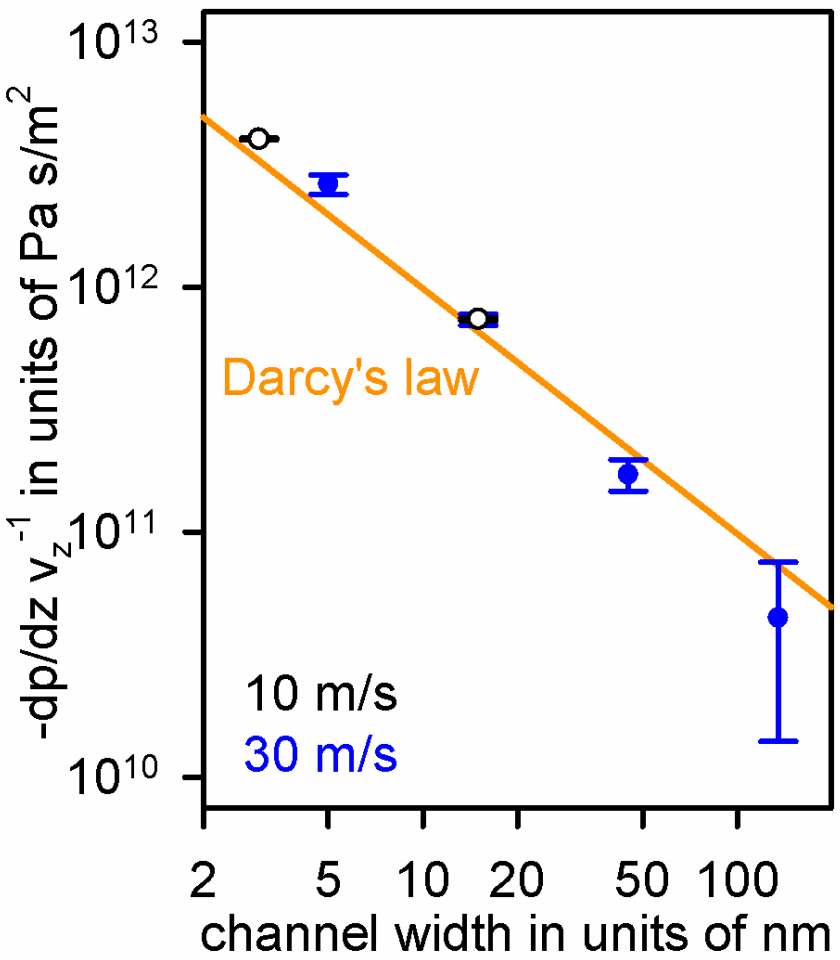
Velocity profile and boundary slip



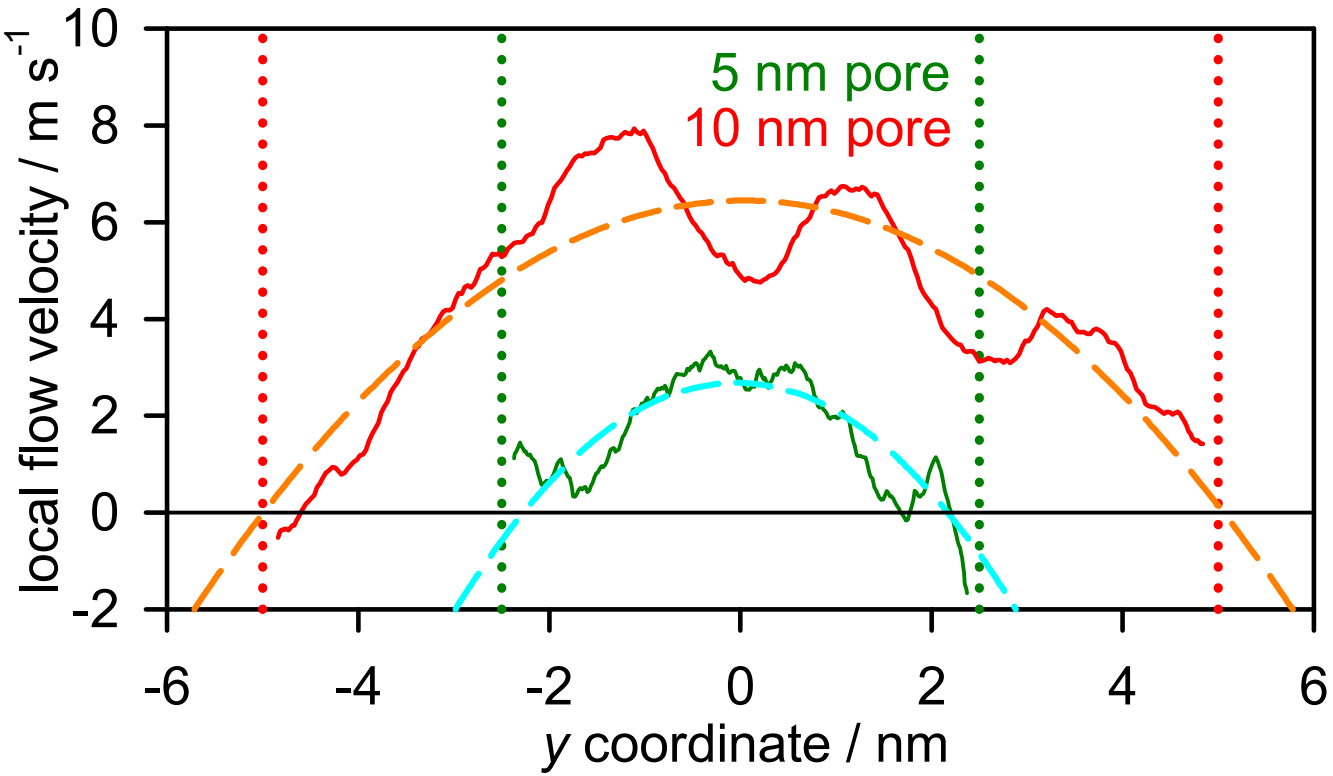
From nanofluidics to microfluidics

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





Water in polar nanofiltration membranes



boundary slip practically negligible, in contrast to the unpolar system

r_{slip} approaches the nm length scale at high flow velocities (200 m/s)

Quantitative water model: TIP4P/2010 (Huang *et al.*)

Qualitative P84 polyimide pore model: Graphite with superimposed point charges

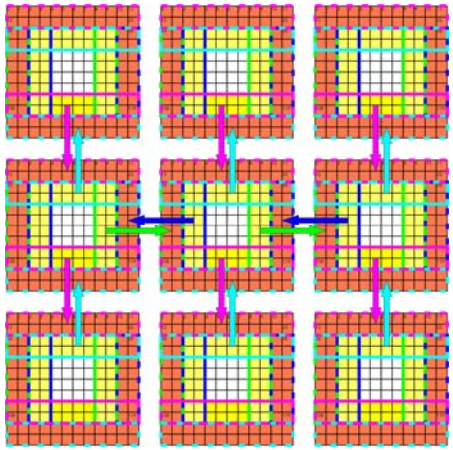
Massively parallel MD simulation

MD code ls1 mardyn (“large systems 1: molecular dynamics”)

spatial domain decomposition

exploits the concurrency due to the limited range of the interactions

central, marginal, and halo cells

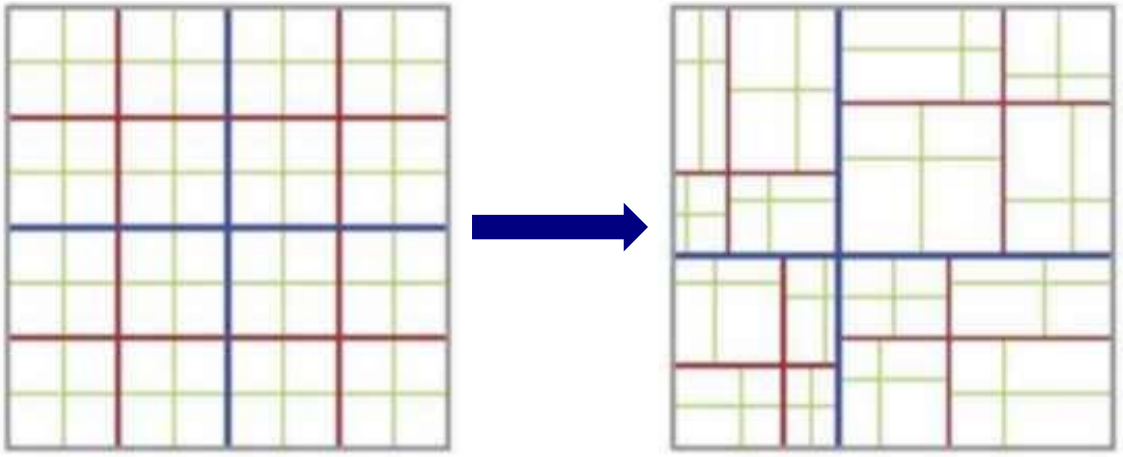


linked-cell algorithm

(dynamic) load balancing

the simulated system and the HPC hardware may be heterogeneous

uses octrees or space-filling curves

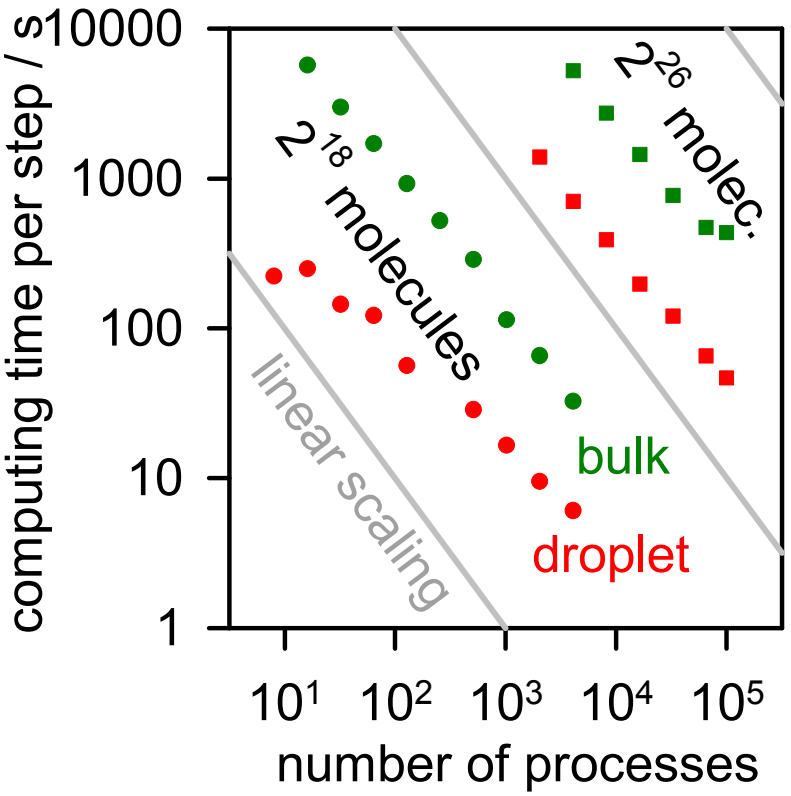


load balancing based on *k*-dimensional trees

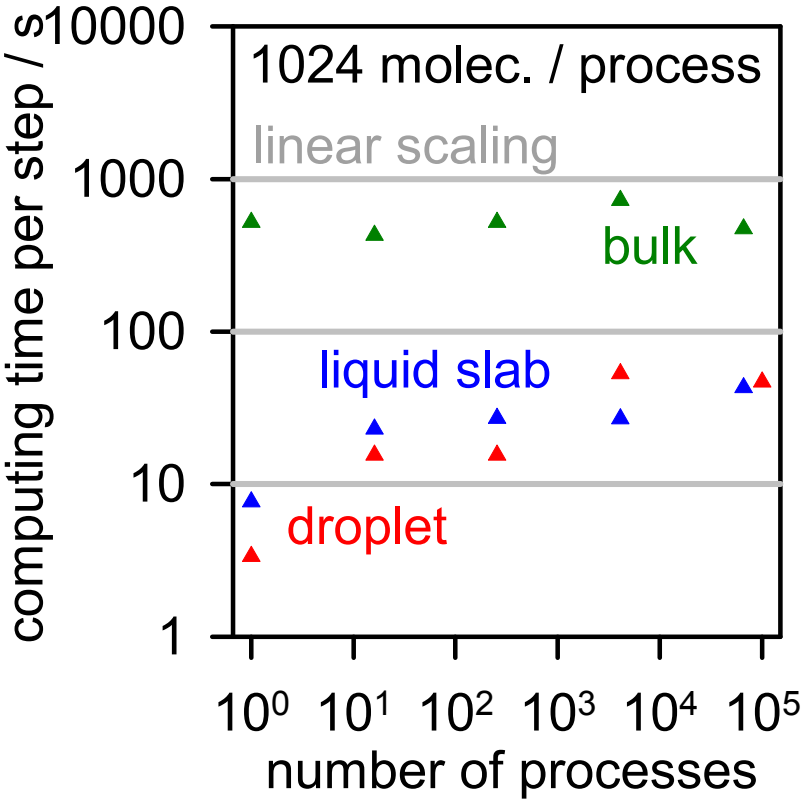
Massively parallel MD simulation

MD code ls1 mardyn: scaling on the *Hermit* (top 12) at HLRS

strong scaling (Amdahl)



weak scaling (Gustafson)



Conclusion

⇒ Poiseuille flow can be investigated by non-equilibrium MD simulation, i.e., by compensating or overcompensating the pressure drop.

⇒ Avendaño's dæmon makes purely diffusive transport (i.e., the mobility coefficient) accessible to NEMD for confined systems.

⇒ For methane in graphite, Darcy's law was found to hold down to the molecular length scale significant boundary slip was present for diameters below 100 nm.

⇒ In case of water in a polar membrane material, no significant boundary slip was detected.

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