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Surface analysis algorithms in the *mardyn* program and the *ls1* project

Stuttgart, 15th December '10

M. T. Horsch

Bundesministerium für Bildung und Forschung

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

ThEt

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Surface tension

The virial route

Bakker-Buff equation:

$$\gamma = R^{-2} \int_{\text{in}}^{\text{out}} dz\, z^2 \left[p_{\text{N}}(z) - p_{\text{T}}(z) \right]$$

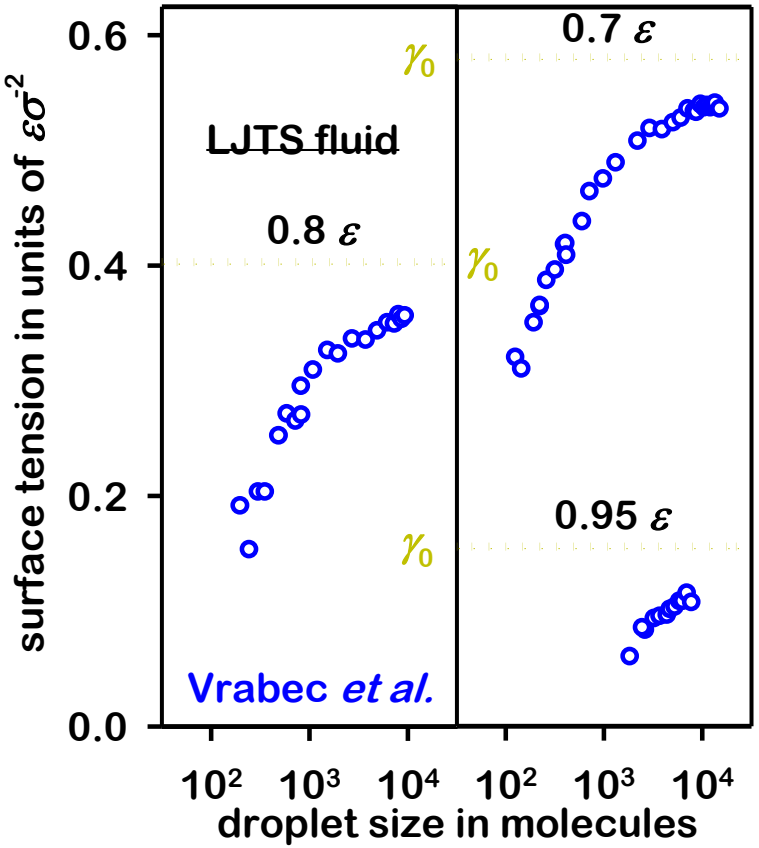
$$(2\gamma)^3 = -\Delta p^2 \int_{\text{in}}^{\text{out}} dp_{\text{N}}(z)\, z^3$$

Irving-Kirkwood pressure tensor:

$$p_{\text{N}}(z) = \sum_{\{i,j\} \in \mathbf{S}(z)} \frac{f_{ij} \left| \mathbf{s} \cdot \mathbf{r}_{ij} \right|}{4\pi z^3 r_{ij}} + kTp(z)$$

Normal pressure decays at R.

Significant decrease of γ due to spherical curvature.



Main advantages of the virial route:

- Equilibrium analysis (no unstable configurations)
- Yields the surface of tension radius $R = 2\gamma/\Delta p$.

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Surface tension

The variational route

Canonical partition function:

$$\Delta F = -T \ln \left\langle \exp\left(-\frac{\Delta U}{T} \right) \right\rangle$$

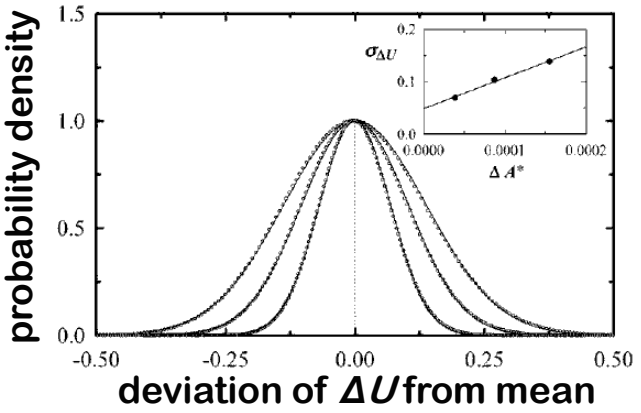
$$= f\left(\langle \Delta U \rangle, \langle \Delta U^2 \rangle, \langle \Delta U^3 \rangle \right) + O\left(\langle \Delta U^4 \rangle \right)$$

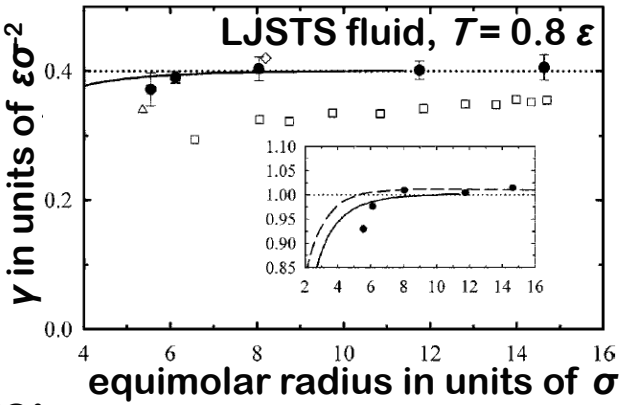
For small deformations:

$$\gamma = \Delta F / \Delta A \text{ with } A = 4\pi Q^2 + O(\delta Q)$$

Nonlinear terms are essential.

Tolman length much smaller than based on other methods.





(Source: Sampayo *et al.*, 2010)

Main advantages of the variational route:

- Free energy differences are considered in a direct way.
- No mechanical equilibrium assumption is applied.

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Discretization of interfaces

Effective radii for a droplet

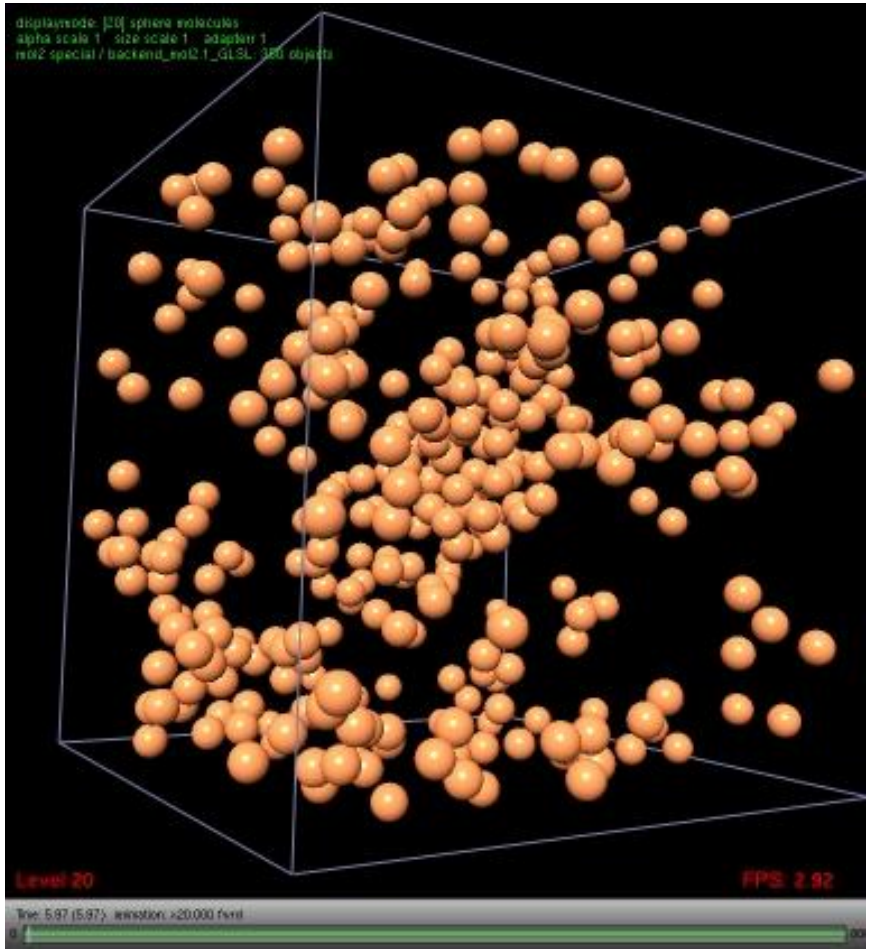
Capillarity radius $P = 2\gamma_0/\Delta p$, from the Laplace equation and the surface tension in the planar case.

Equimolar radius Q, from condition $\Gamma = 0$ for the excess density.

Laplace radius $R = 2\gamma/\Delta p$, based on a known value of the surface tension for the curved interface.

Conservative radius R_C for which the excess free energy is $4\pi R_C^2 \gamma_0$.

Radii $R(\rho)$ for a density $\rho' > \rho > \rho''$.



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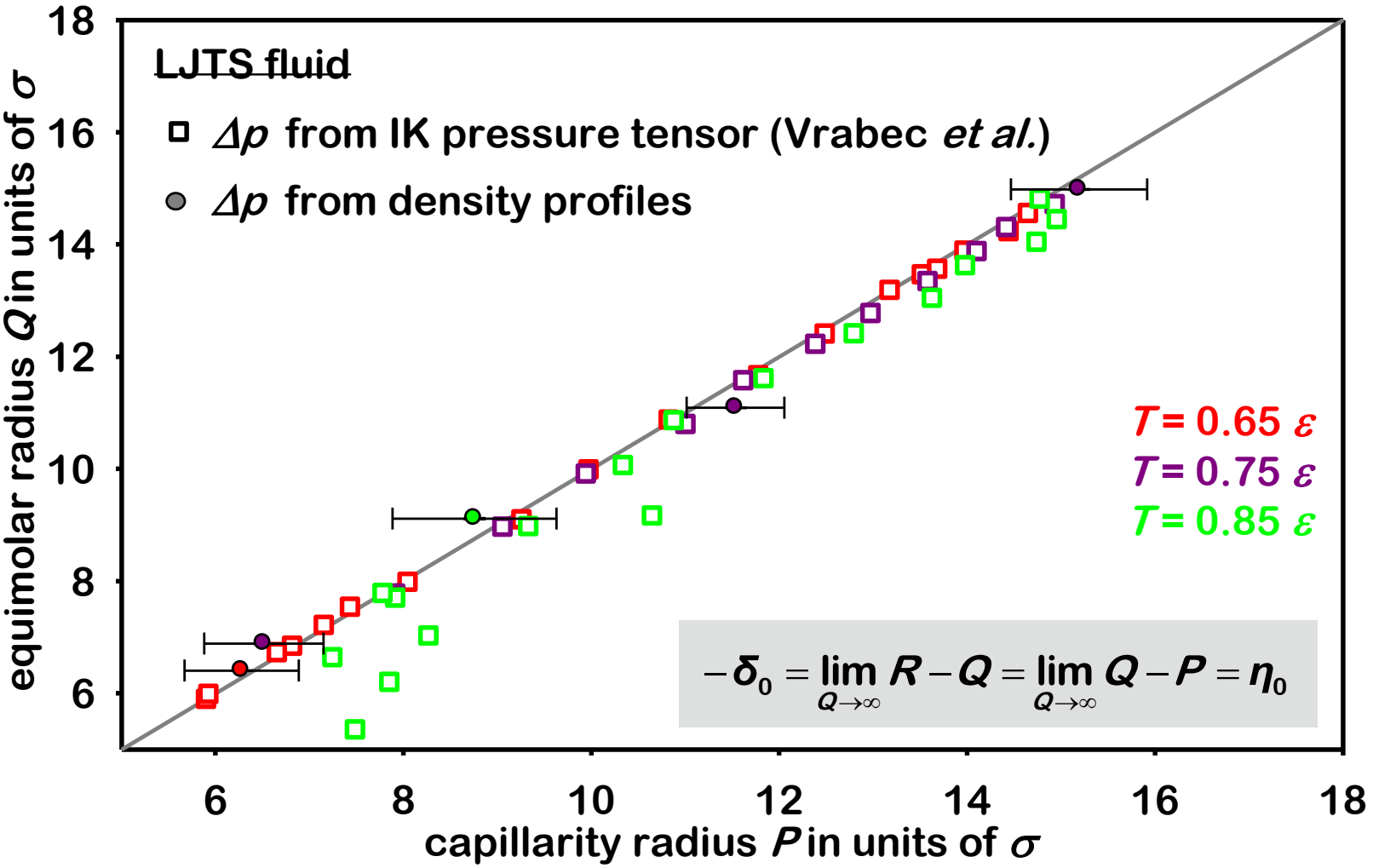
Discretization of interfaces



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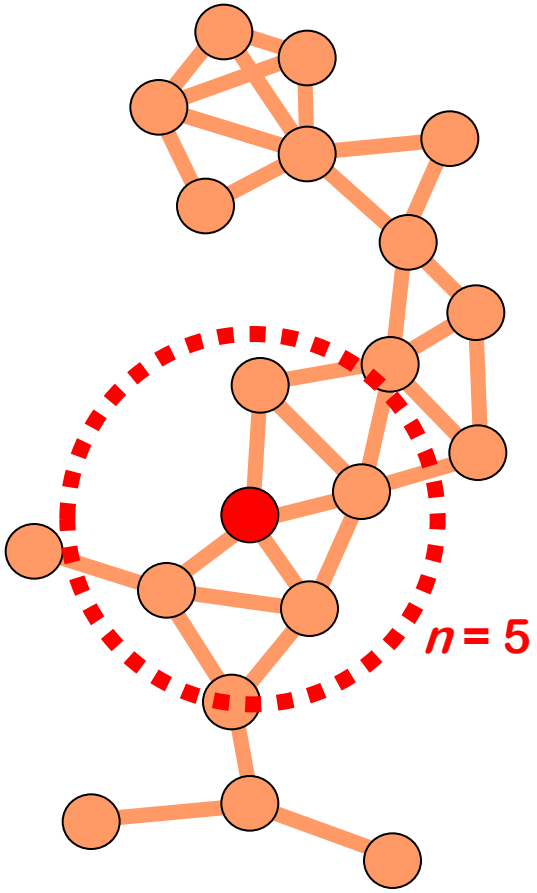
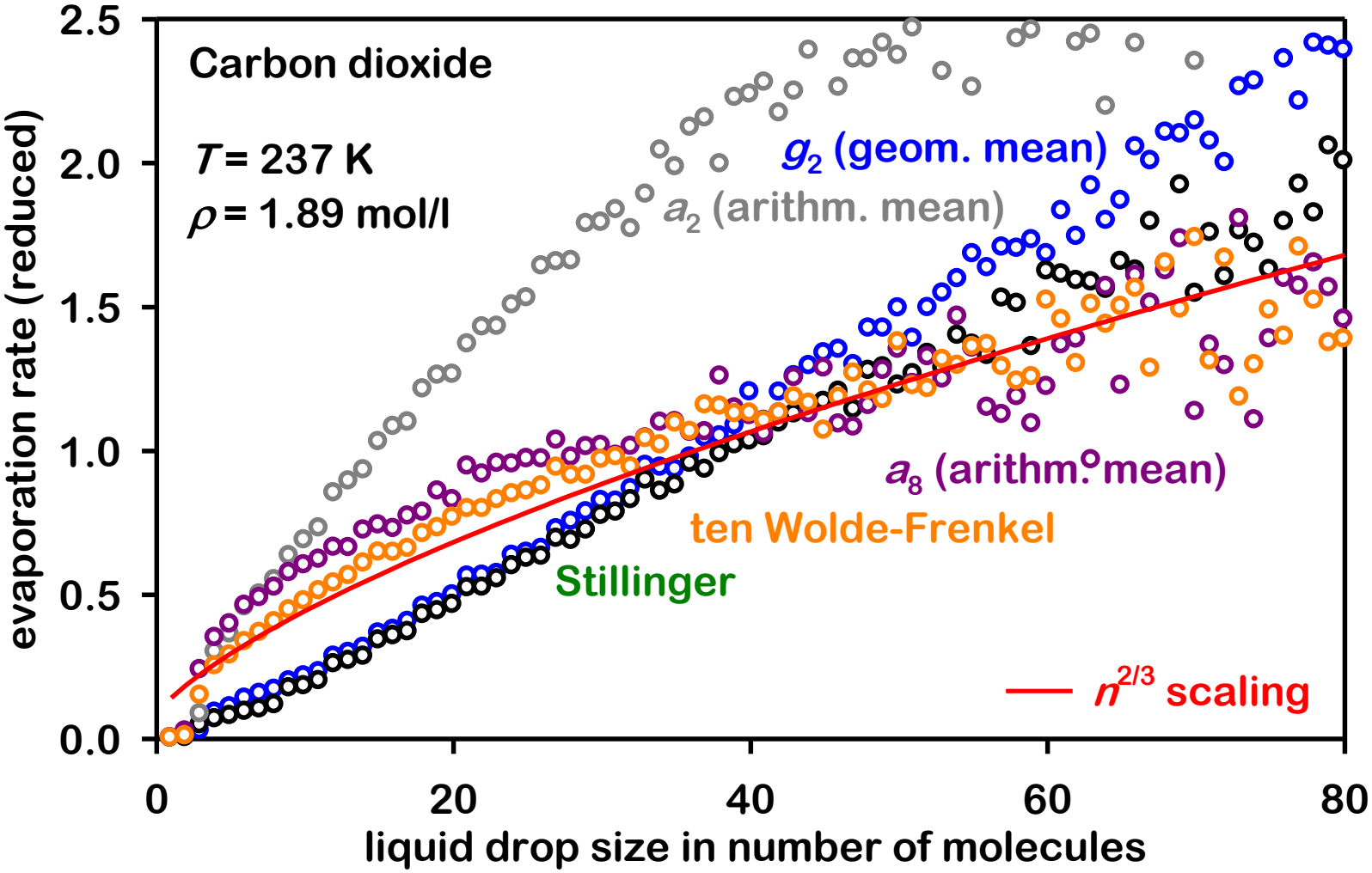
Clustering

Cluster critieria for the dispersed liquid phase

- Molecules with a distance between the centres of mass $r_{ij} < r_{St}$ are regarded as part of the liquid phase (Stillinger).
- At least $n = 4$ neighbours are required within a sphere with the radius r_{St} around the centre of mass (ten Wolde-Frenkel).
- A molecule is liquid if the sphere around its n nearest neigbours has an average density greater than the arithmetic (a_n) or the geometric (g_n) mean between ρ' and ρ''.



Clustering

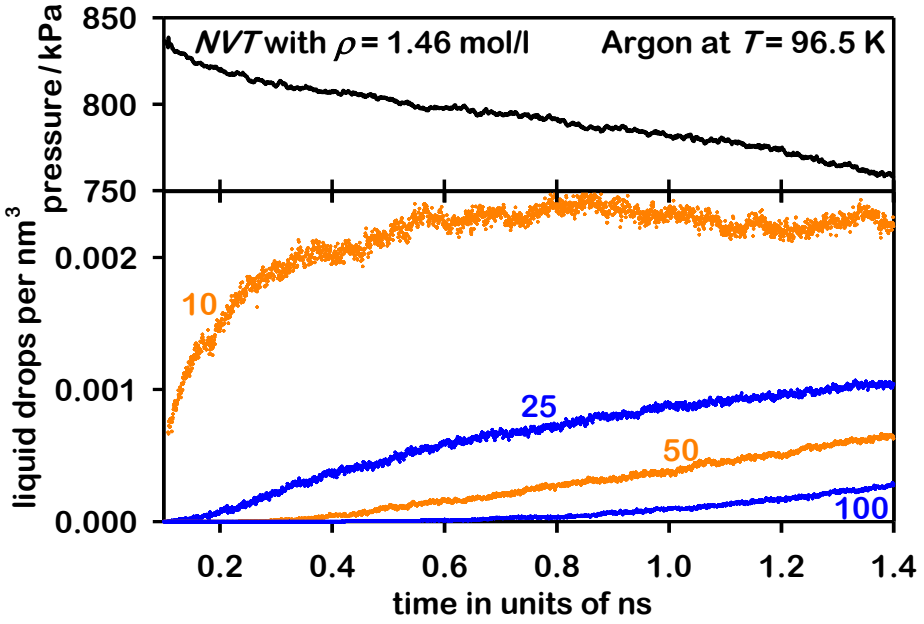

Carbon dioxide
T = 237 K
ρ = 1.89 mol/l
g2 (geom. mean)
a2 (arithm. mean)
a8 (arithm. mean)
ten Wolde-Frenkel
Stillinger
n^2/3 scaling
evaporation rate (reduced)
liquid drop size in number of molecules
0.0
0.5
1.0
1.5
2.0
2.5
0
20
40
60
80

Population statistics

Nucleation in supersaturated vapours

Yasuoka and Matsumoto (1998):

- Canonical MD simulation
- Limited time interval
- Conditions change over time



Higher-level evaluation subsequent to cluster detection:

- Population statistics, yielding a nucleation rate
- Cluster identification and tracking of growth and decay
- Evaluation of cluster temperature to analyze the heat transfer

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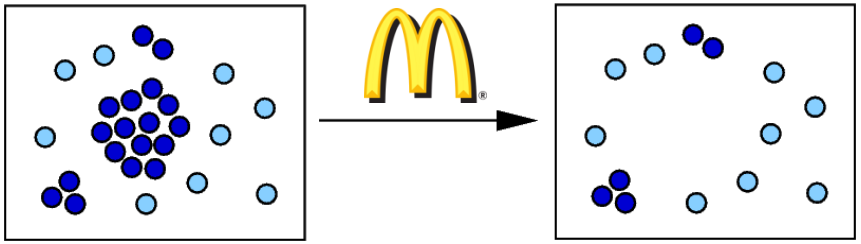
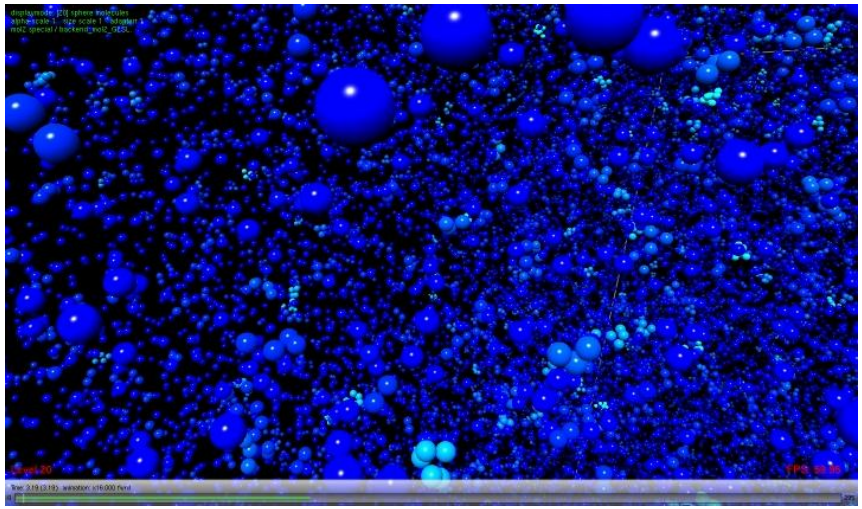
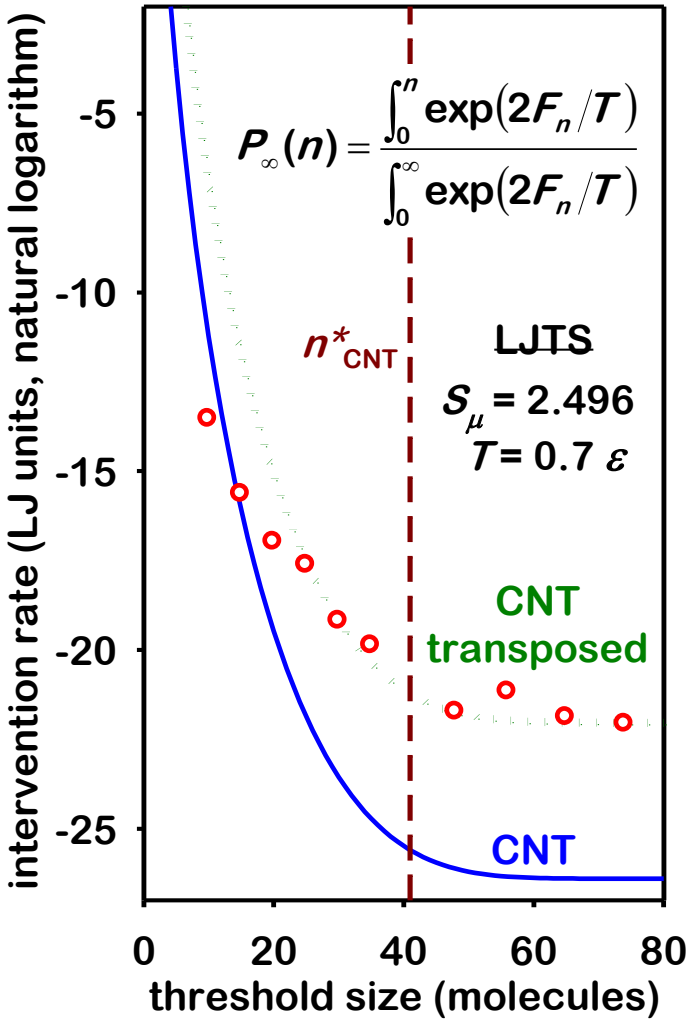
Population statistics

Requirement for a steady state:

Elimination of liquid drops …







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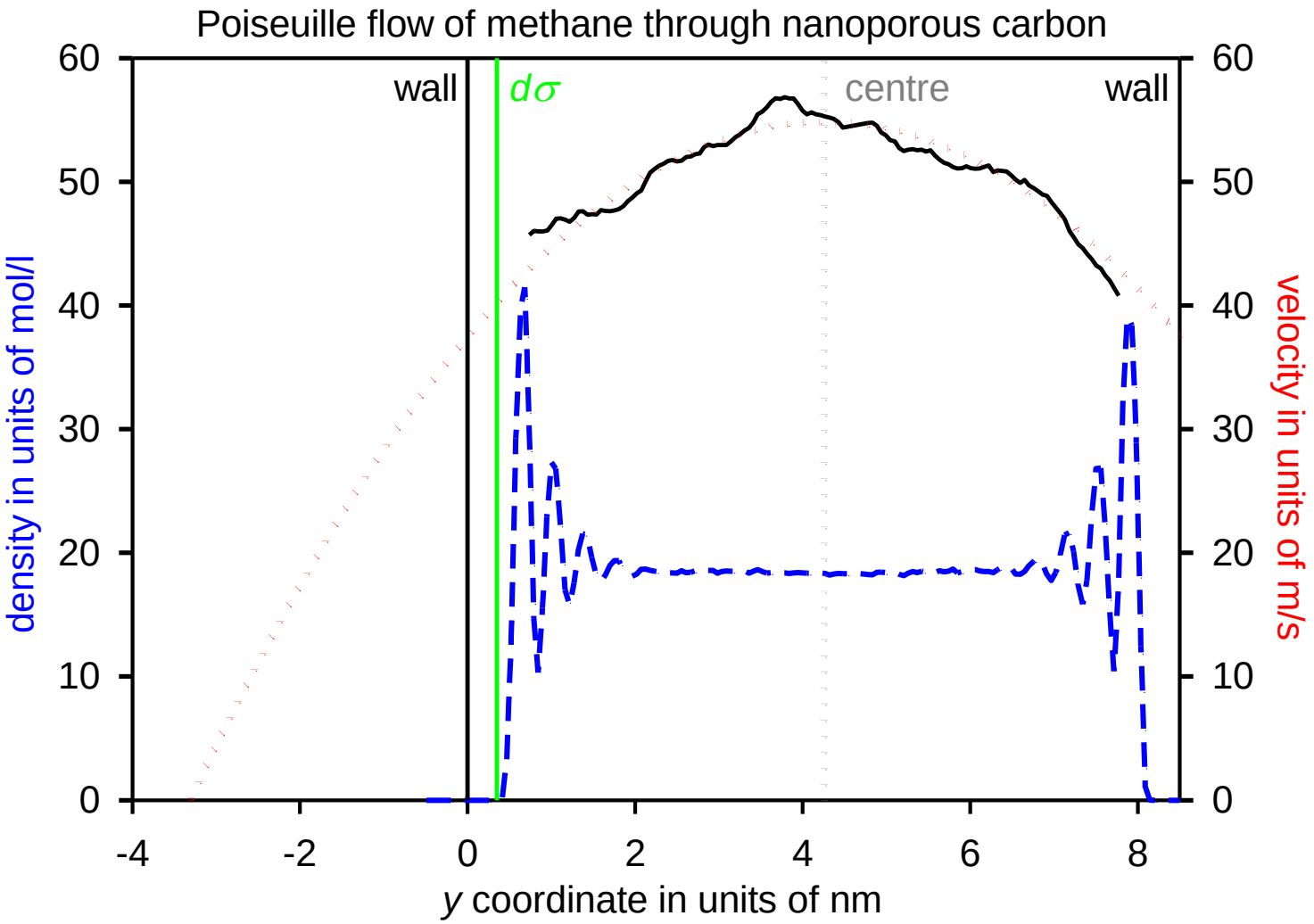
Confined fluid systems



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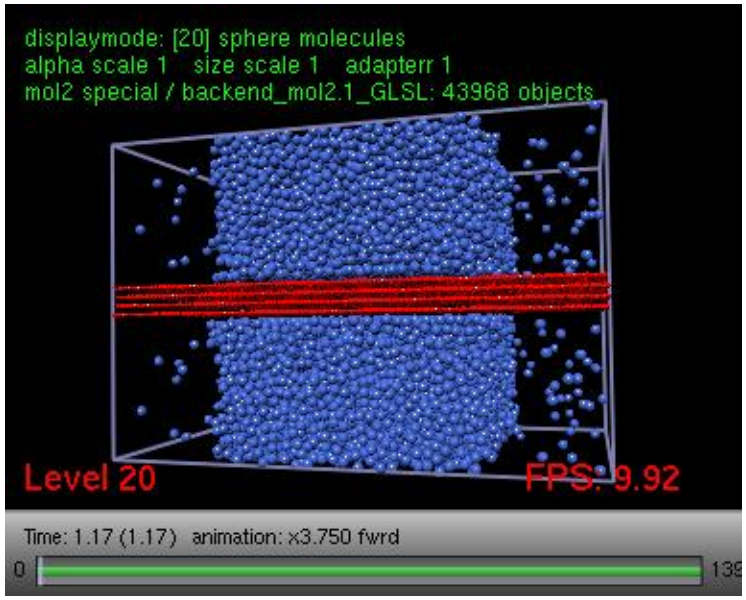
Confined fluid systems

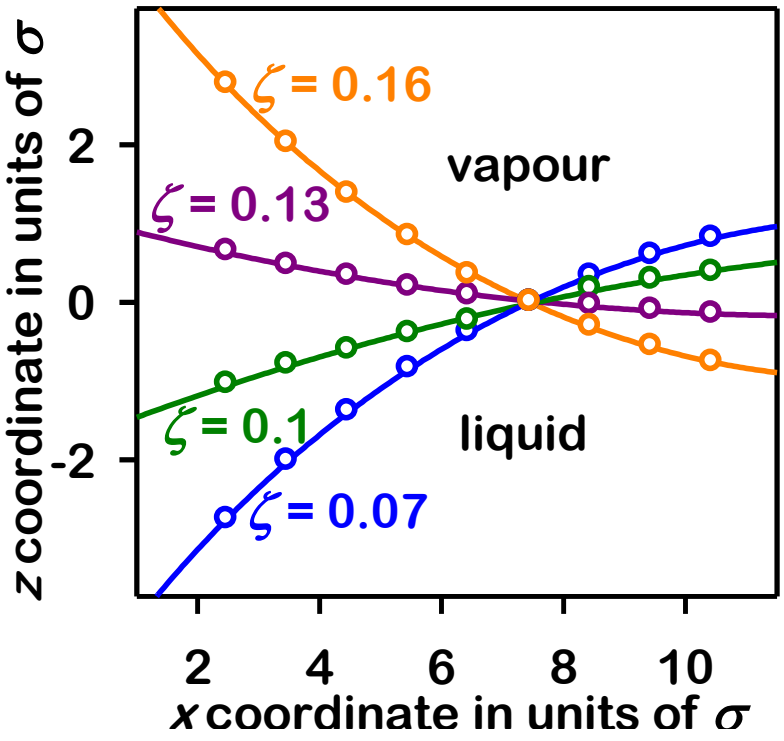
Simulation approach

LJTS fluid, generic wall model,
Dispersive energy $\varepsilon_{fw} = \zeta\varepsilon$



Equilibrium state

Cylindrical meniscus,
based on arithm. mean density



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Functionality within the *ls1* project

Main initial application of *ls1 mardyn:*

"structure and properties of fluids at interfaces"

	moldy	mardyn b´	b´´	trunk
Interfacial profiles	–	planar	spherical	planar
Surface tension	–	virial	variational	both
Cluster detection	o	arith. mean	local ρ	local ρ
Population statistics	o	–	–	–
Adsorption	–	o	o	o
Nanoscopic flow	–	o	o	o