Thermo
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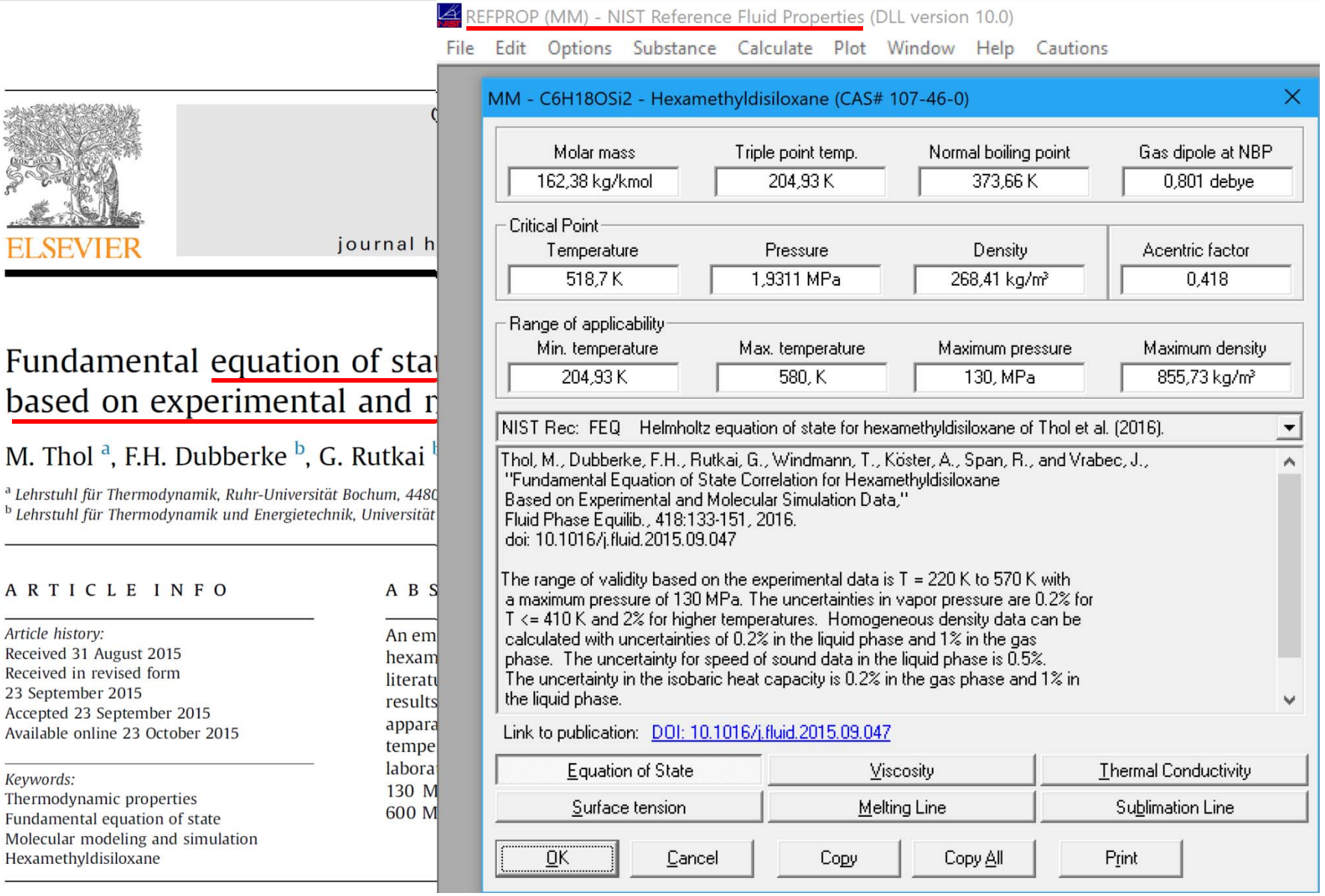
Fakultät III – Prozesstechnik

Atomistic Molecular Simulations for Engineering Applications

Jadran Vrabec *et al.*

Computational Molecular Engineering

Thermodynamic data from force fields gained recognition



ELSEVIER

journal h

Fundamental equation of sta
based on experimental and r

M. Thol [a], F.H. Dubberke [b], G. Rutkai [

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ABS

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130 M
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REFPROP (MM) - NIST Reference Fluid Properties (DLL version 10.0)

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MM - C6H18OSi2 - Hexamethyldisiloxane (CAS# 107-46-0)

Molar mass	Triple point temp.	Normal boiling point	Gas dipole at NBP
162,38 kg/kmol	204,93 K	373,66 K	0,801 debye

Critical Point

Temperature	Pressure	Density	Acentric factor
518,7 K	1,9311 MPa	268,41 kg/m³	0,418

Range of applicability

Min. temperature	Max. temperature	Maximum pressure	Maximum density
204,93 K	580, K	130, MPa	855,73 kg/m³

NIST Rec: FEQ Helmholtz equation of state for hexamethyldisiloxane of Thol et al. (2016).

Thol, M., Dubberke, F.H., Rutkai, G., Windmann, T., Köster, A., Span, R., and Vrabec, J.,
"Fundamental Equation of State Correlation for Hexamethyldisiloxane
Based on Experimental and Molecular Simulation Data,"
Fluid Phase Equilib., 418:133-151, 2016.
doi: 10.1016/j.fluid.2015.09.047

The range of validity based on the experimental data is T = 220 K to 570 K with a maximum pressure of 130 MPa. The uncertainties in vapor pressure are 0.2% for T <= 410 K and 2% for higher temperatures. Homogeneous density data can be calculated with uncertainties of 0.2% in the liquid phase and 1% in the gas phase. The uncertainty for speed of sound data in the liquid phase is 0.5%. The uncertainty in the isobaric heat capacity is 0.2% in the gas phase and 1% in the liquid phase.

Link to publication: DOI: 10.1016/j.fluid.2015.09.047

Equation of State | Viscosity | Thermal Conductivity
Surface tension | Melting Line | Sublimation Line

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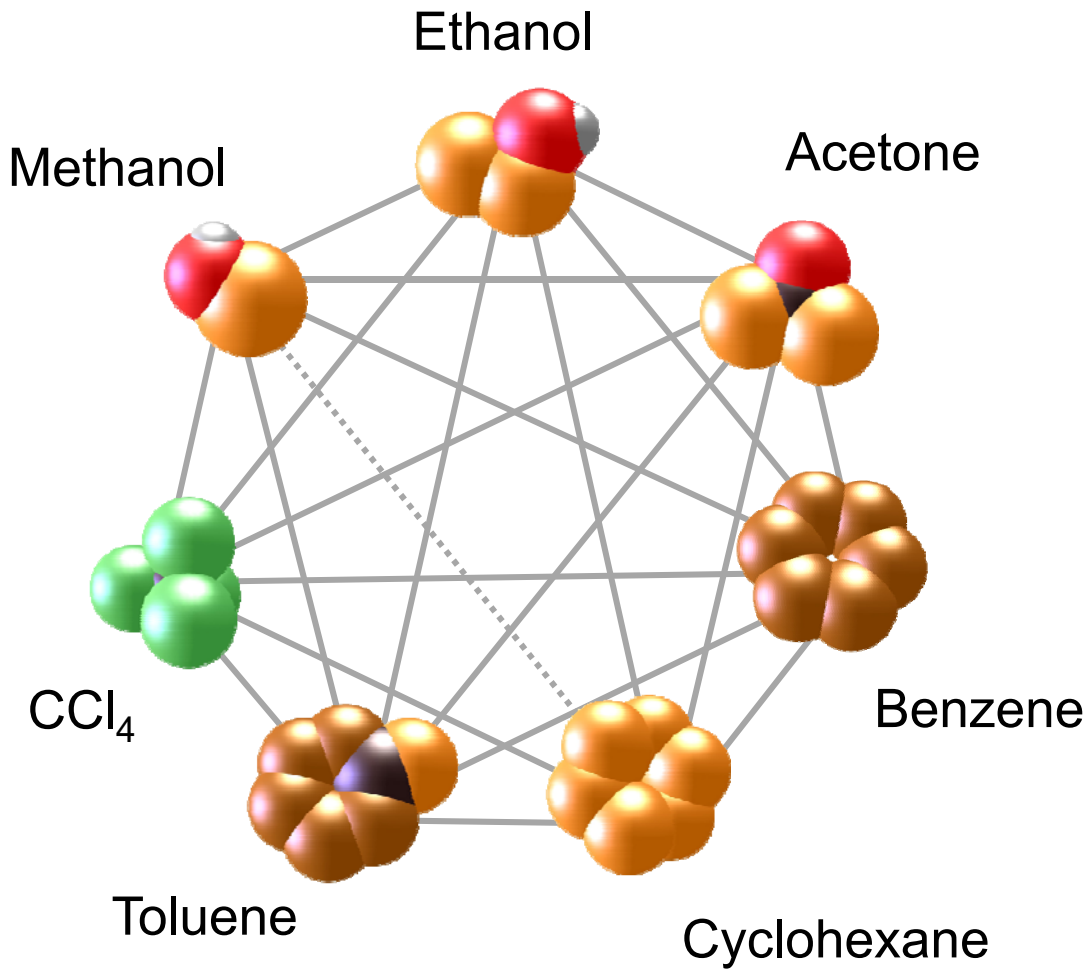
Transport properties



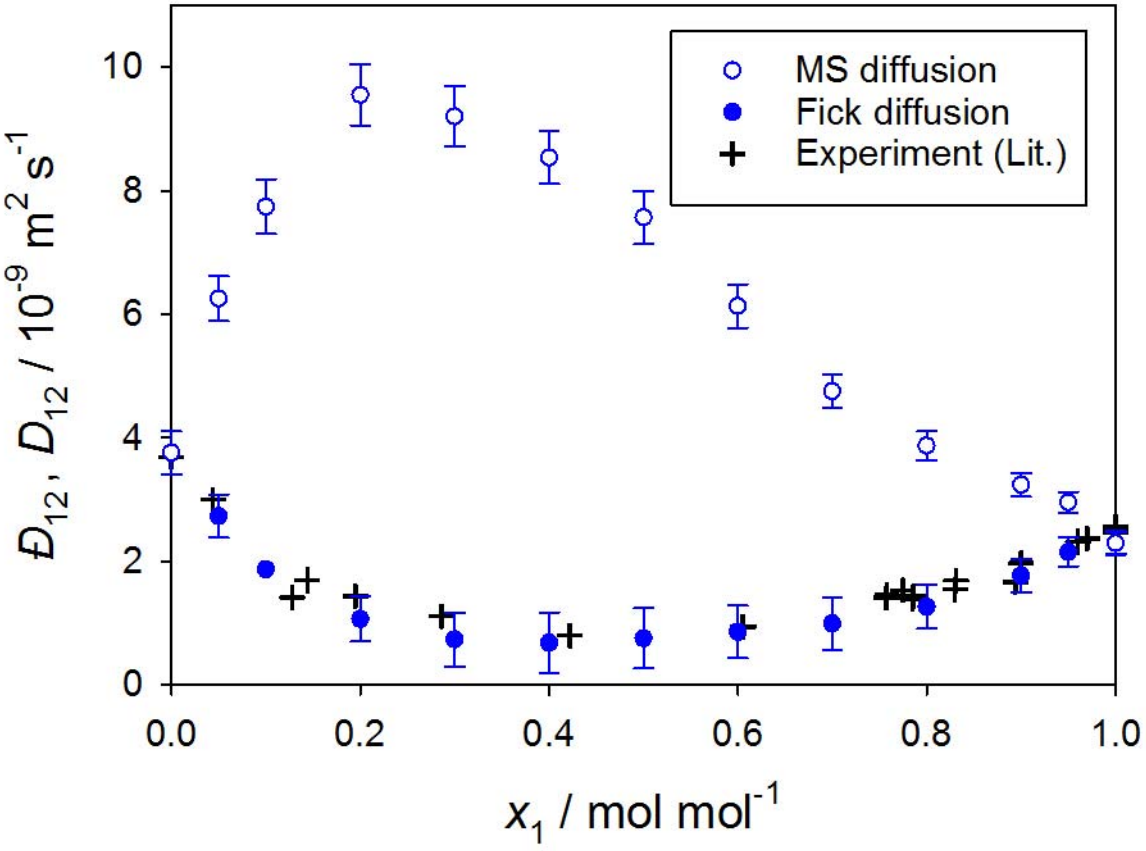
- Molecular models
- Rigid molecules (united atom)
- Lennard-Jones sites, point charges, dipoles, quadrupoles
- Parameters optimized to saturated liquid density and vapor pressure (partly also self-diffusion)
- Mixing behavior: predicted

20 binary mixtures

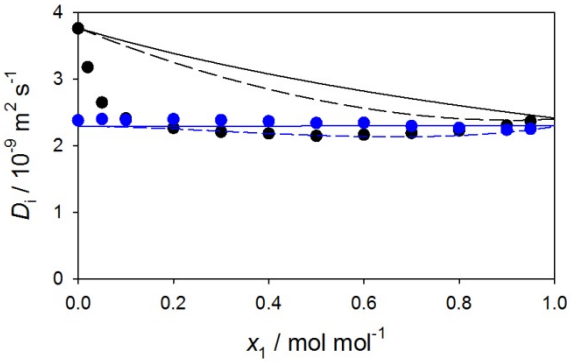
Guevara-Carrion et al.,
J. Chem. Phys. **144**, 124501 (2016)

Example: Methanol + Toluene

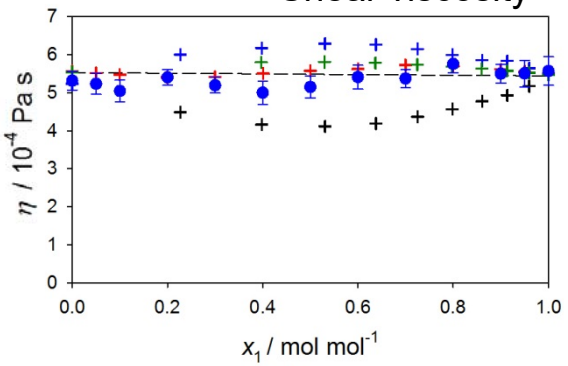
Diffusion coefficients



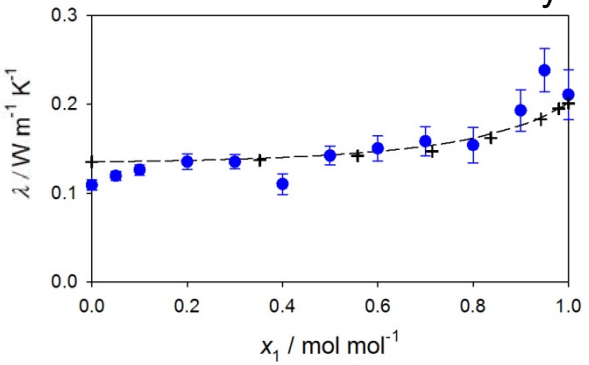
Self-diffusion



Shear viscosity



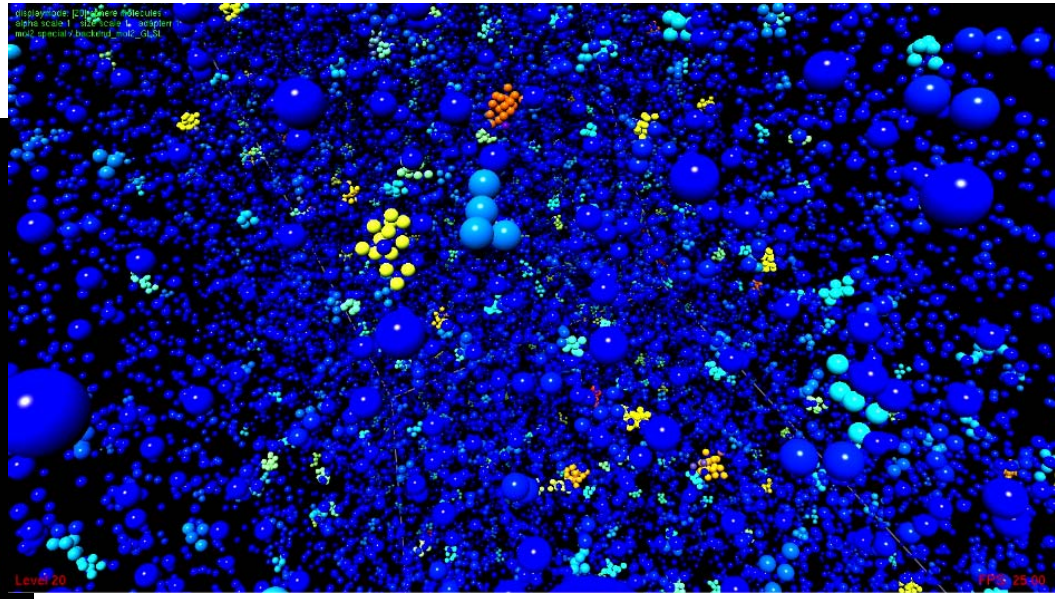
Thermal conductivity



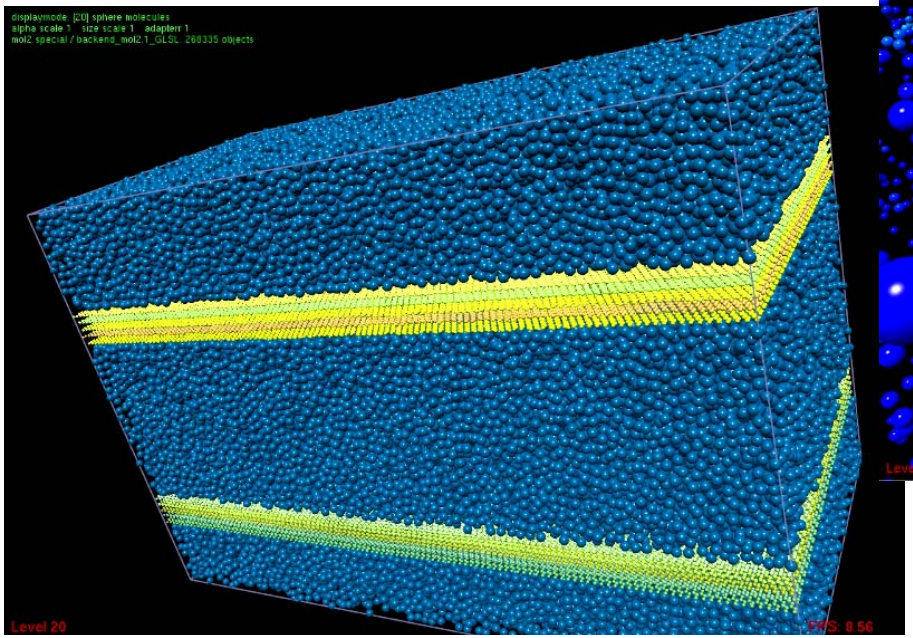
Massively parallel molecular dynamics code: *ls*1

- Force fields: Rigid, Lennard-Jones based, incl. electrostatics
- Tersoff potential for solids
- „Large“ systems, „long“ time scales
- Concurrency in space, not in time

Nucleation



Flow

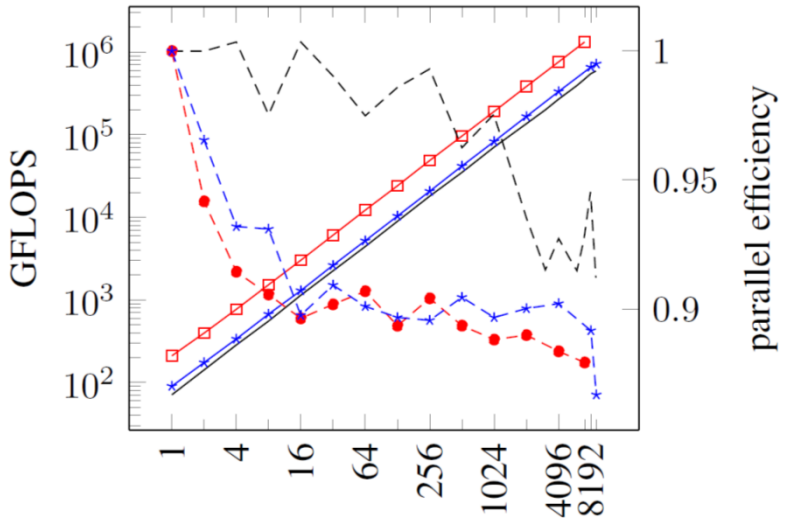


Niethammer et al.,
J. Chem. Theory Comput. **10** (2014) 4455

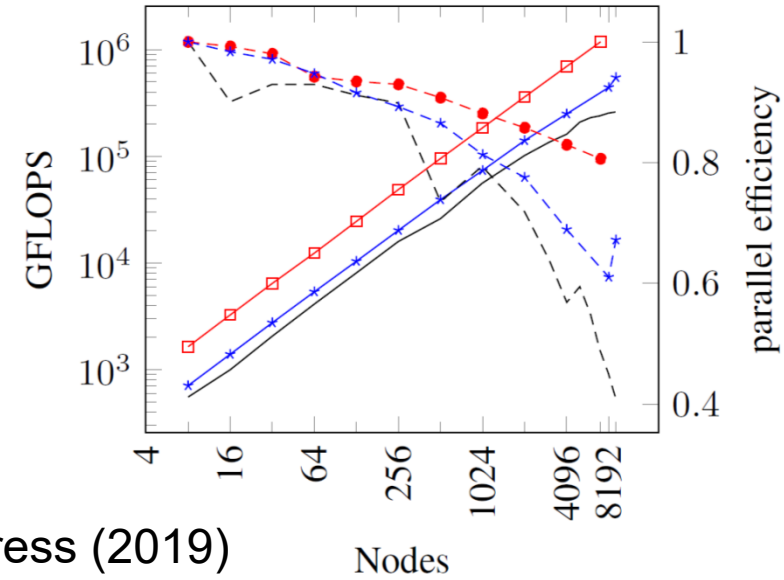
21 trillion molecules simulation on Hazel Hen

- **max. $2.1 \cdot 10^{13}$ molecules**
- 1.33 PFLOPS absolute performance
- 88% weak scaling efficiency
- 80% strong scaling efficiency
- 9% of single precision peak performance

weak scaling

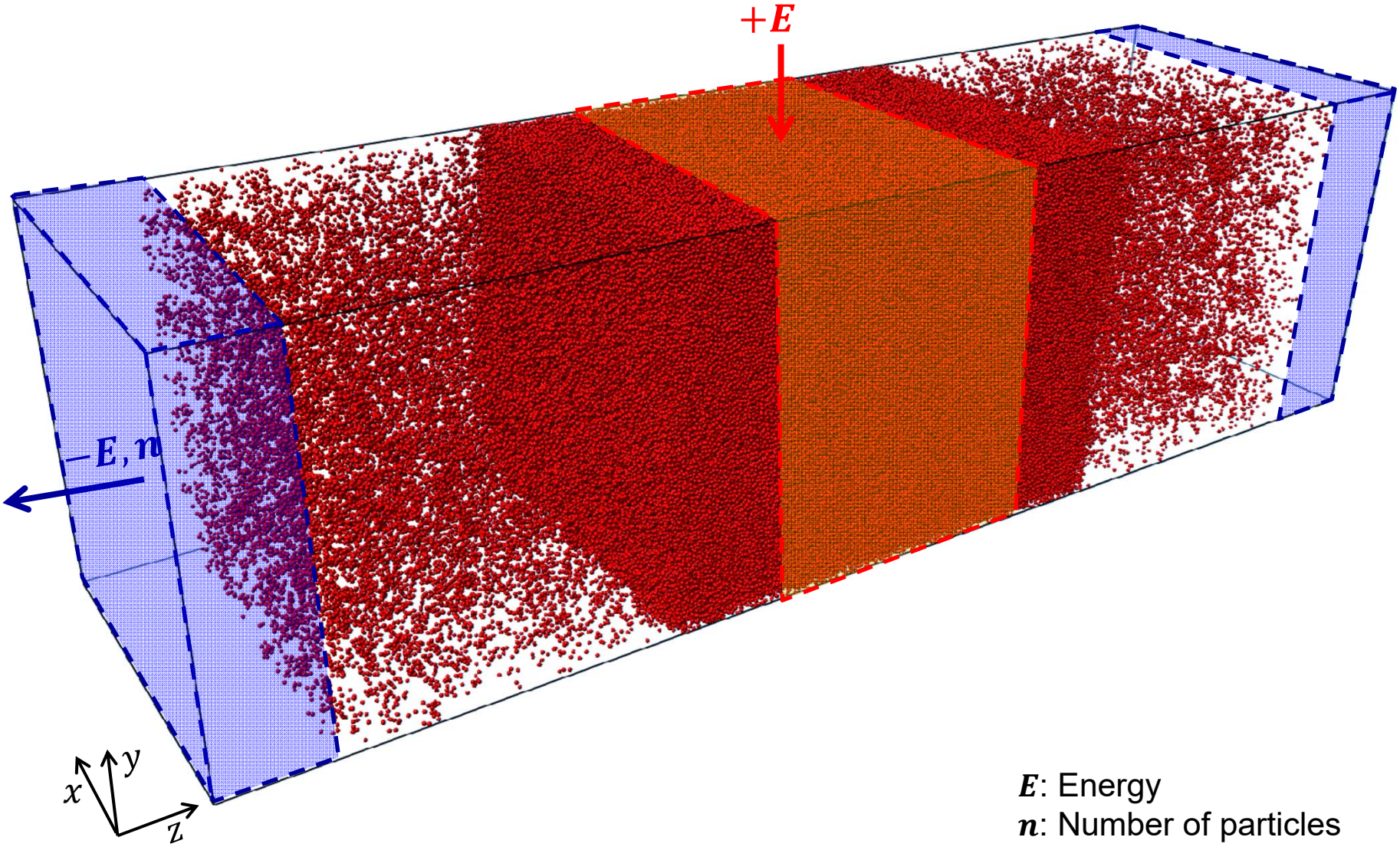


strong scaling



Tchipev et al., *Int. J. High Perf. Comput. Appl.*, in press (2019)

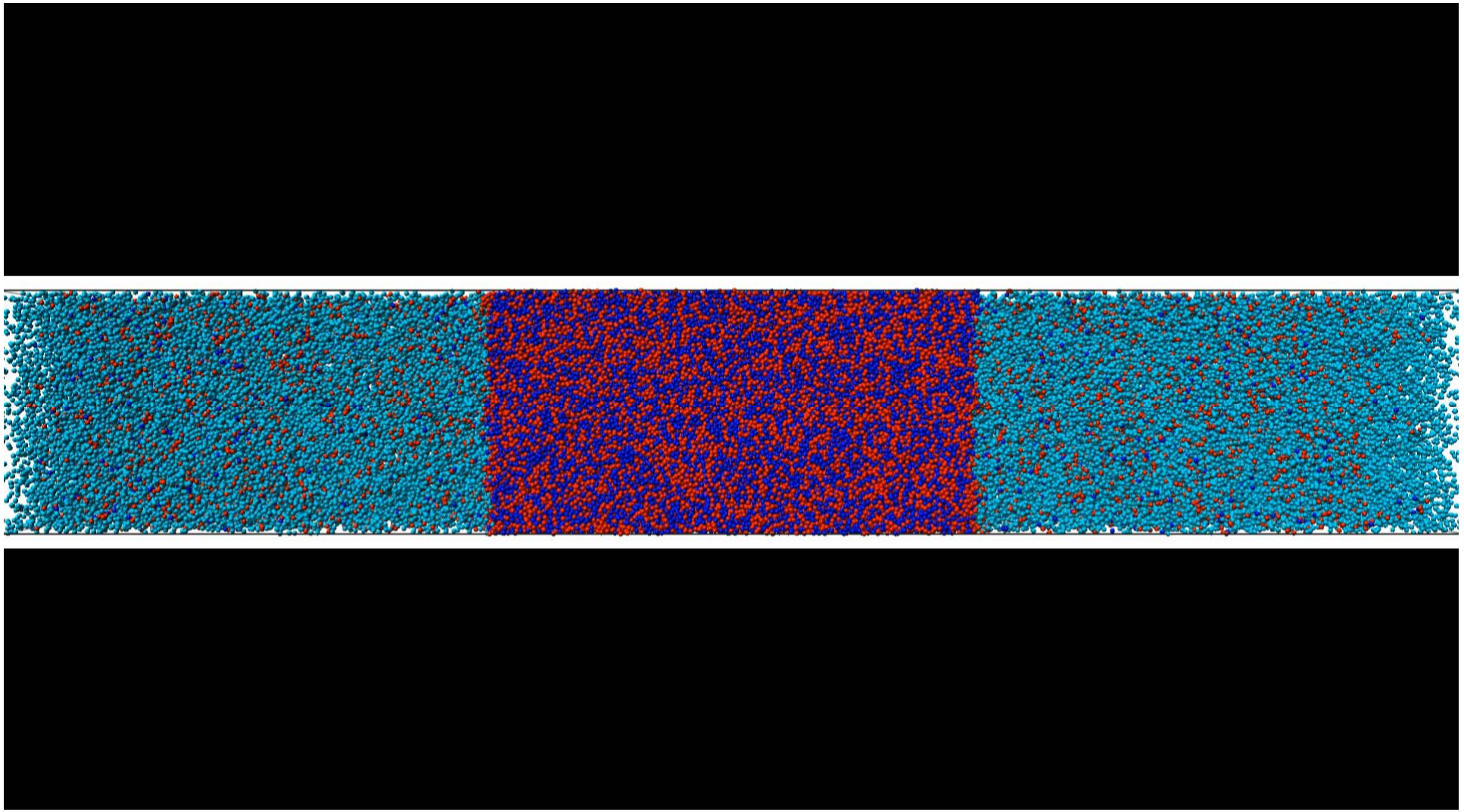
Simulation of evaporation with *ls*1



$\boldsymbol{E}$: Energy
$\boldsymbol{n}$: Number of particles

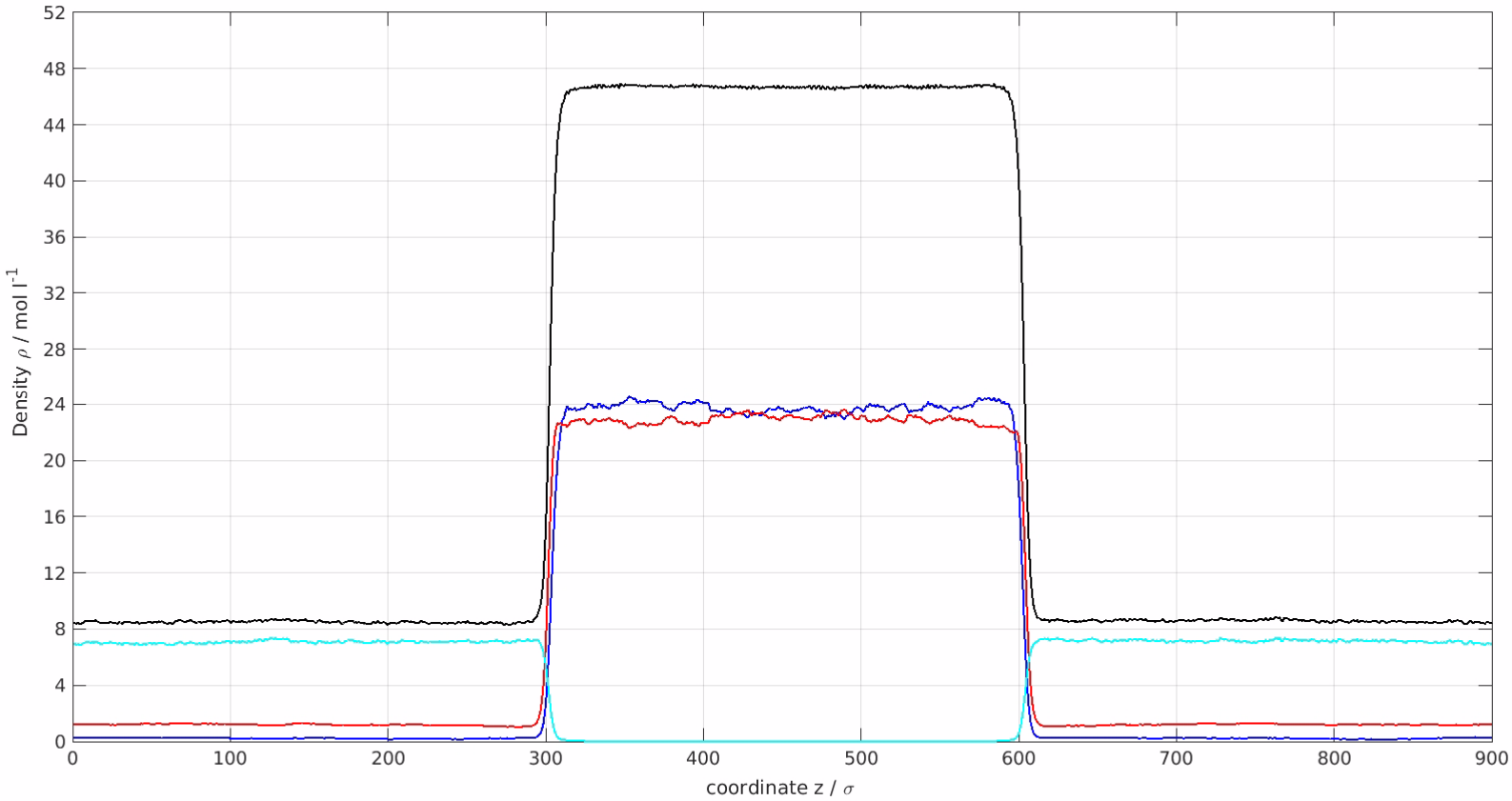
Simulation of evaporation with *ls*1

Equimolar LJ mixture evaporating through a very dense gas (~isothermal)



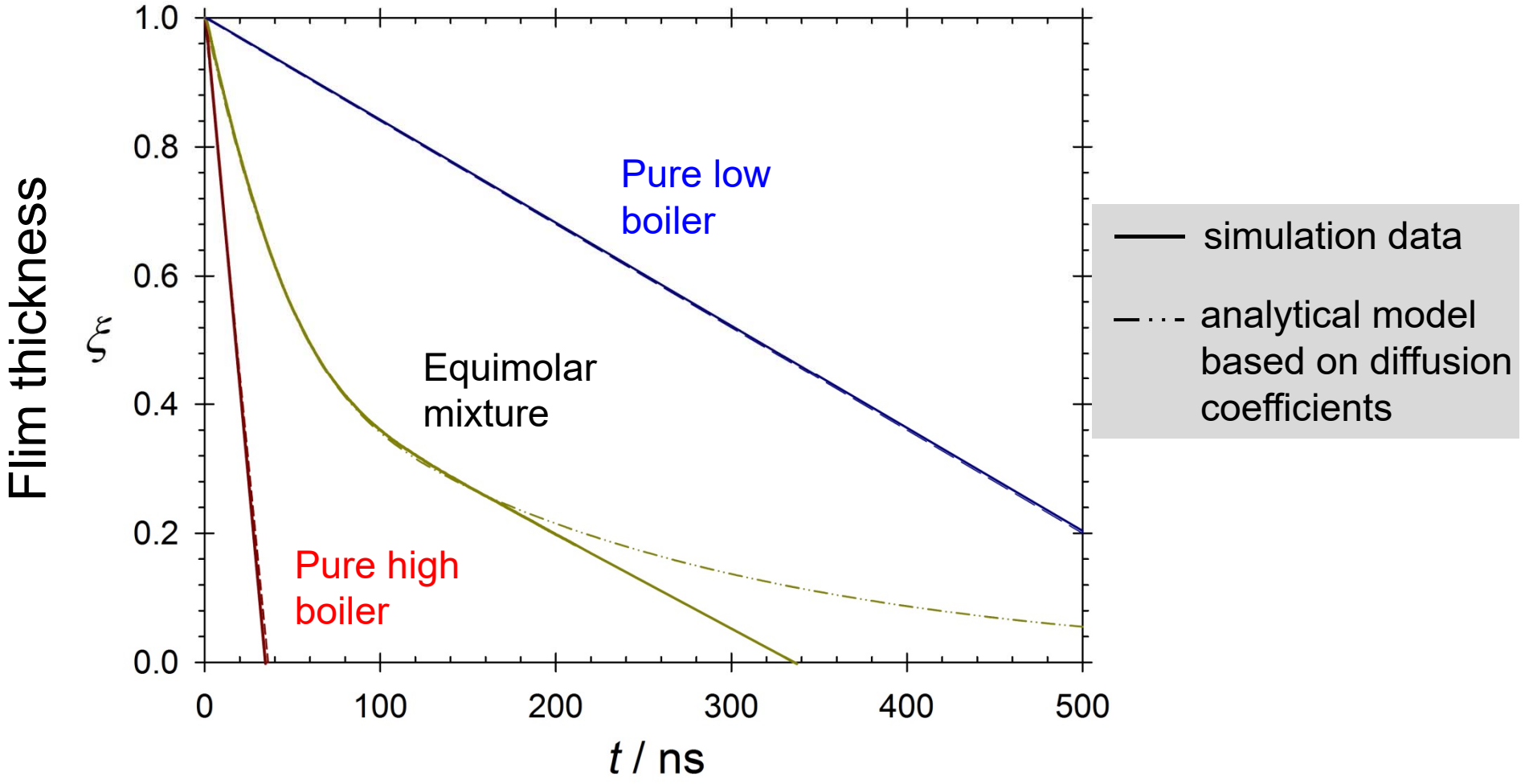
Time dependence of partial densities during evaporation

... spatially resolved



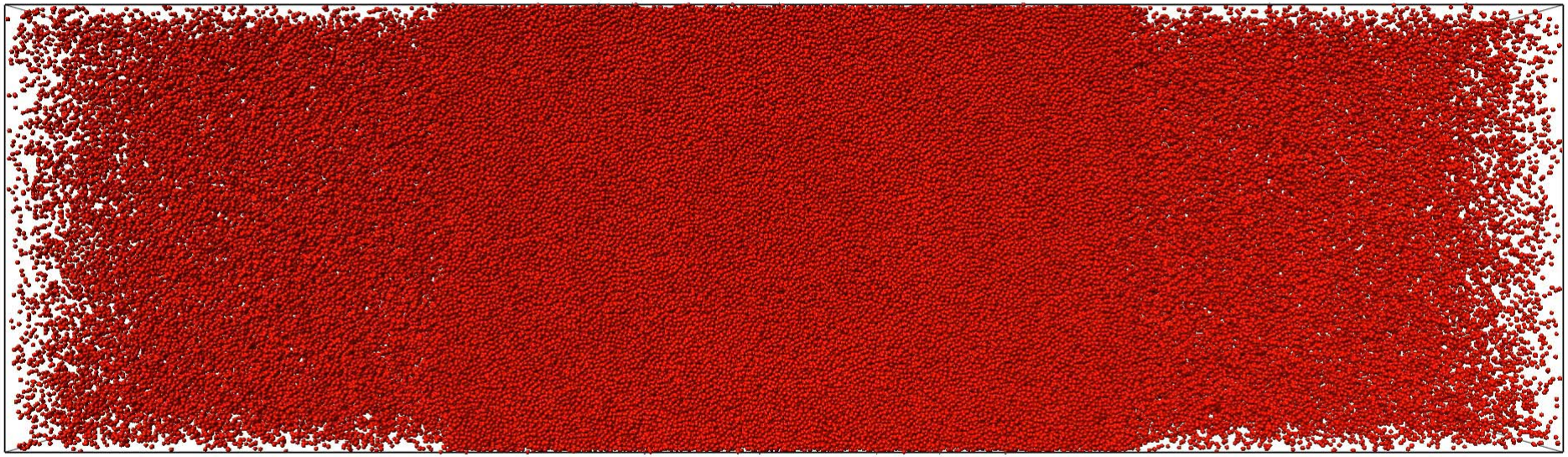
Coordinate / σ

"D-squared law" for planar film

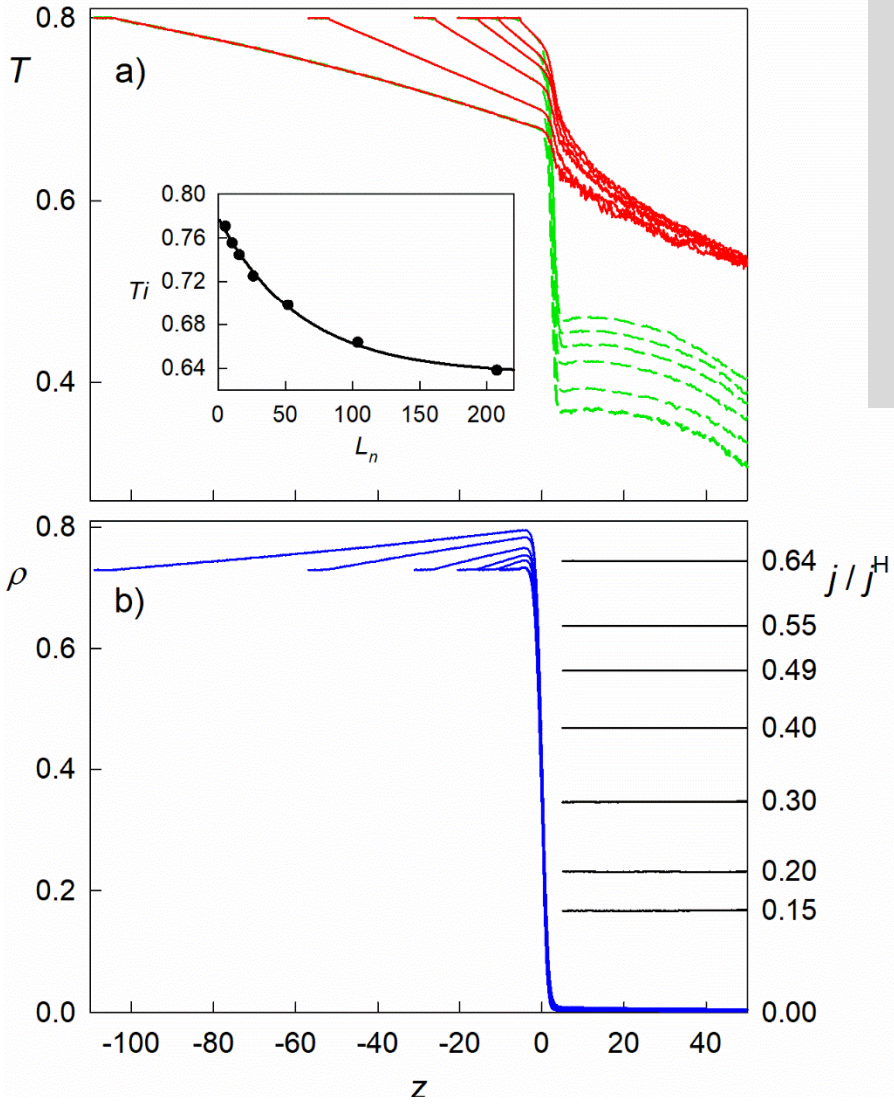


Chatwell et al., *Int. J. Heat Mass Transf.*, in press (2019)

Quasi-stationary simulation of evaporation



Distance between thermostat region and interface L_n



	L_n	Distance to thermostat
———	T_{xy}	Temperature in x, y directions
- - - - -	T_z	Temperature in z direction
———	T_i	Interface temperature
———	ρ	Density
———	j / j^H	Molar flux / Hertz flux

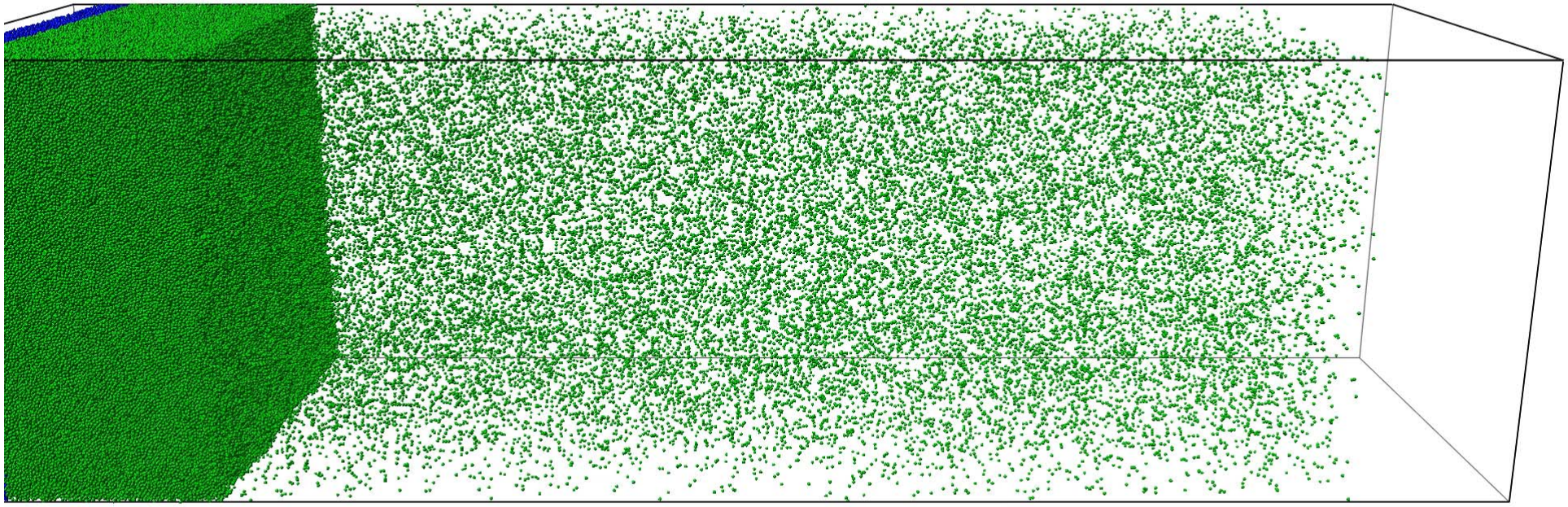
Molar flux j only depends on interface temperature T_i

L_n	T_l	T_i	$j \cdot 10^3$
5.2	0.8000	0.7705	4.504
10.4	0.8240	0.7740	4.523
15.6	0.8466	0.7712	4.496

Heinen et al.,
J. Chem. Phys. **145**: 081101 (2016)

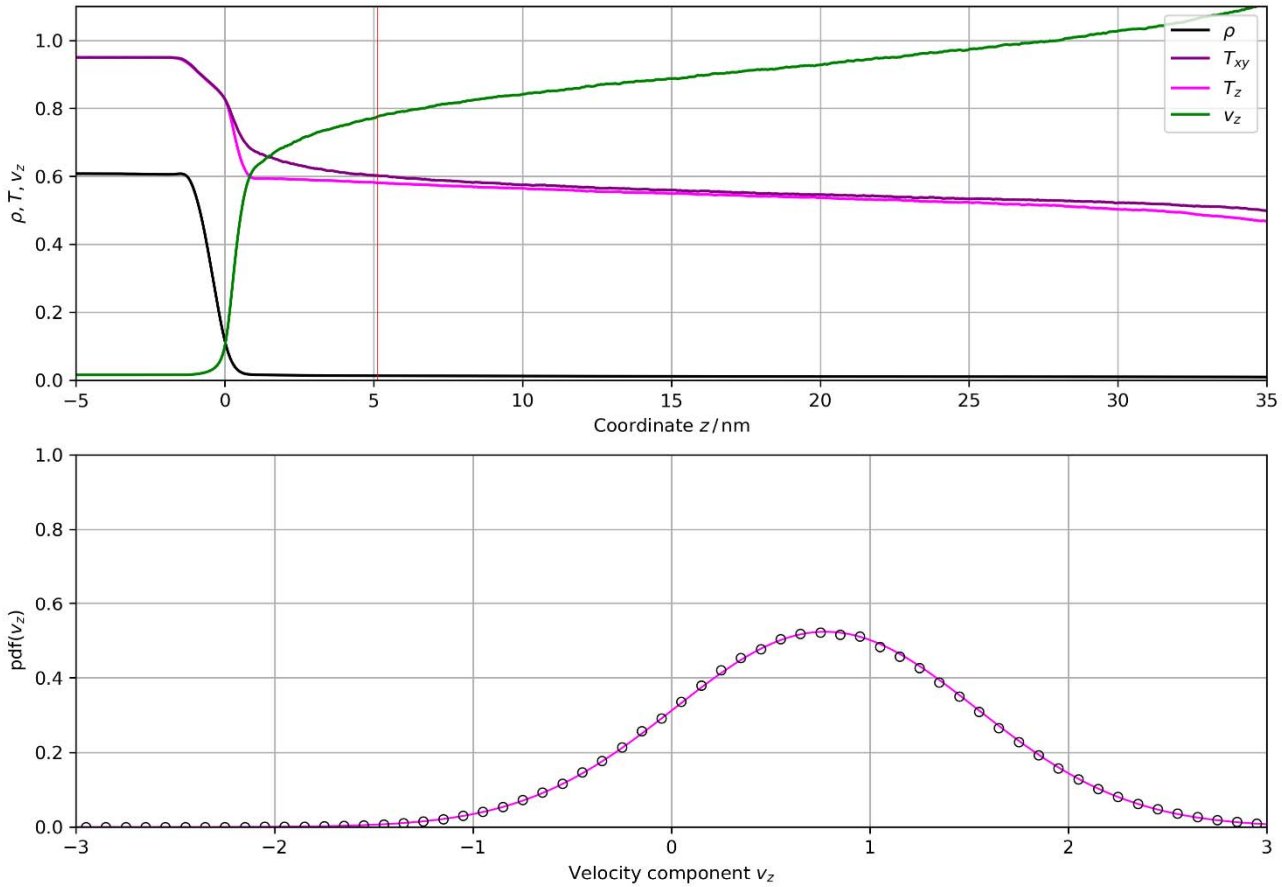
Stationary simulation of evaporation

Fresh liquid is supplied from the left side to attain constant interface position



Temperature, density and velocity profiles @ T_l*=0.95

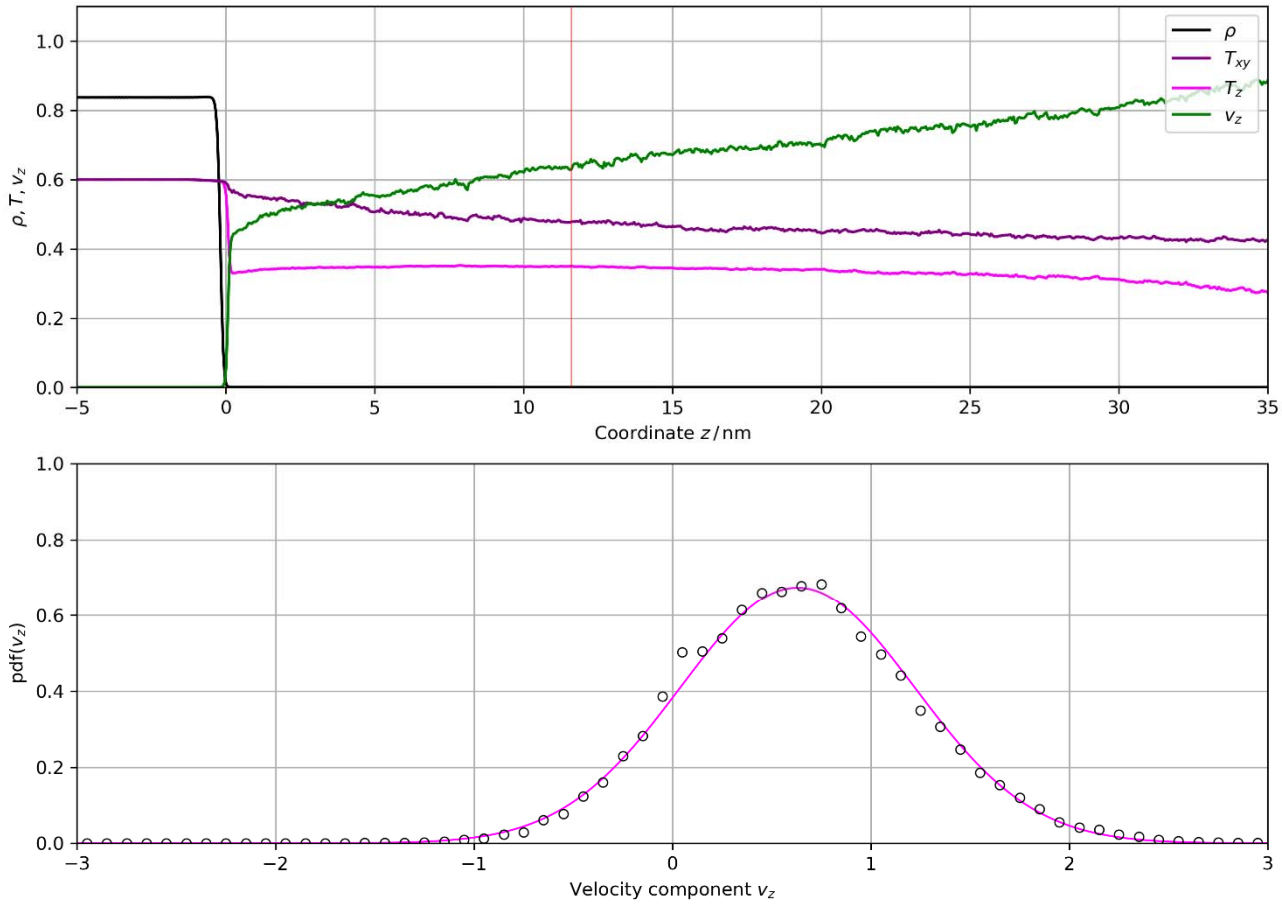
Velocity distribution function is Maxwellian everywhere



Temperature, density and velocity profiles @ T_l*=0.6

Velocity distribution function is not Maxwellian at the interface

A thermalization region can be define in which the Maxwellian is re-attained



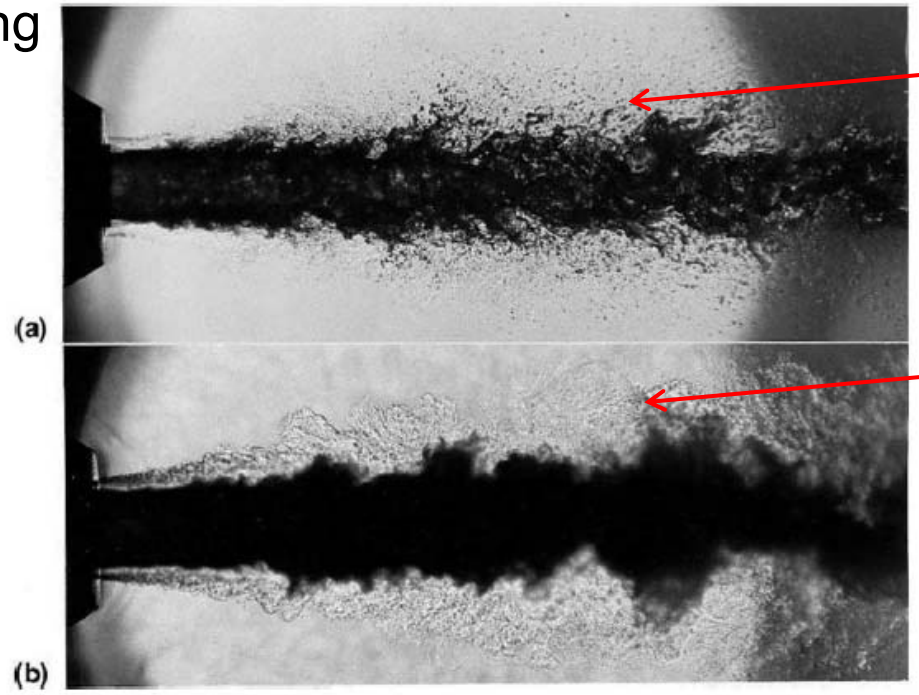
Liquid nitrogen injection (instead of oxygen)

Dahms, Oefelein: Phys. Fluids 25 (2013)

Injector operating pressure:

$p = 1$ MPa

$p = 6$ MPa



Spray

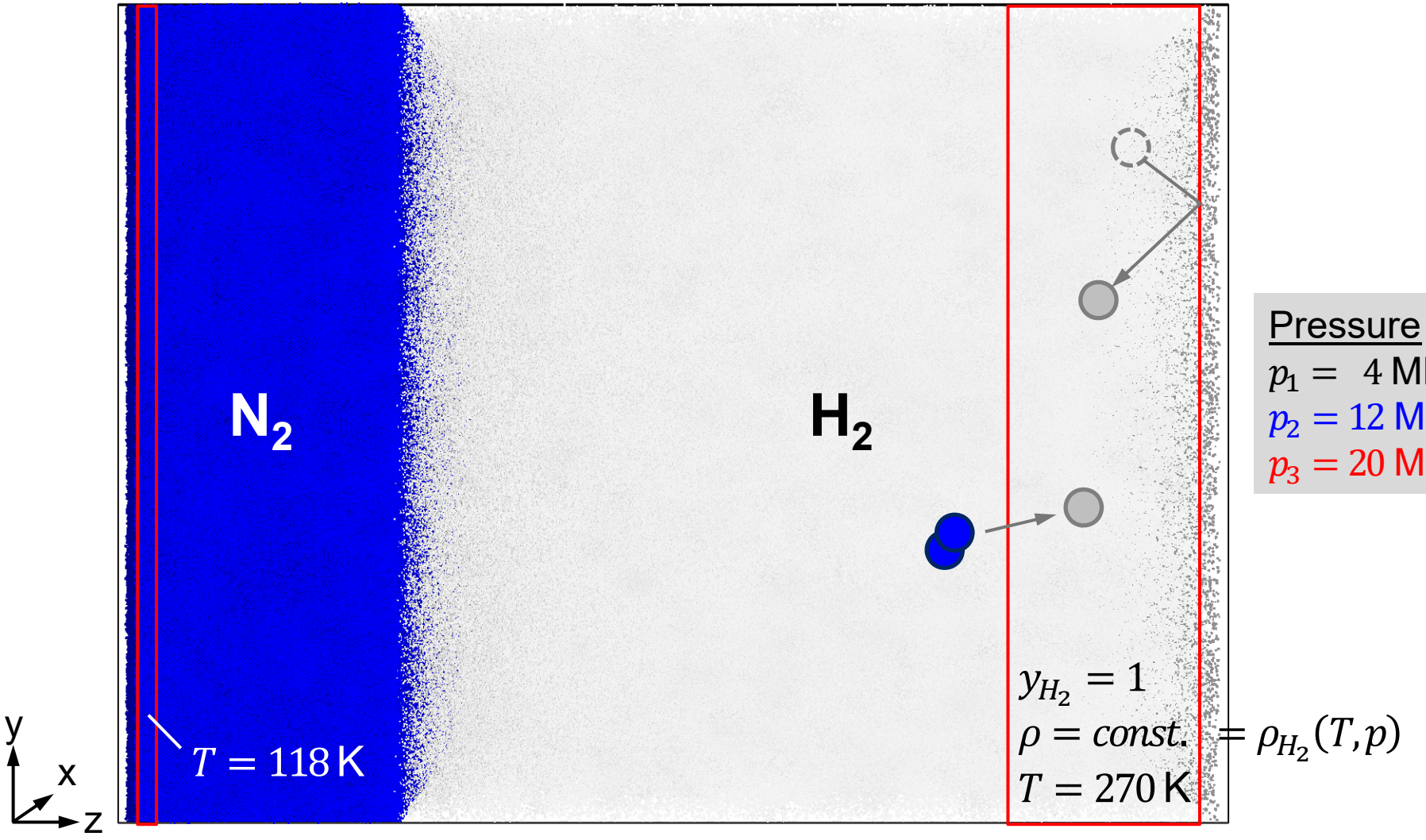
Diffuse mixing

FIG. 1. Nonreacting shear-coaxial liquid-nitrogen–helium injector operating at (a) 1.0 MPa and (b) 6.0 MPa. T_{N2} = 97 K, T_{He} = 280 K into GHe at T = 300 K. Reprinted with permission from W. Mayer, A. Schik, B. Vieille, C. Chaveau, I. Gökalp, D. Talley, and R. Woodward, J. Propul. Power **14**, 835 (1998). Copyright 1998, American Institute of Aeronautics and Astronautics.

Also, helium instead of hydrogen …

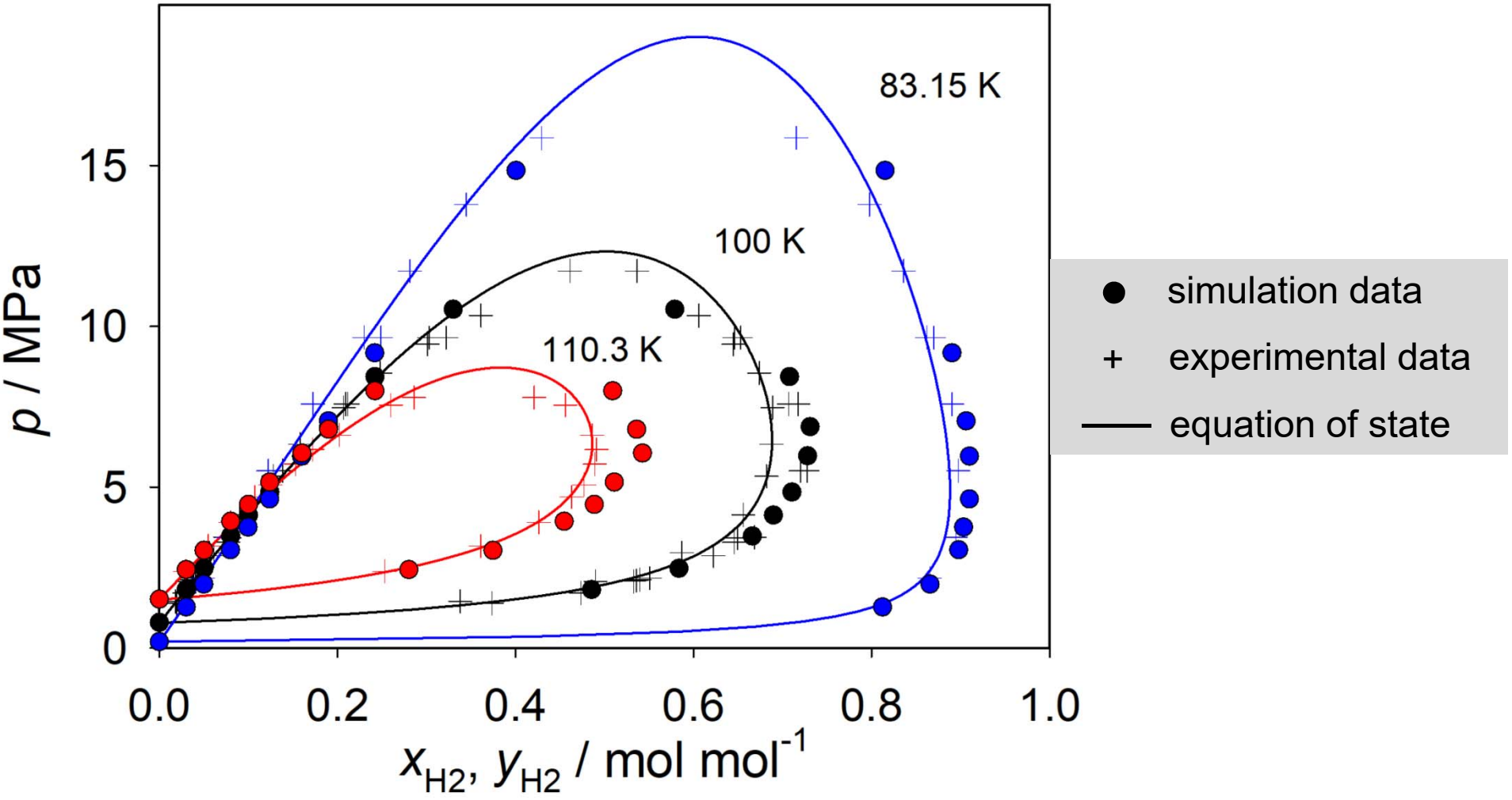
Dual Control Volume (DCV)

$N \approx 10^7$

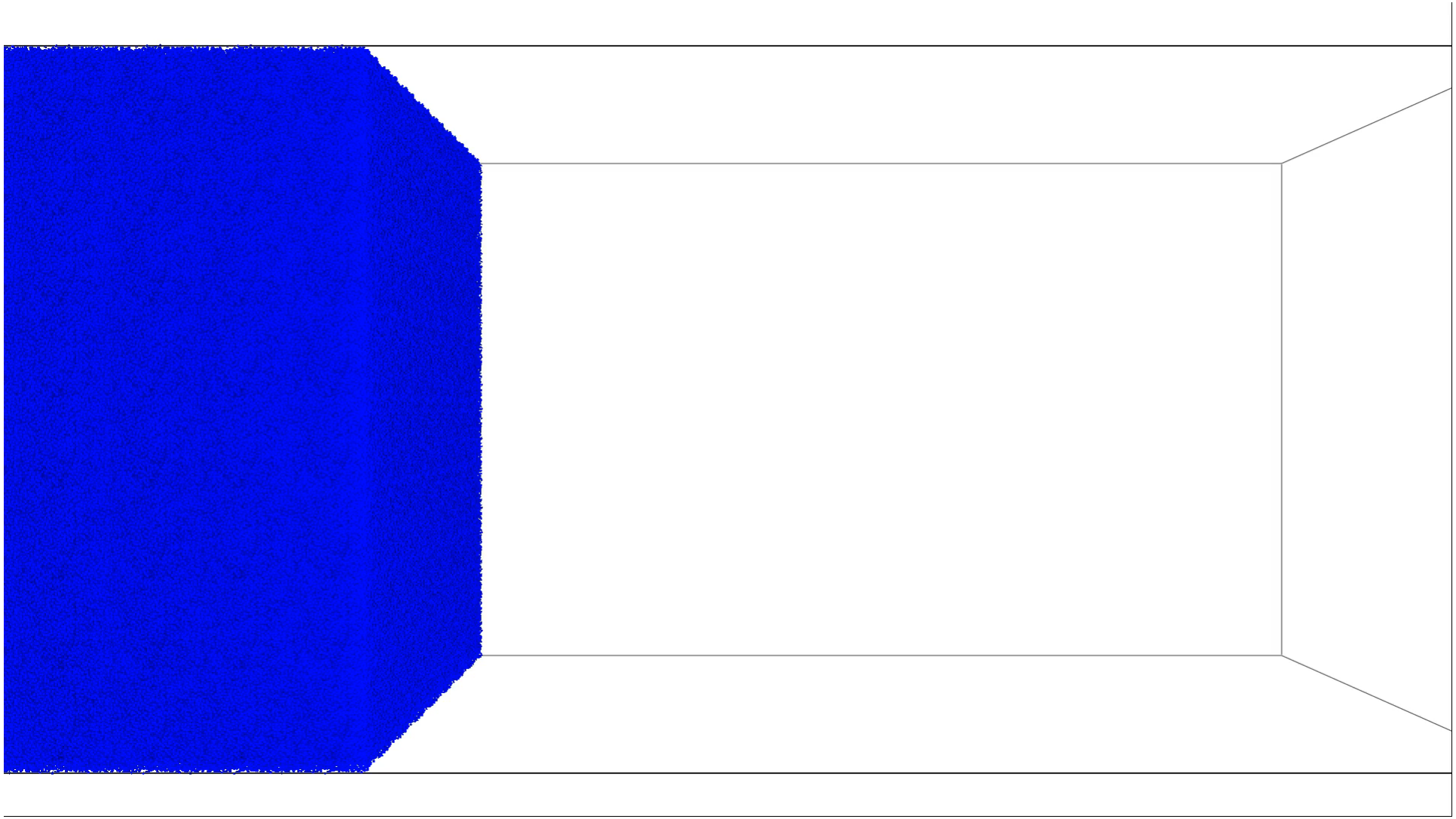


Pressure
$p_1 = 4$ MPa
$p_2 = 12$ MPa
$p_3 = 20$ MPa

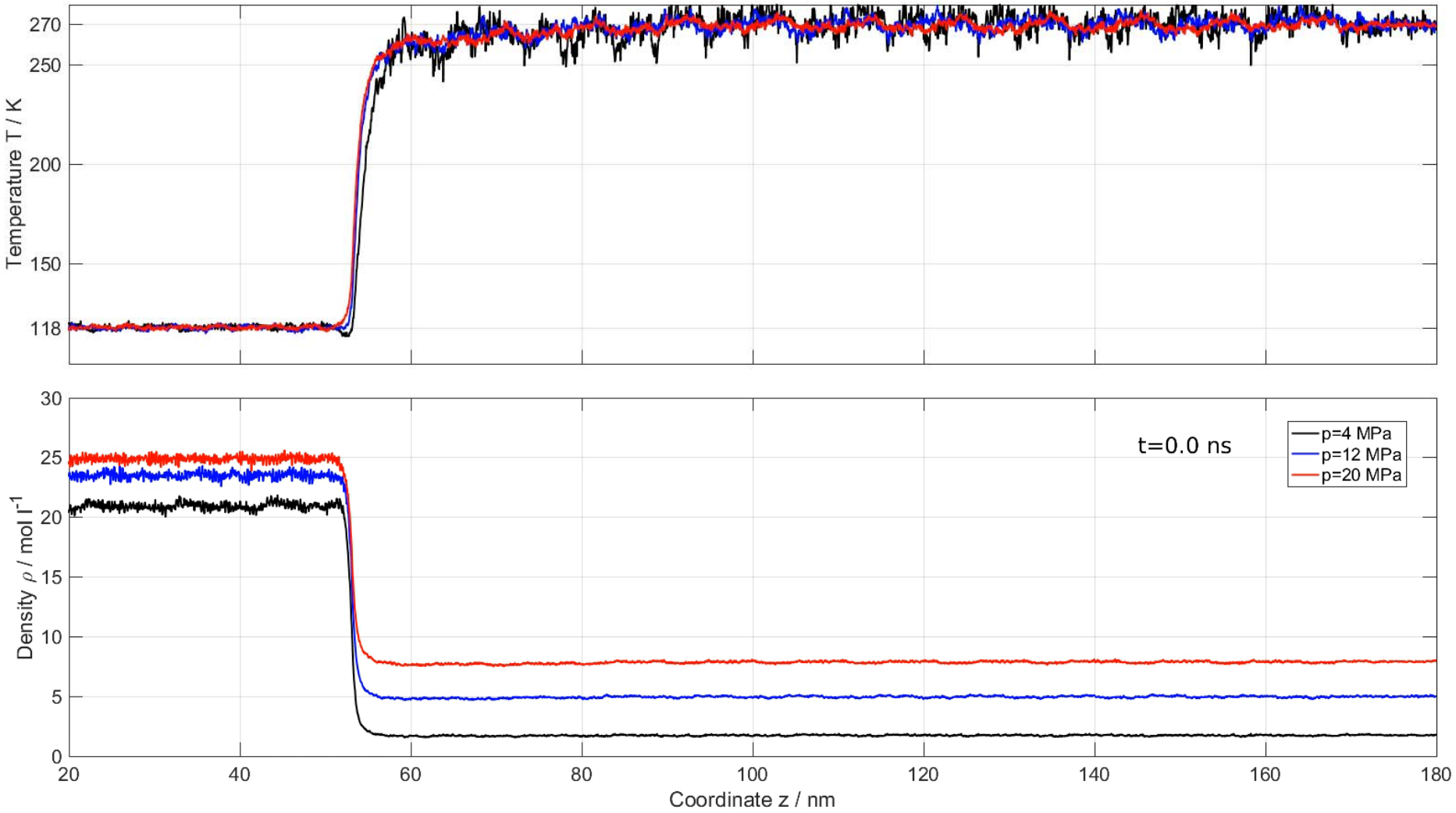
Vapor-liquid phase diagram of N_2 + H_2



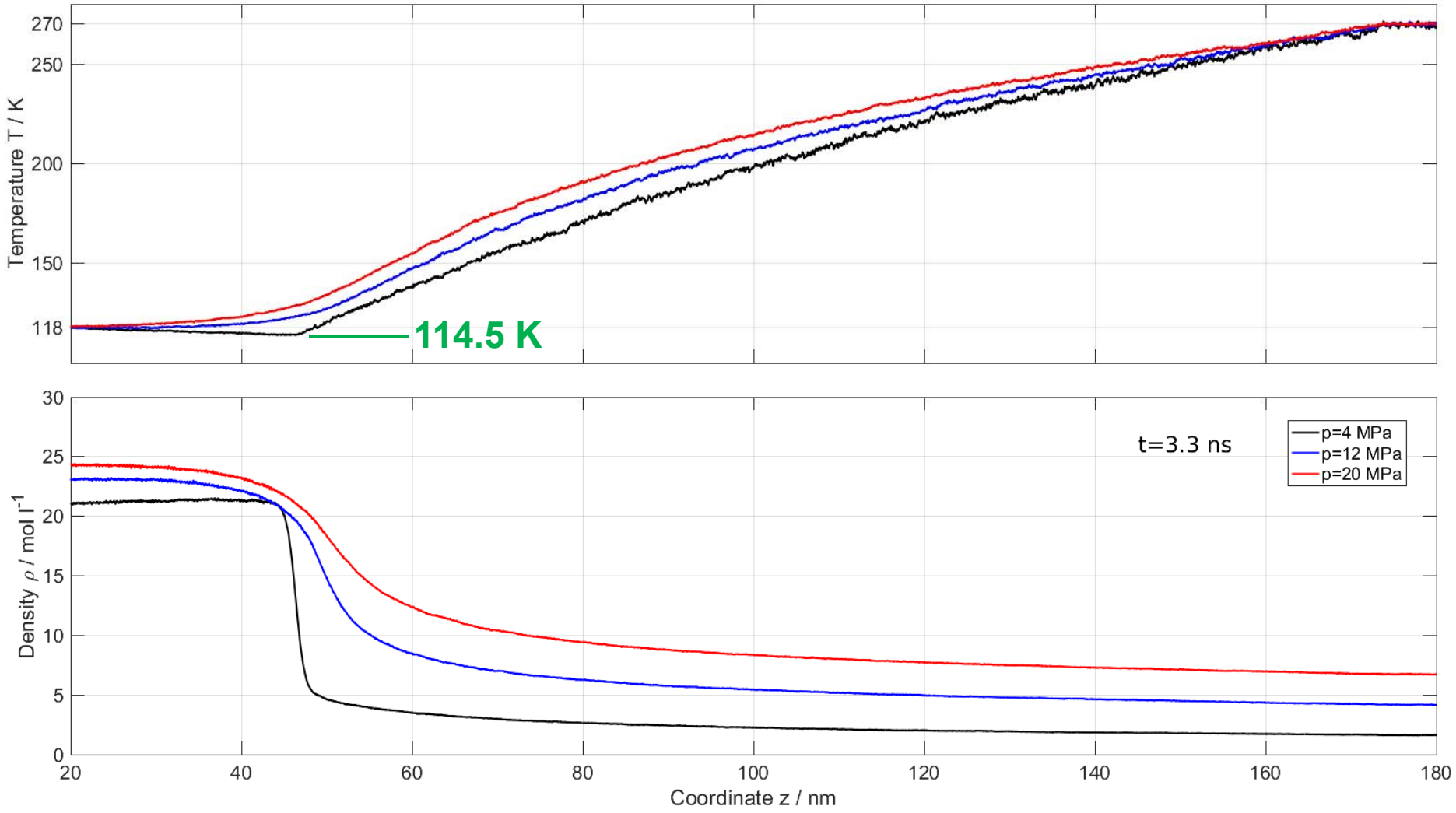
Visualization: Liquid N_2 evaporating into H_2



Evolution of temperature and density

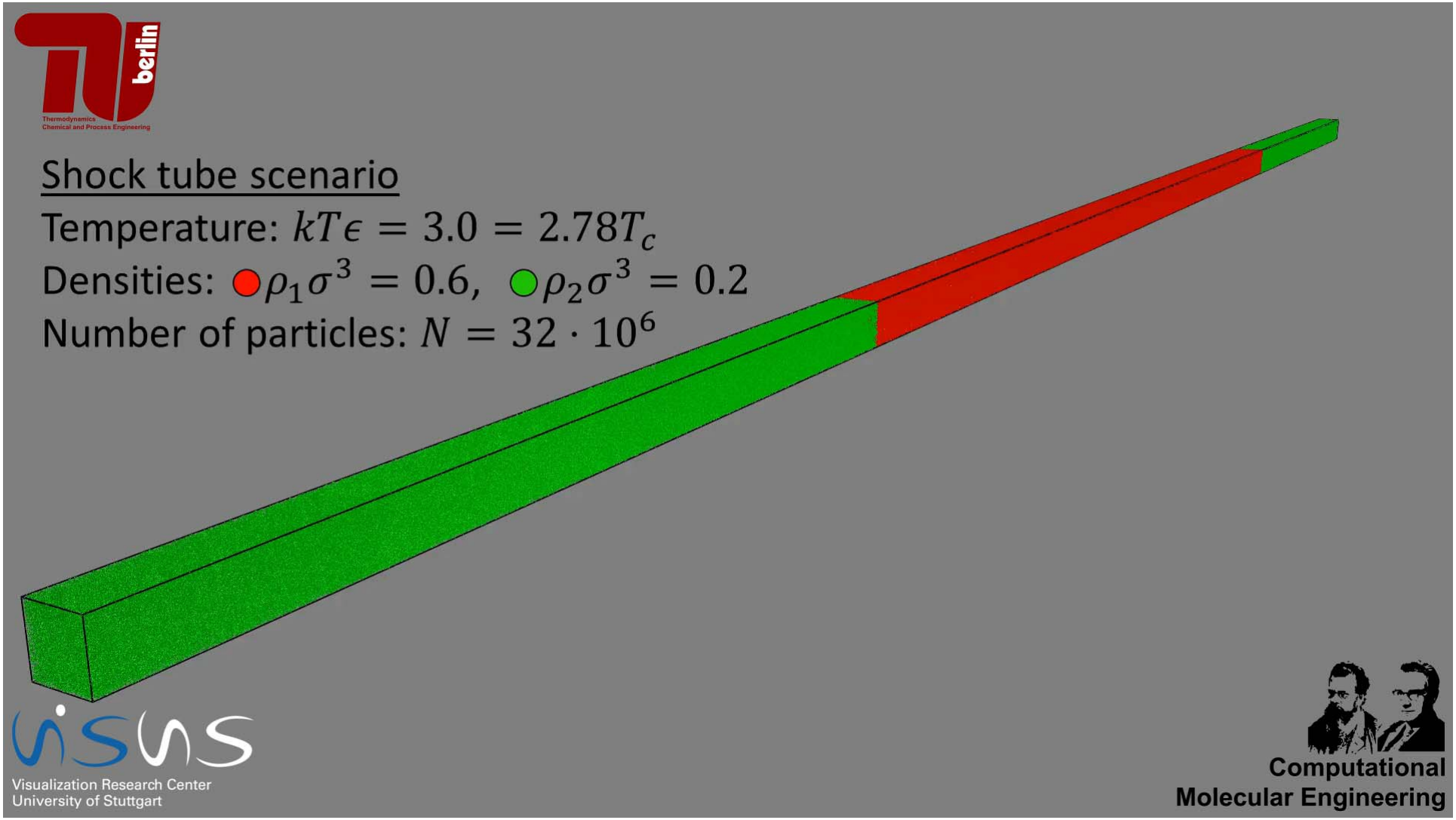


Evolution of temperature and density



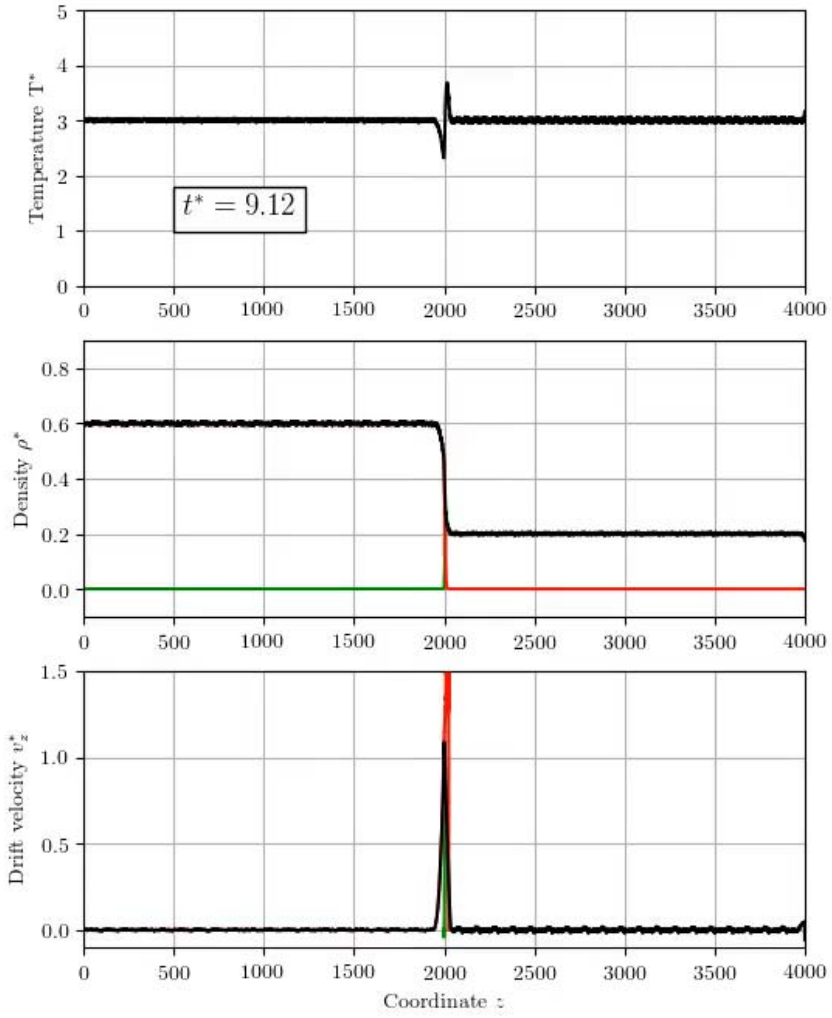
Instationary simulation of a shock tube

A pure fluid at different densities interacts with itself



Shock wave results

Circular marks are visible where the expanding spherical atmospheric shockwaves from the gun firing meet the water surface



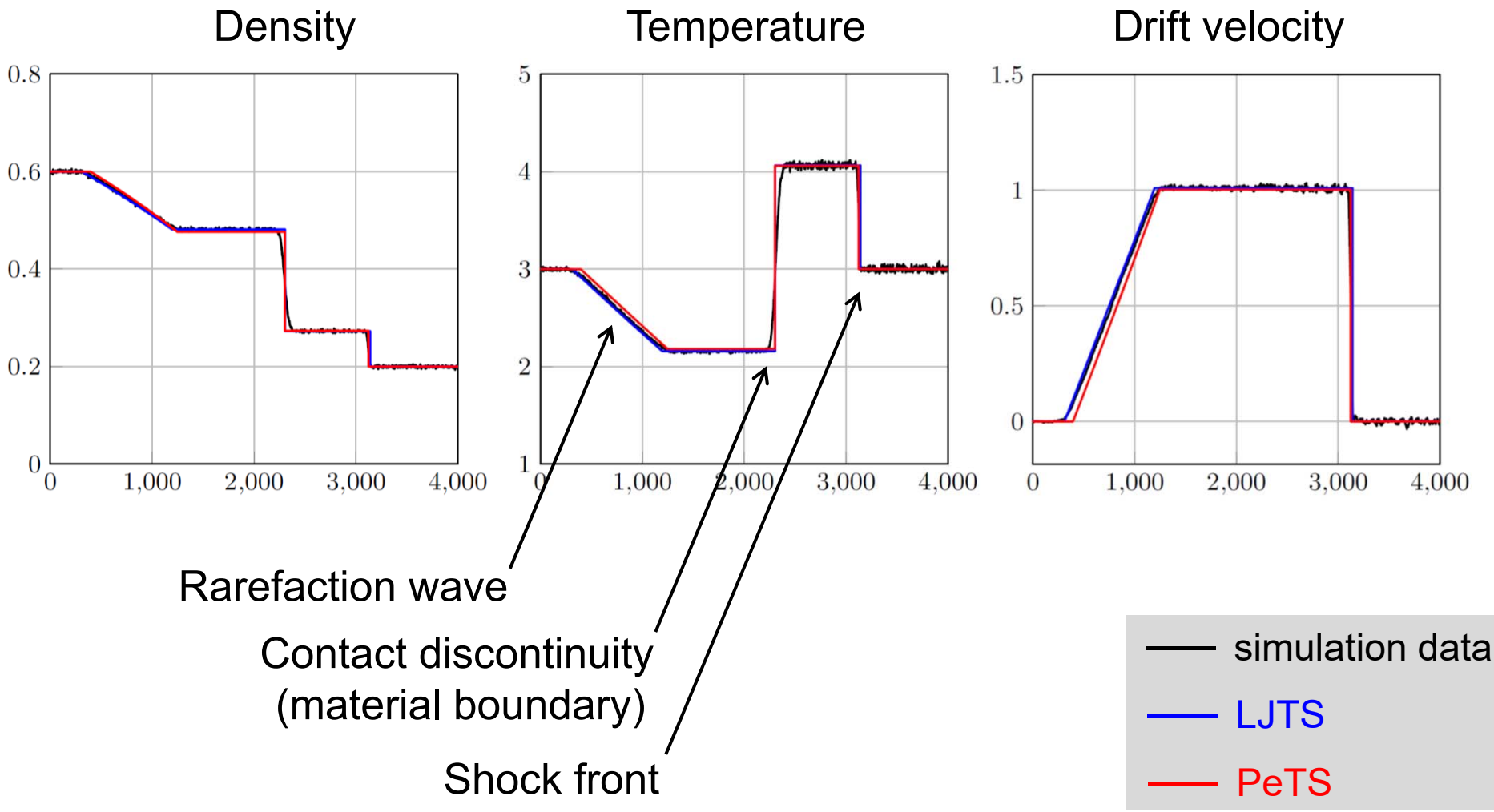
— expanding phase

— stationary phase

— overall

Results for shock wave …

agree very well with discontinuous Galerkin spectral element solution
of the multiphase Riemann problem (Hitz, Munz, IAG, University of Stuttgart)



Summary

- Classical force fields contain thermodynamic properties adequately
- Molecular dynamics simulations of inhomogeneous fluids may efficiently use large machines
- The spectrum of possible applications of molecular modeling and simulation is very wide