MD simulation of methane in nanochannels

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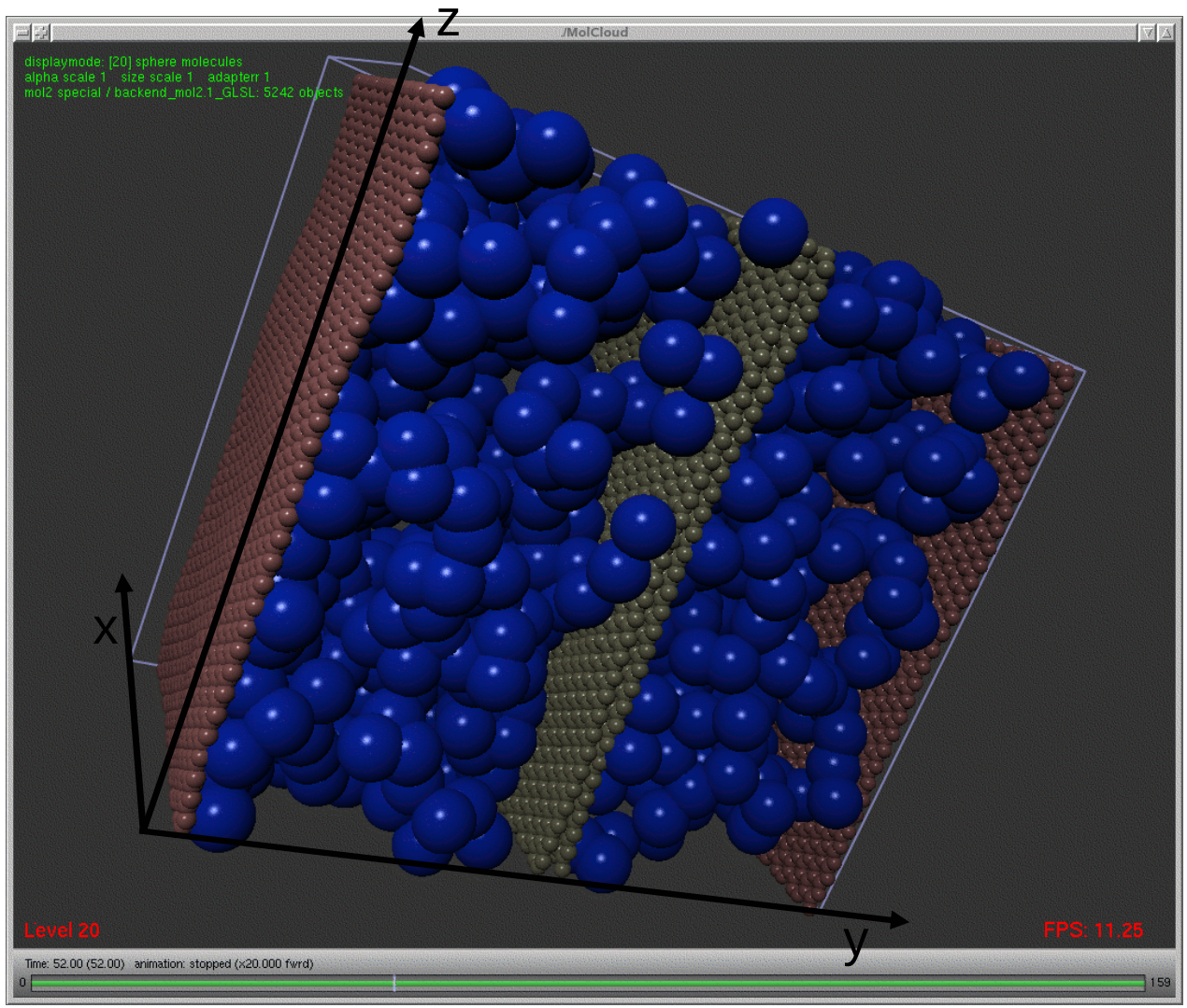
Scope and structure

- Molecular model for graphite and the fluid-wall interaction
- Scalability of the MD simulation
- Poiseuille/Couette flow of methane through graphite channels
- Cluster criteria for systems with vapor-liquid coexistence
- Vapor-liquid equilibria of methane under confinement
- Contact angle dependence on the fluid-wall interaction

Methane confined in a nanochannel



Poiseuille flow:

The fluid is accelerated in *z* direction

Couette flow:

The walls are accelerated in *z* direction

Contact angle:

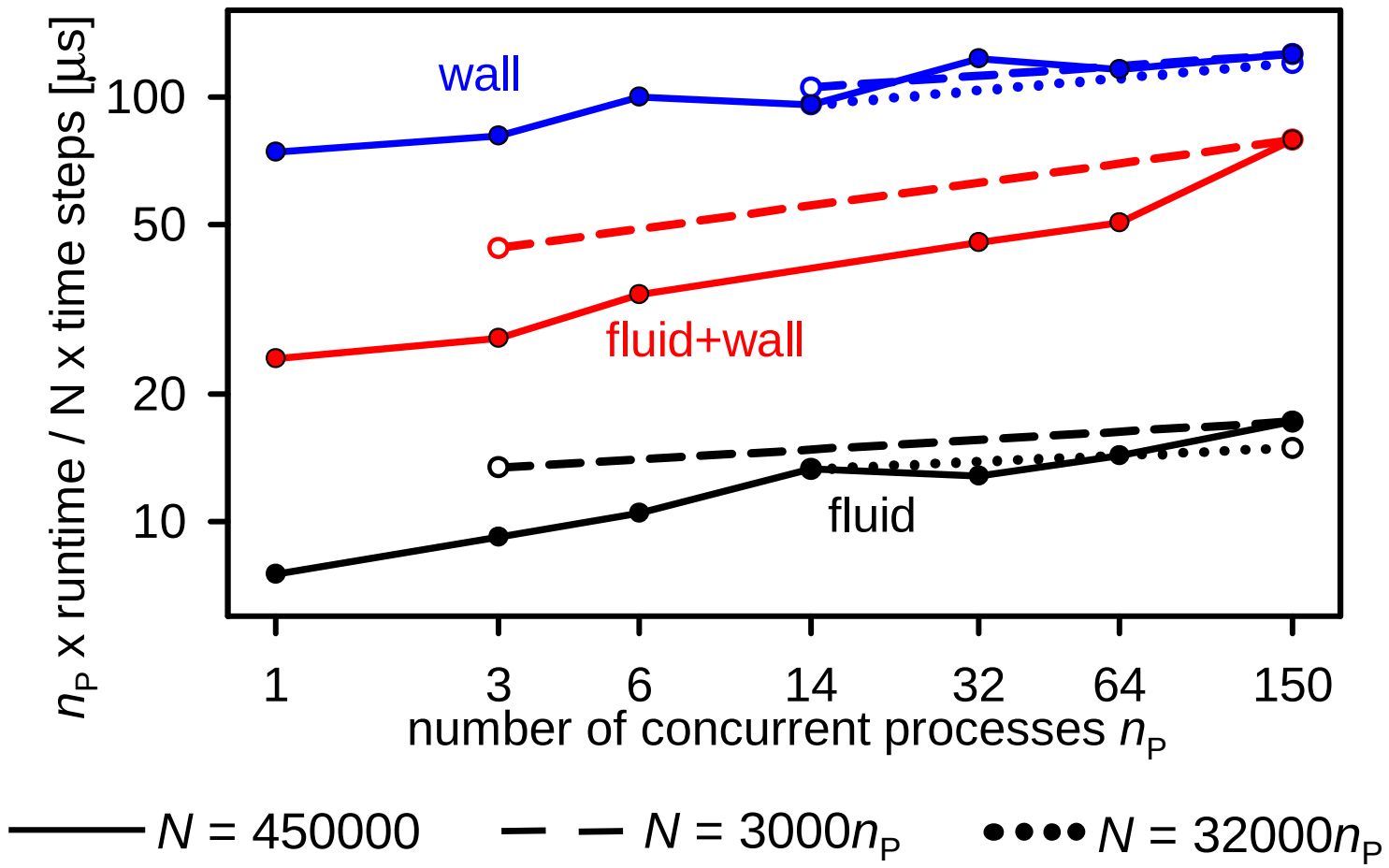
Meniscus perpendicular to the *z* axis

State of the art: system size

		Diameter / number of particles	
Vishnyakov *et al.* *Langmuir* 15: 8736	1999	$L \leq 1{,}5$ nm	
Werder *et al.* *Nano Lett.* 1: 697	2001	$L \leq 7{,}5$ nm	
Sokhan *et al.* *J. Chem. Phys.* 117: 8531	2002	$L \leq 2{,}8$ nm	$N_{wall} = 2000$
Cui und Cochran *Mol. Sim.* 30: 259	2004	$L \leq 200$ nm ($\rho_{Ionen} \leq 0{,}02$ mol/l)	
Dimitrov *et al.* *PRL* 99: 054501	2007	$L \leq 20\ \sigma_{LJ} \equiv 6$ nm	$N_{fluid} = 25000$
Present work	2008	L up to 75 nm	N up to 4,8 million

Scaling with isotropic domain decomposition

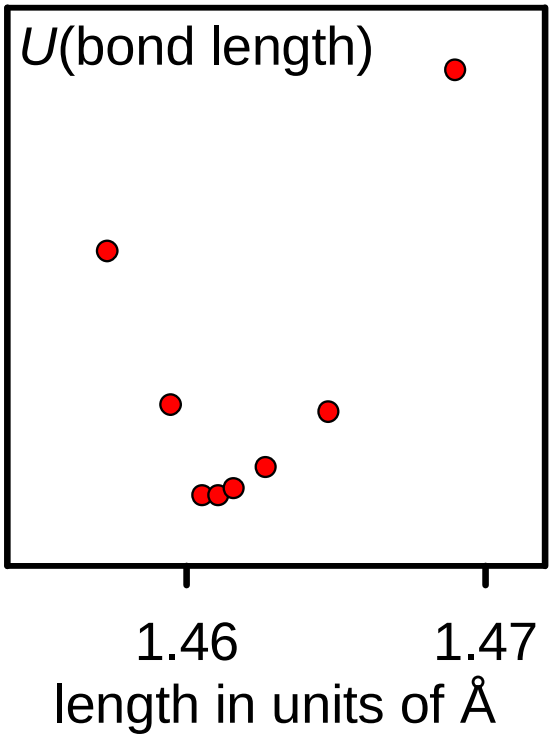
Molecul**ar dyn**amics code *Mardyn* (developed by the *ls*$_1$ project):



State of the art: potential models

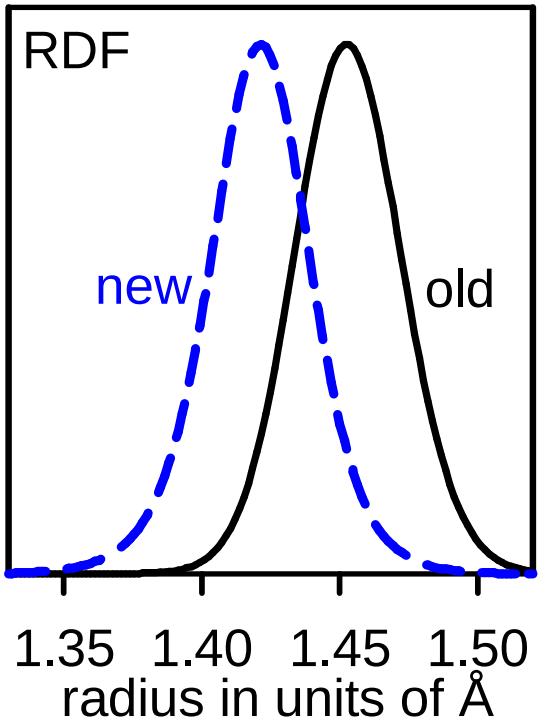
		fluid	wall	fluid-wall
Vishnyakov *et al.* *Langmuir* 15: 8736	1999	3CLJQ (CO_2)	rigid	Steele (10-4-3)
Werder *et al.* *Nano Lett.* 1: 697	2001	SPC (water)	Walther *et al.* (carbon)	LJ
Sokhan *et al.* *J. Chem. Phys.* 117: 8531	2002	LJ	Tersoff-Brenner (carbon)	LJ
Liu und Wang *Phys. Rev. B* 72: 085420	2005	SPC (water)	rigid	LJ
Dimitrov *et al.* *PRL* 99: 054501	2007	LJTS	LJTS, elastic	LJTS
		(LJTS ≡ LJ, truncated and shifted at $r_{ij} = 2{,}5\sigma$)		
Present work	2008	LJTS	Tersoff (also: springs)	LJTS

Reparametrization of the Tersoff potential



Bond length

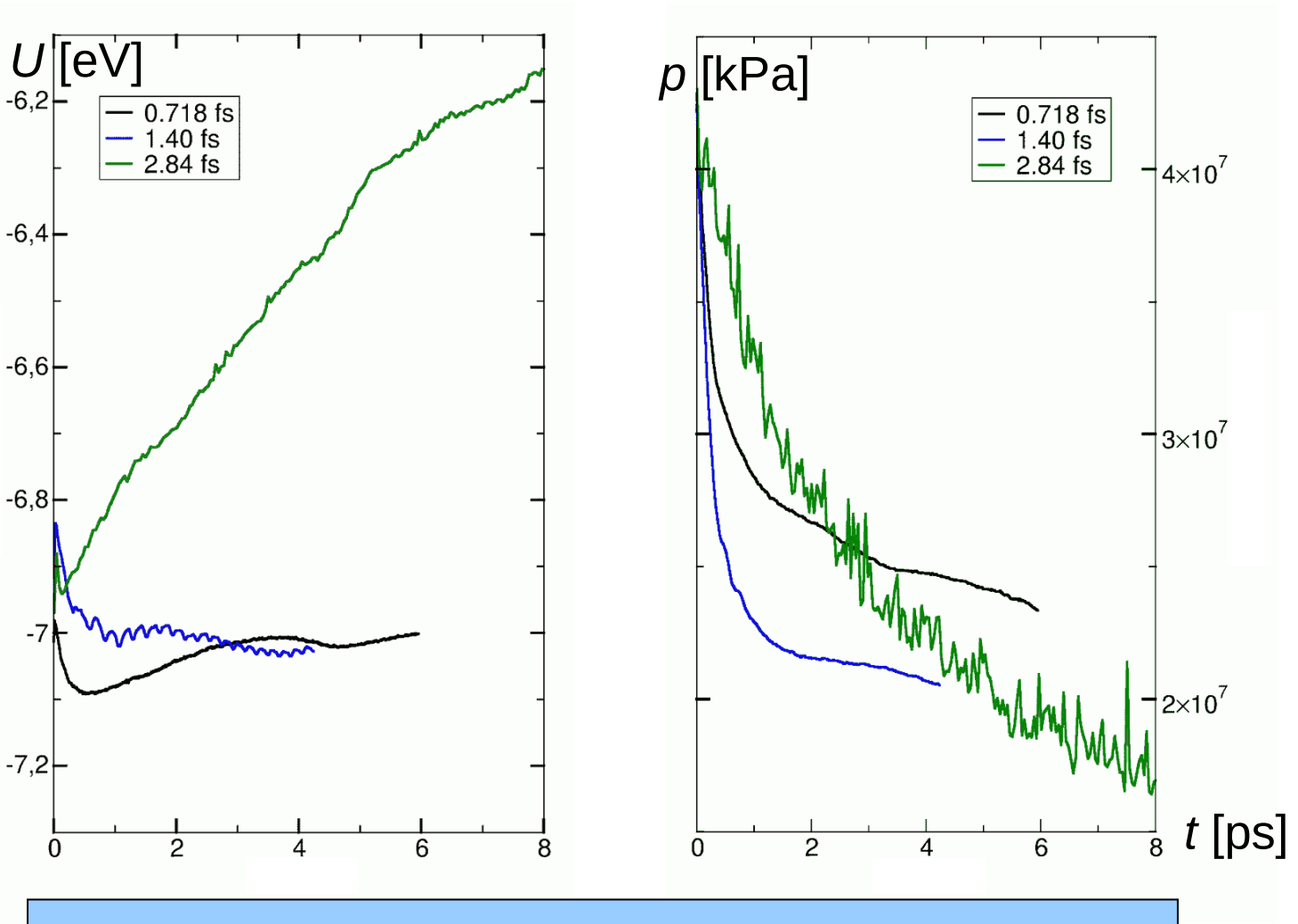
Tersoff potential: 1.461 Å
Actual graphite: 1.421 Å



More adequate 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})

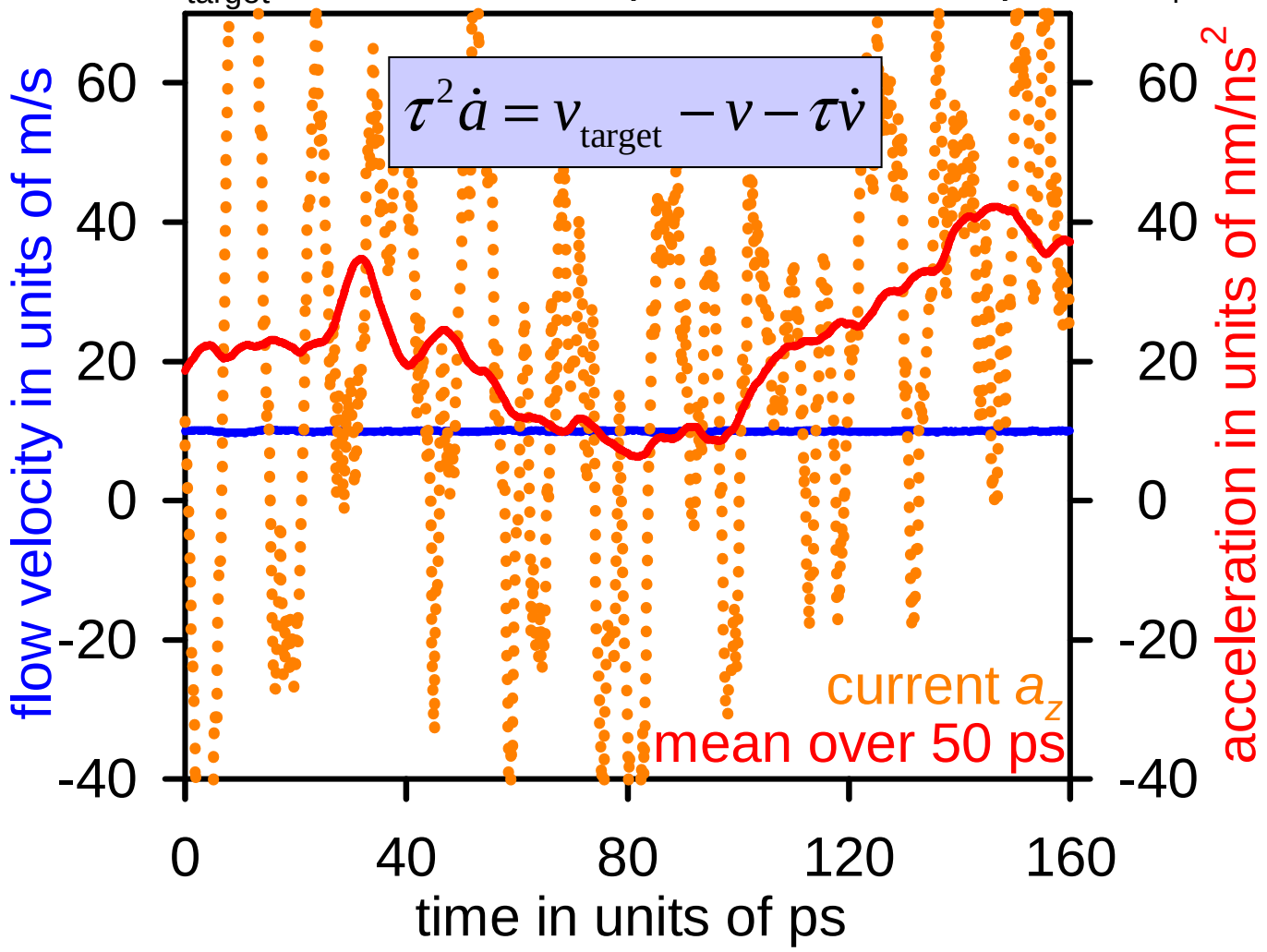
Integration time step



A time step of 1 fs leads to an acceptable accuracy.

Uniform acceleration (PI controller)

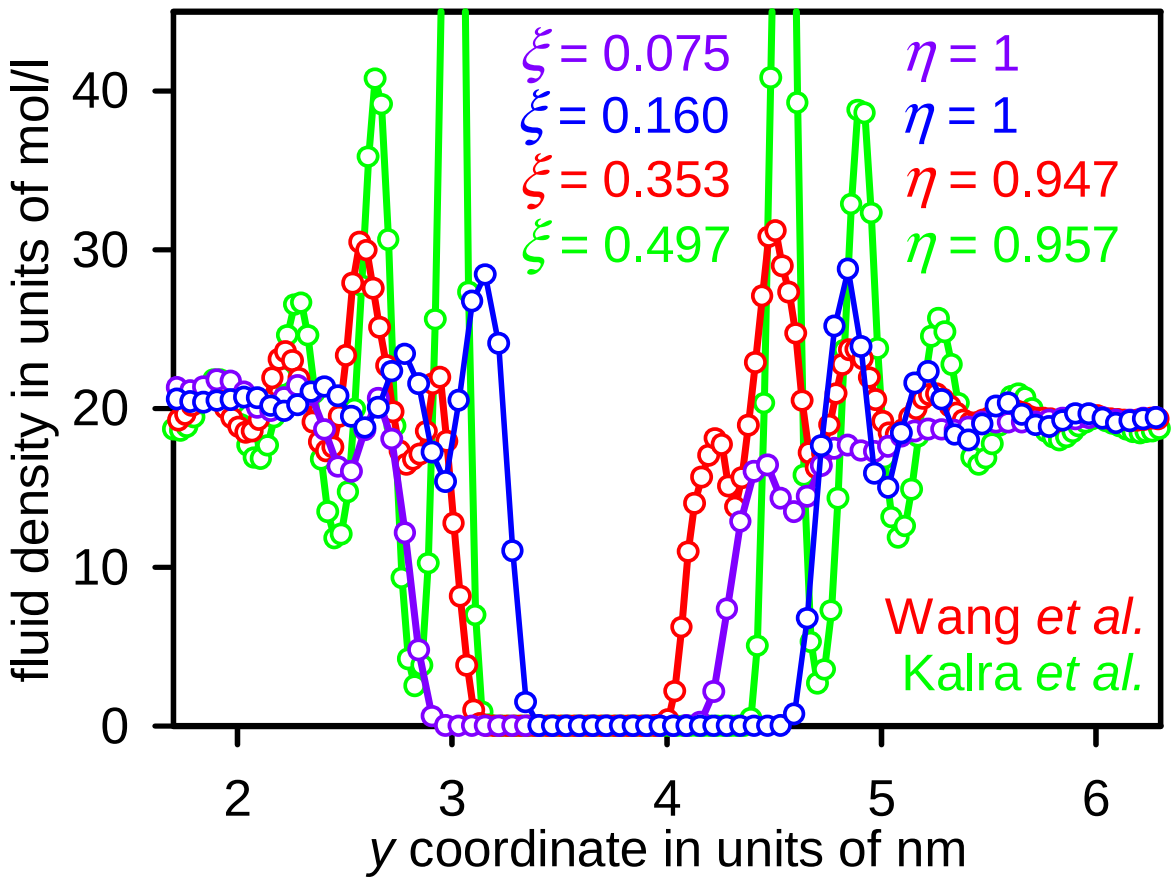
Poiseuille, v_{target} = 10 m/s, τ = 3 ps, L = 15 nm, liquid CH_4 at 166 K



Fluid-wall interaction

Lennard-Jones energy parameter: $\varepsilon_{FW} = \xi \cdot \varepsilon_{FF}$

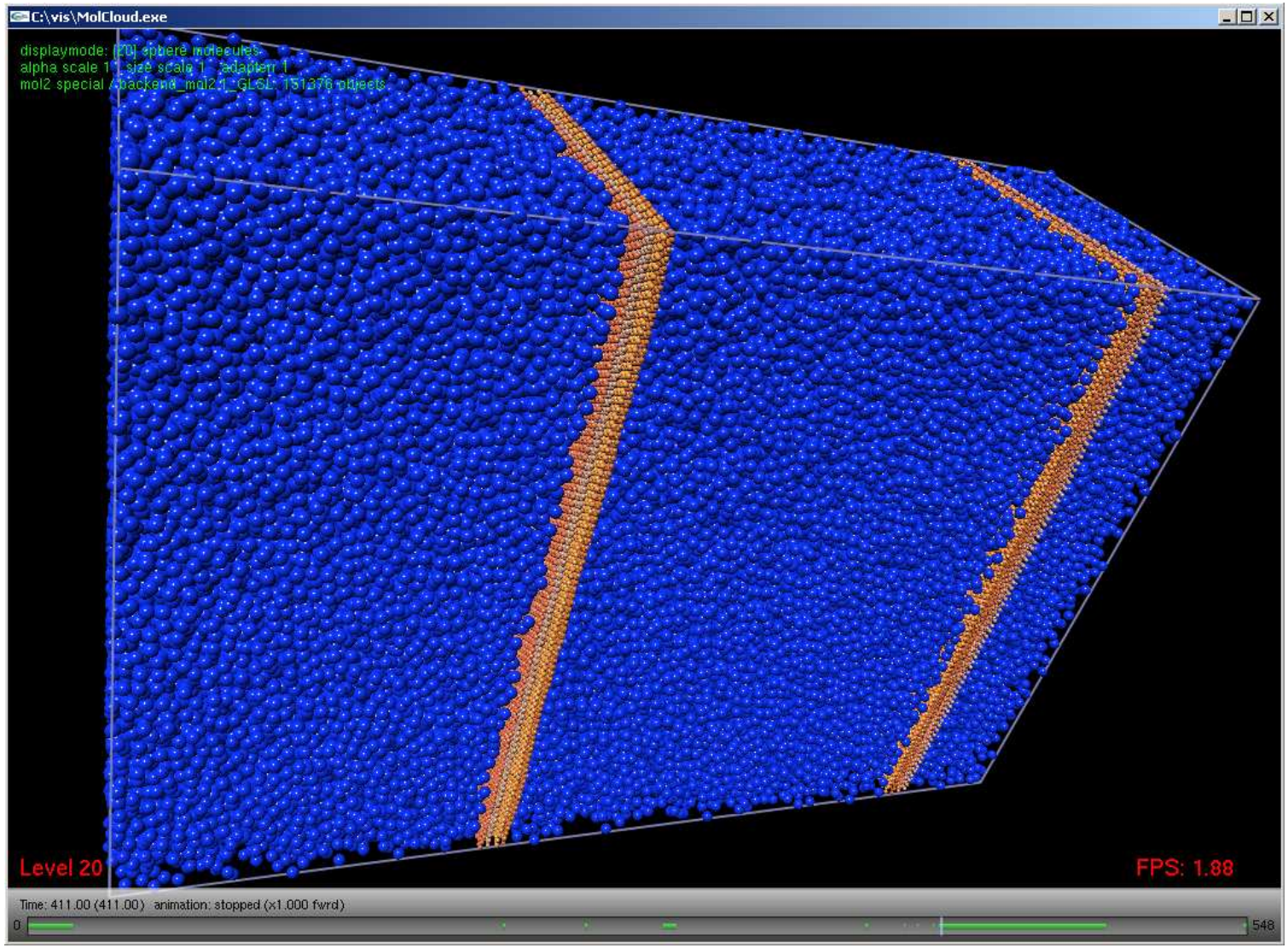
Lennard-Jones size parameter: $\sigma_{FW} = \eta \cdot \sigma_{FF}$



$T = 0.95\ \varepsilon/k$

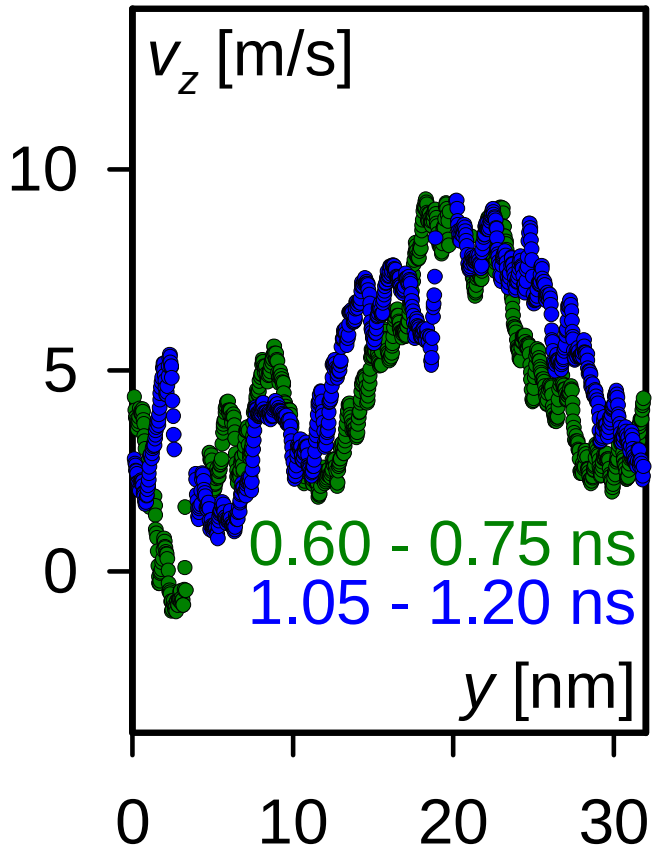
$\rho = 1.005\ \rho'$

MD simulation of Couette flow

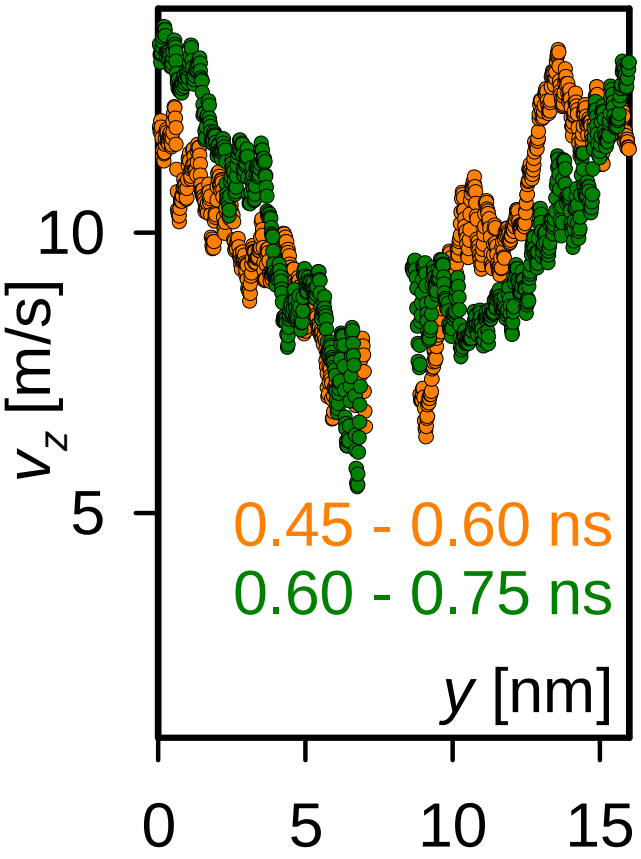


Poiseuille and Couette flow: velocity profile

$T = 0.95\ \varepsilon/k$, $\rho = 1.005\ \rho'$, $v_{target} = 10$ m/s, $\xi = 0.353$, $\eta = 0.9466$ (Wang et al.)

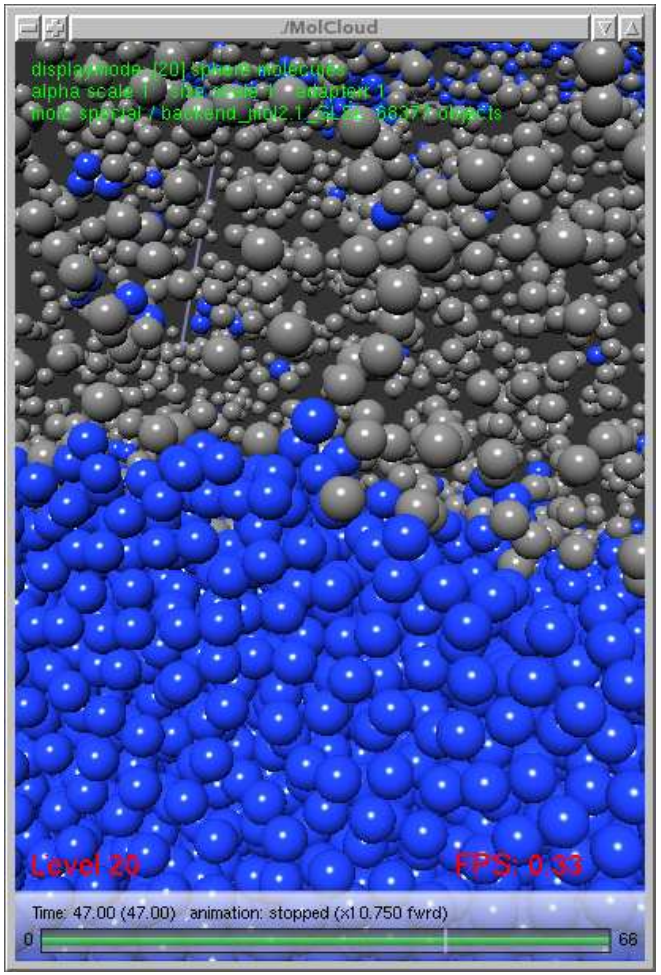


Couette flow

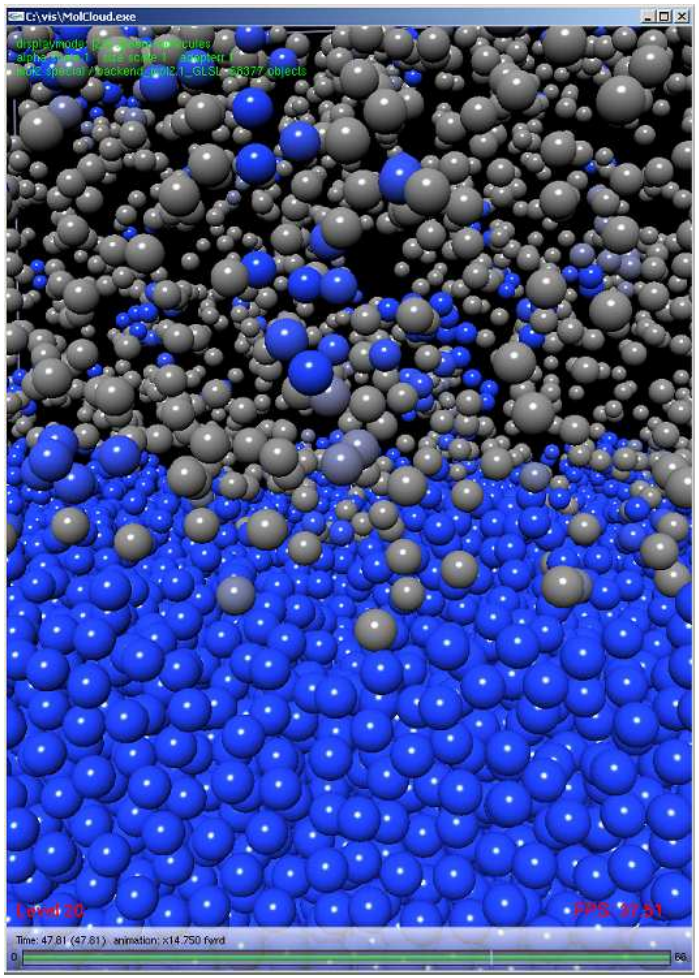


Poiseuille flow

Comparison of cluster criteria

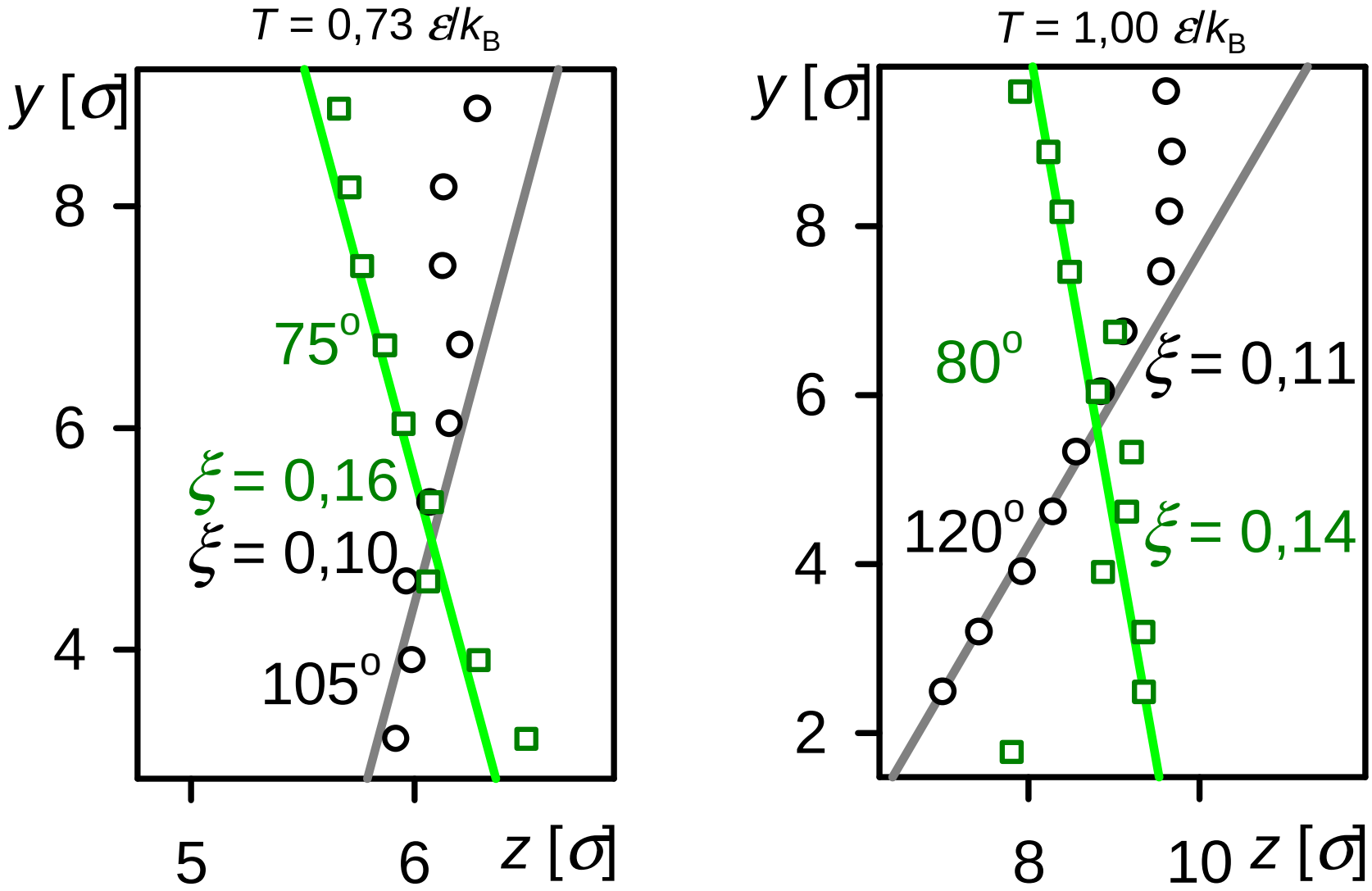


criterion a_2



criterion g'_2

Dependence of the contact angle on ξ



Conclusion

System size: acceptable scaling of *Mardyn*, *L* up to 75 nm easily possible

the system geometry requires (at least static) load balancing

Flow simulations: were carried out in the canonical ensemble

unknown interaction parameters ξ and η

Vapor-liquid interface: dependence of the contact angle on ξ was studied

suitable criterion for the interface: $\rho \geq \sqrt{\rho' \rho''}$

J. Chem. Phys. **128**: 164510

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