

CCP5 Annual Meeting



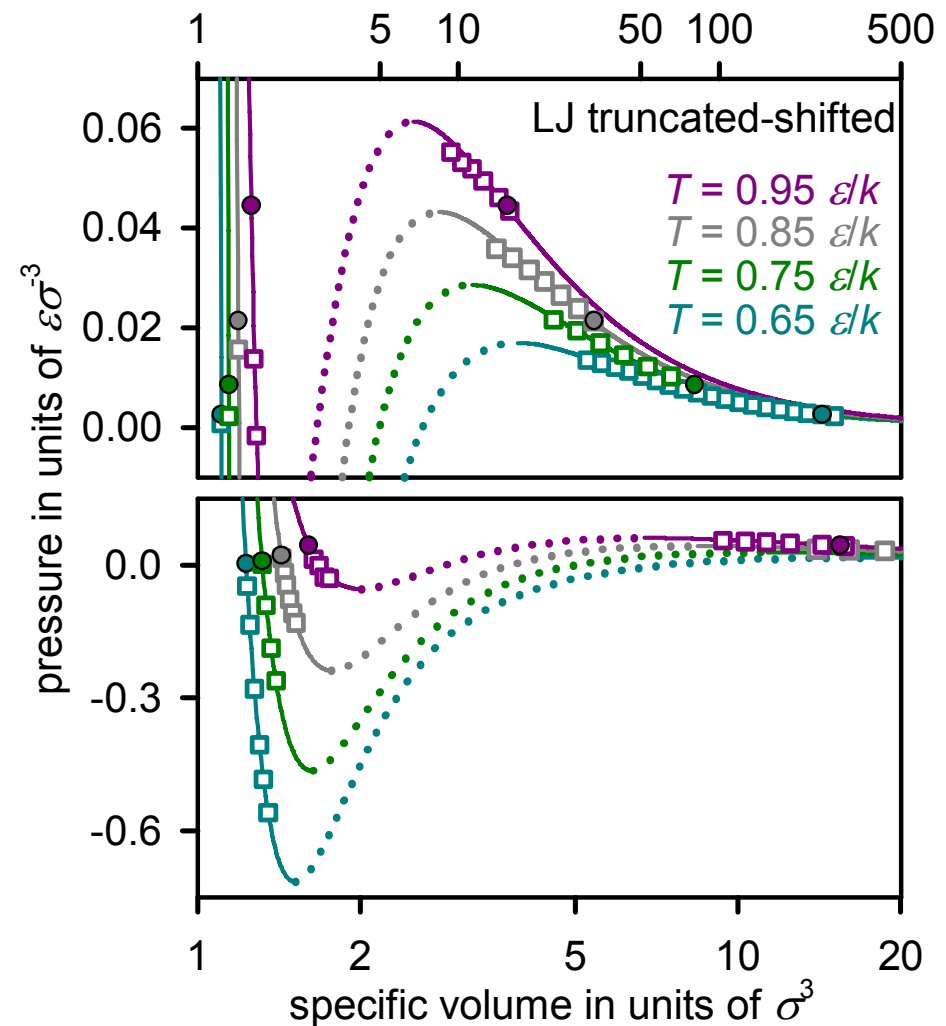
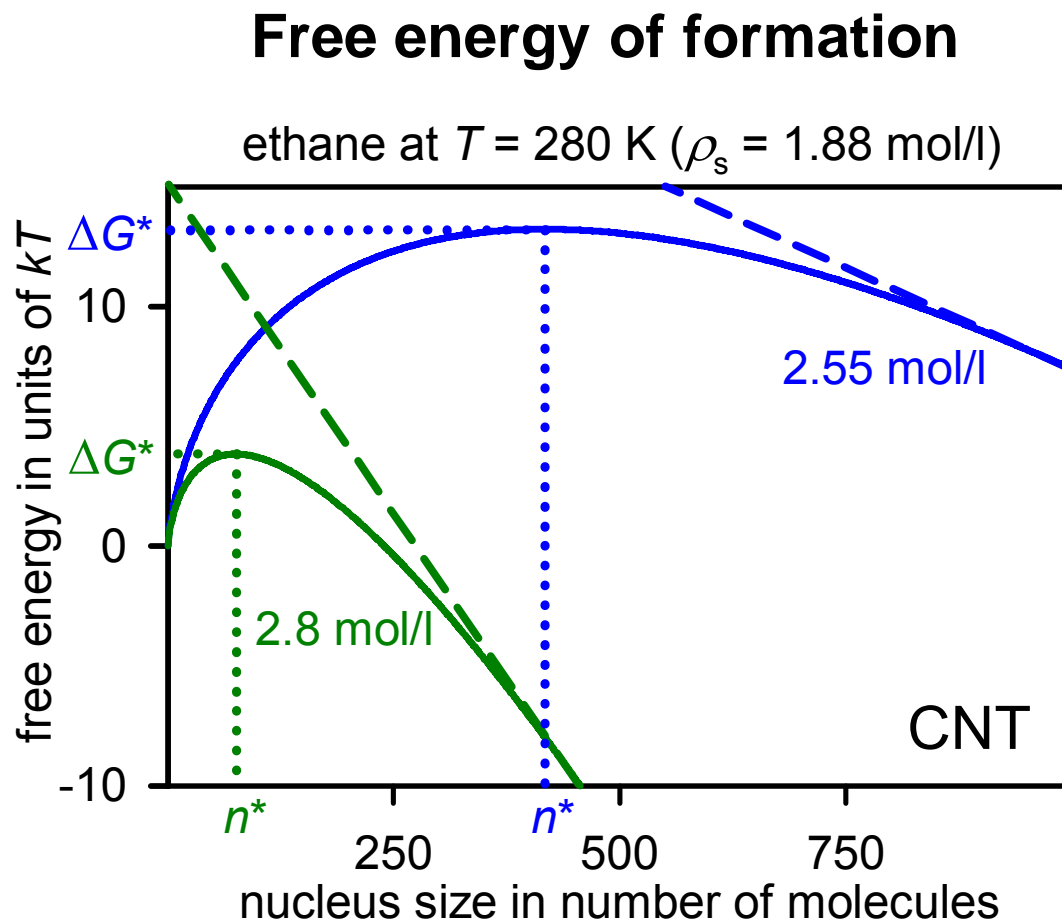
Surface property corrected modification of the classical nucleation theory

Sheffield Hallam University, September 15, 2010

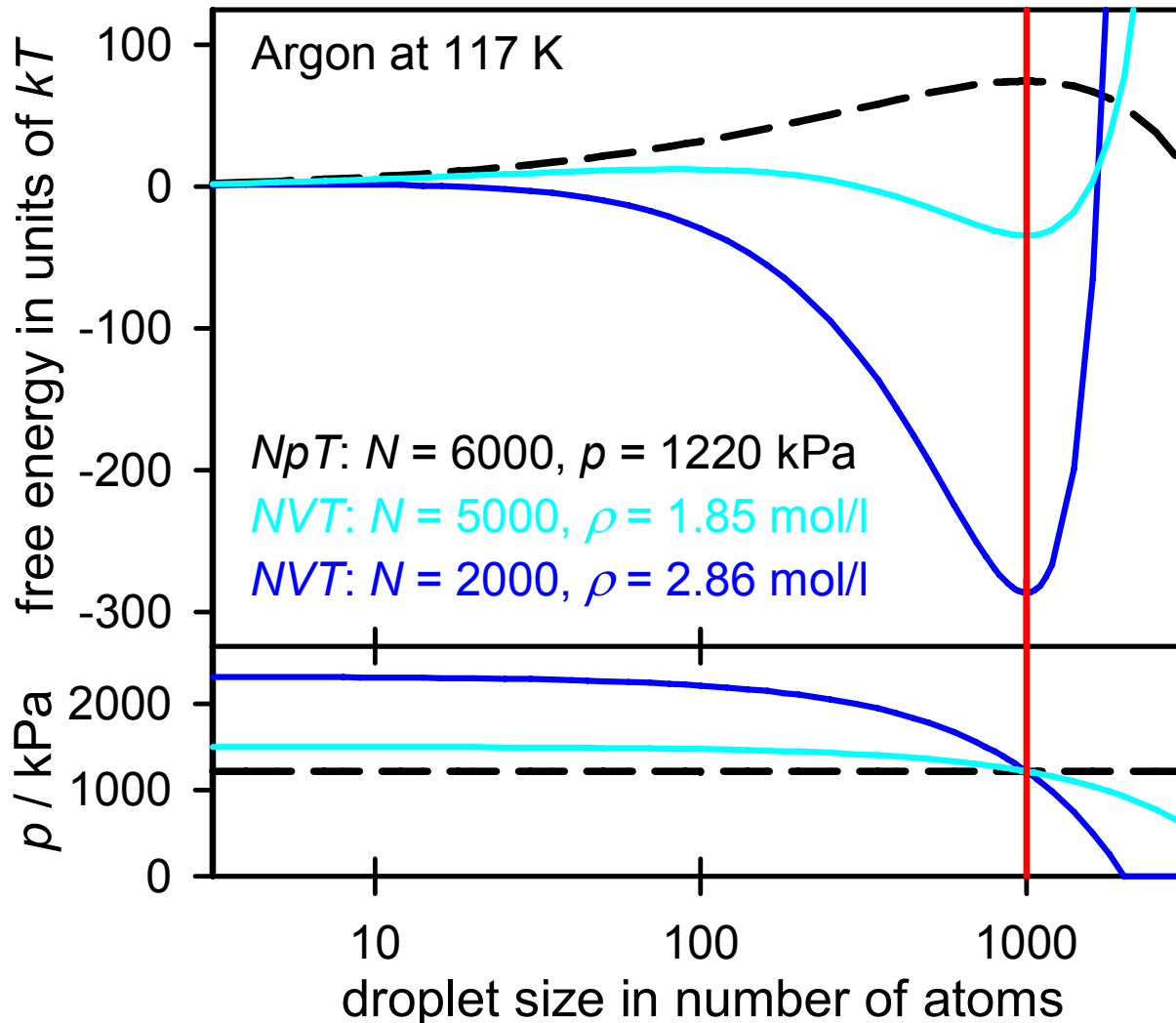
Martin Horsch, Hans Hasse, and Jadran Vrabec

The critical droplet

... is defined by a *stable* or *unstable* equilibrium with the vapour phase.



Equilibrium vapour pressure



Equilibrium condition for a droplet containing n atoms:

$$p = p(T, n)$$

ΔG at constant p and T :

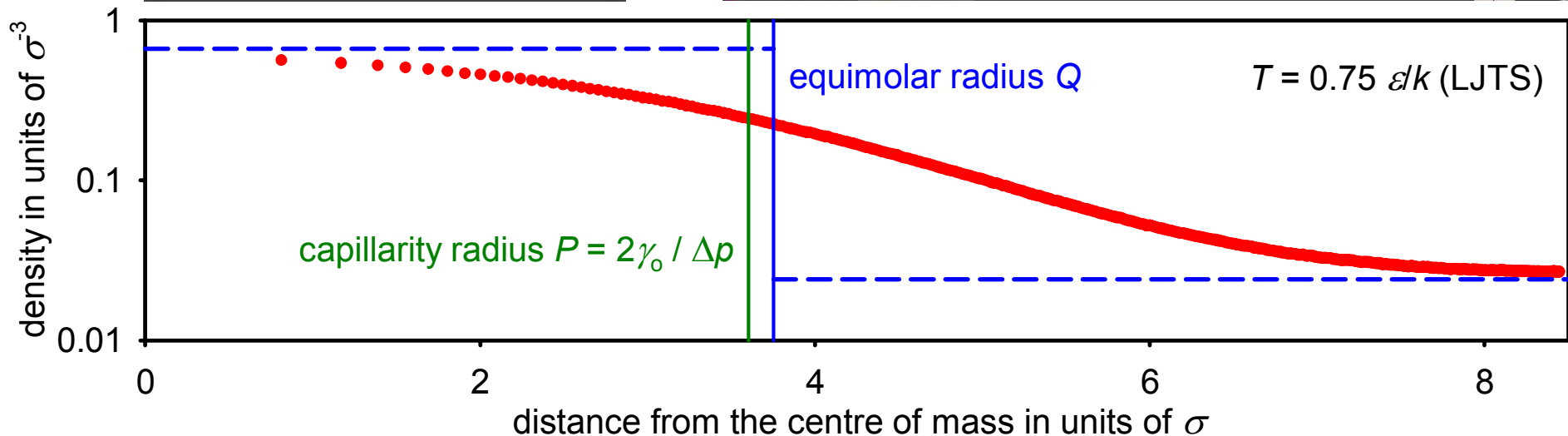
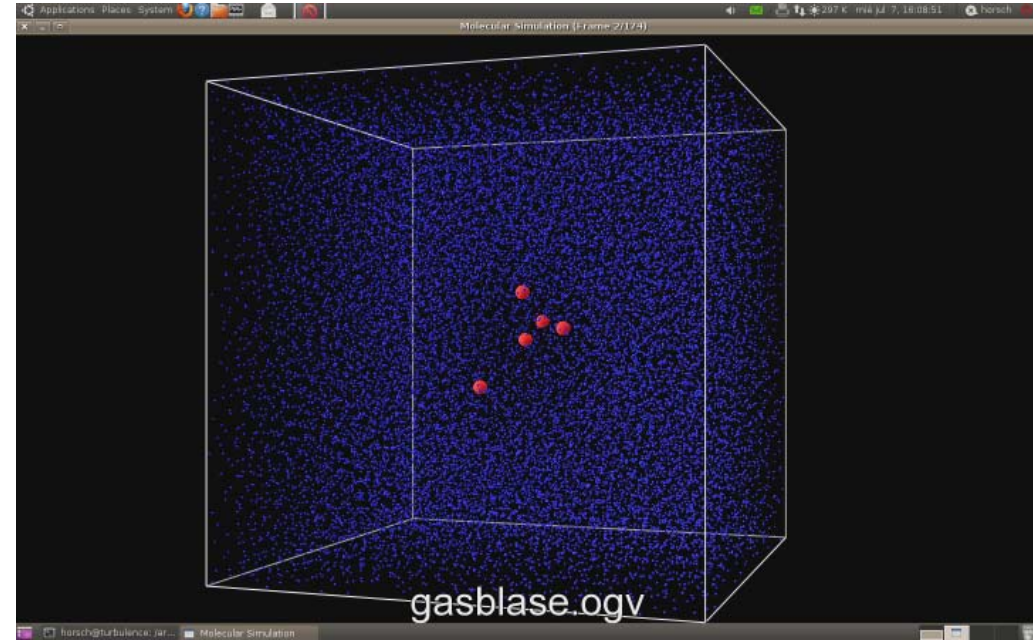
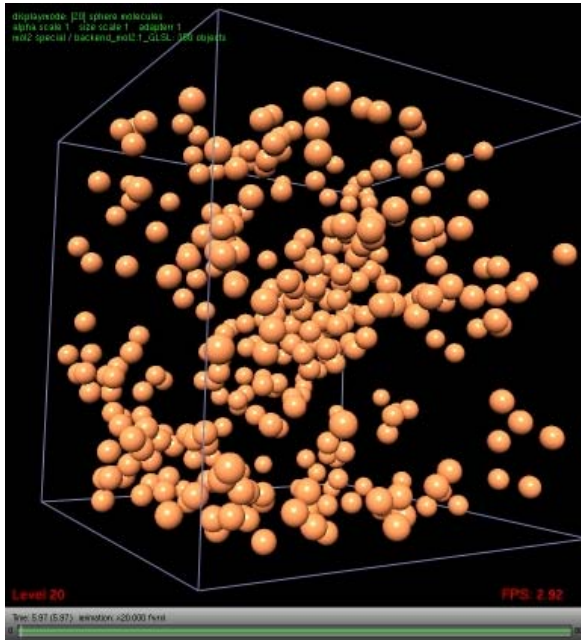
1 unstable equilibrium

ΔF at constant V and T :

1 unstable equilibrium

1 stable equilibrium

Canonical MD simulation of curved interfaces



Droplet properties in equilibrium

Irving-Kirkwood tensor:

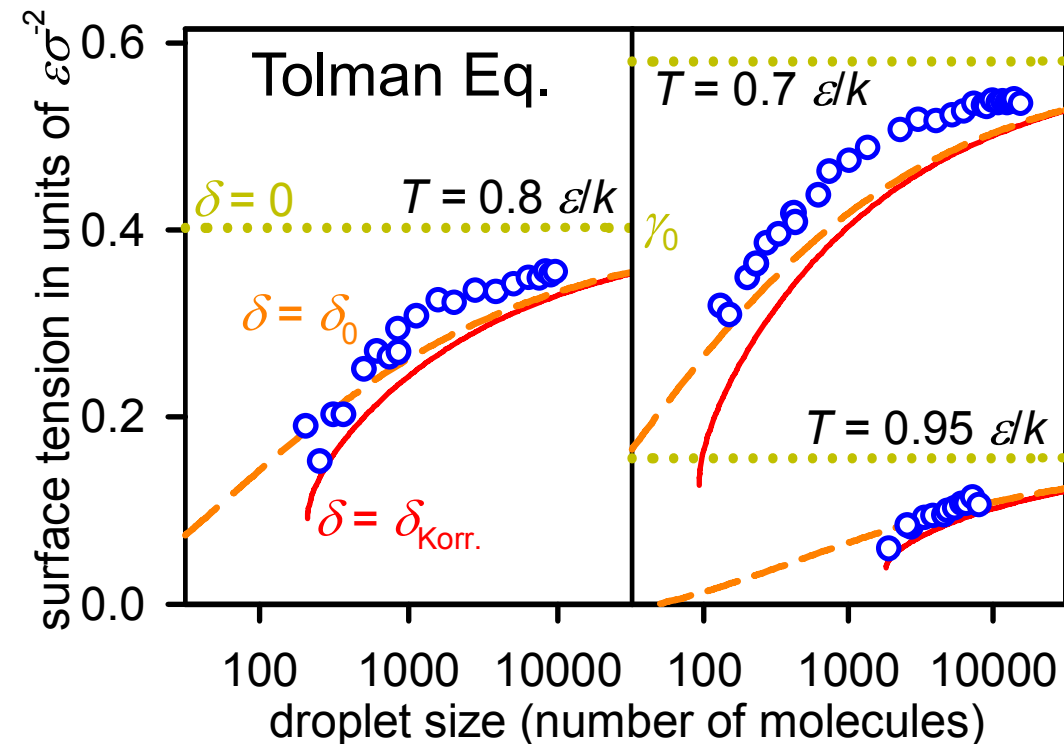
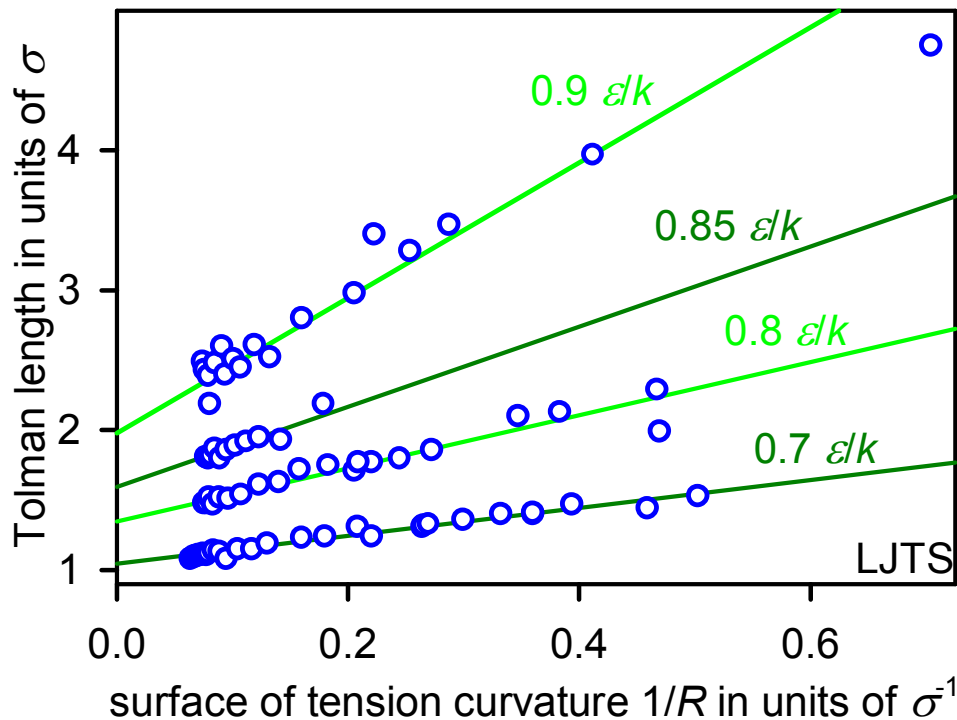
- normal pressure $p_N(R)$
- tangential pressure $p_T(R)$

surface tension

$$(2\gamma)^3 = -\Delta p^2 \int_{\text{inside}}^{\text{outside}} r^3 dp_N$$

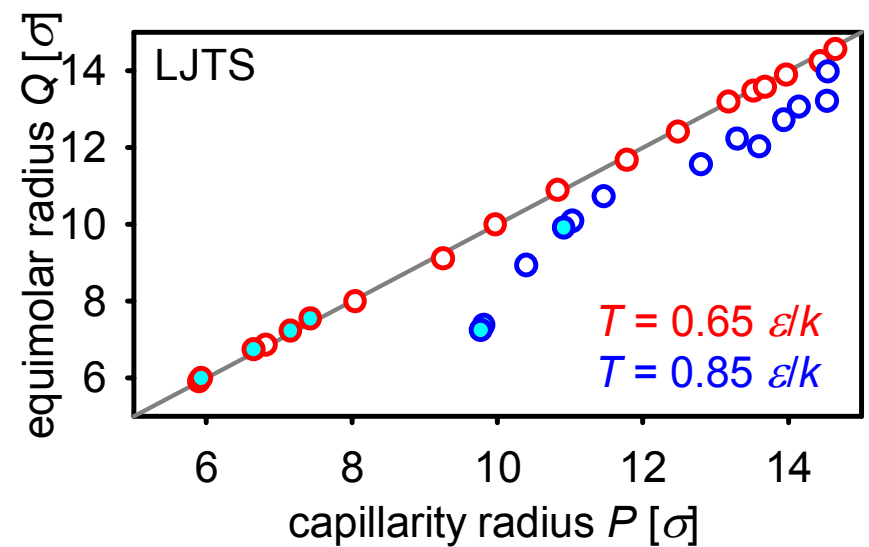
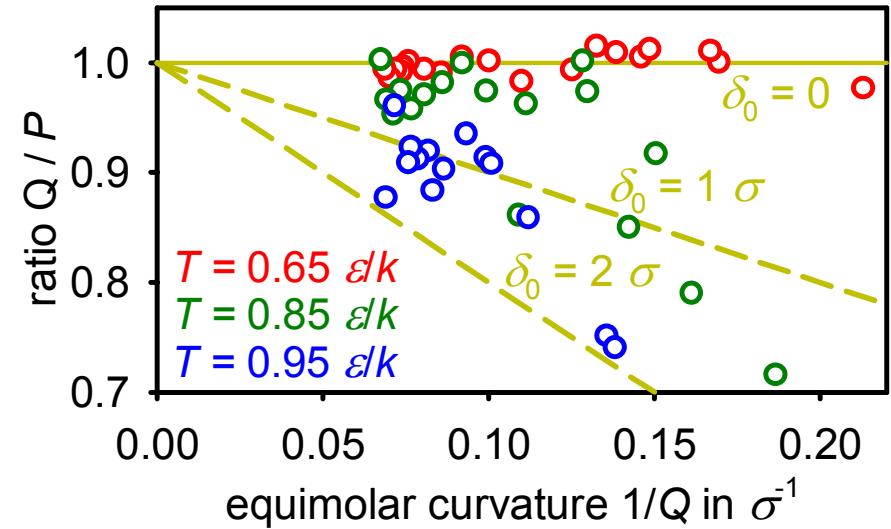
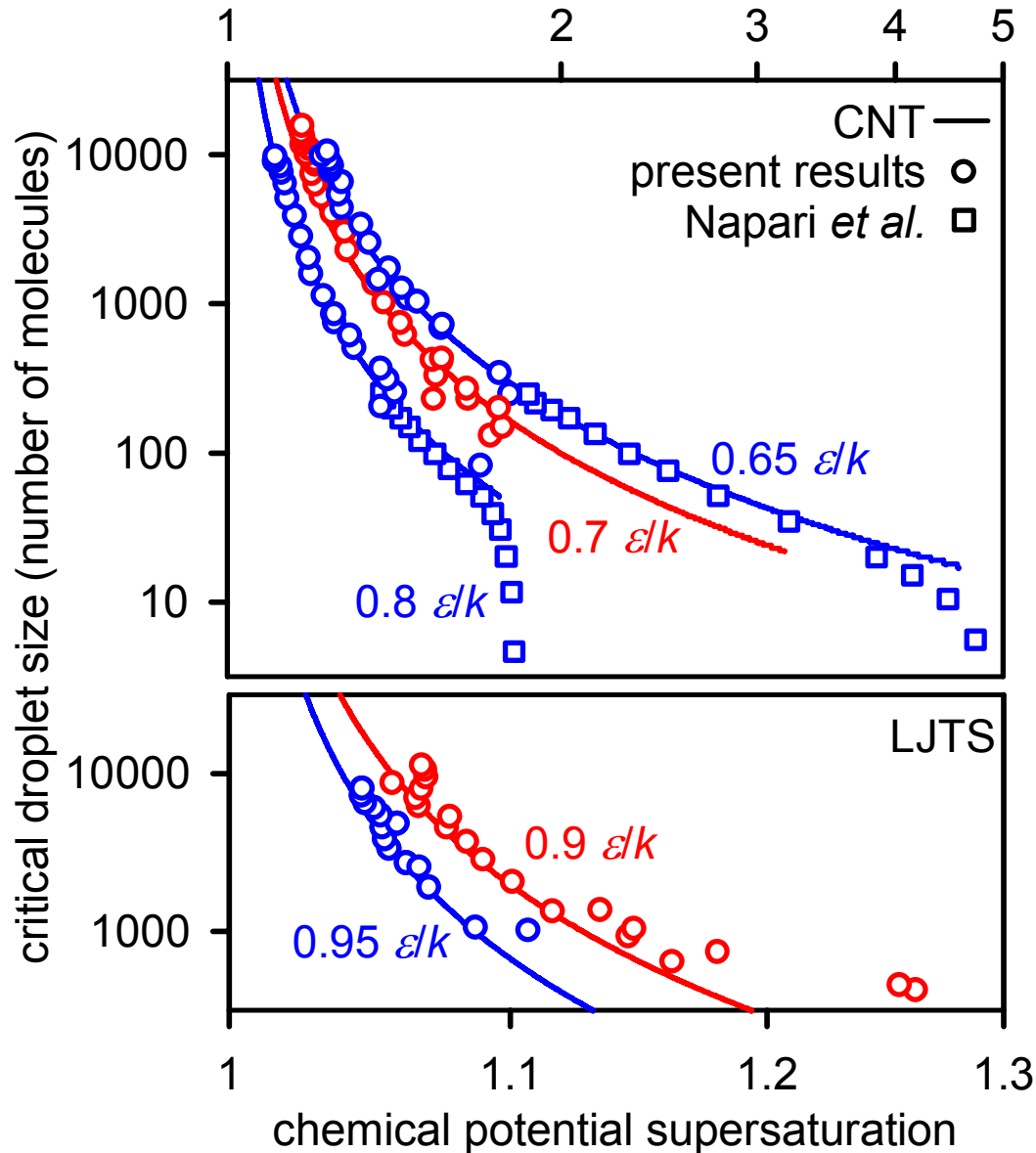
Laplace radius

$$R = \frac{2\gamma}{\Delta p} = Q - \delta$$



Mol. Phys. **104**: 1509 (2006).

Droplet properties in equilibrium: Discussion



Nucleation: Direct simulation vs. experiment

- Integration time step typically between 1 and 5 fs;
Feasible simulation time: on the order of nanoseconds.
- A saturated vapor with $V = 10^{-20} \text{ m}^3$ contains:
 - 800 000 molecules (saturated methane at 114 K)
 - 7 000 000 molecules (saturated CO_2 at 253 K)
- Minimal nucleation rate accessible by direct simulation:

$$\begin{aligned} \# \text{nuclei} / (\text{volume } V \times \text{time } \Delta t) &= \text{nucleation rate } J \\ 10 / (10^{-20} \text{ m}^3 \times 10^{-9} \text{ s}) &= 10^{30} / \text{m}^3\text{s} \end{aligned}$$

Direct MD simulation
above $10^{30} / \text{m}^3\text{s}$



Experiment
up to $10^{23} / \text{m}^3\text{s}$

Innovative HPC Methods and Applications for Highly Scalable Molecular Simulation (IMEMO)



Bundesministerium
für Bildung
und Forschung

2008 –2011

Project associates:



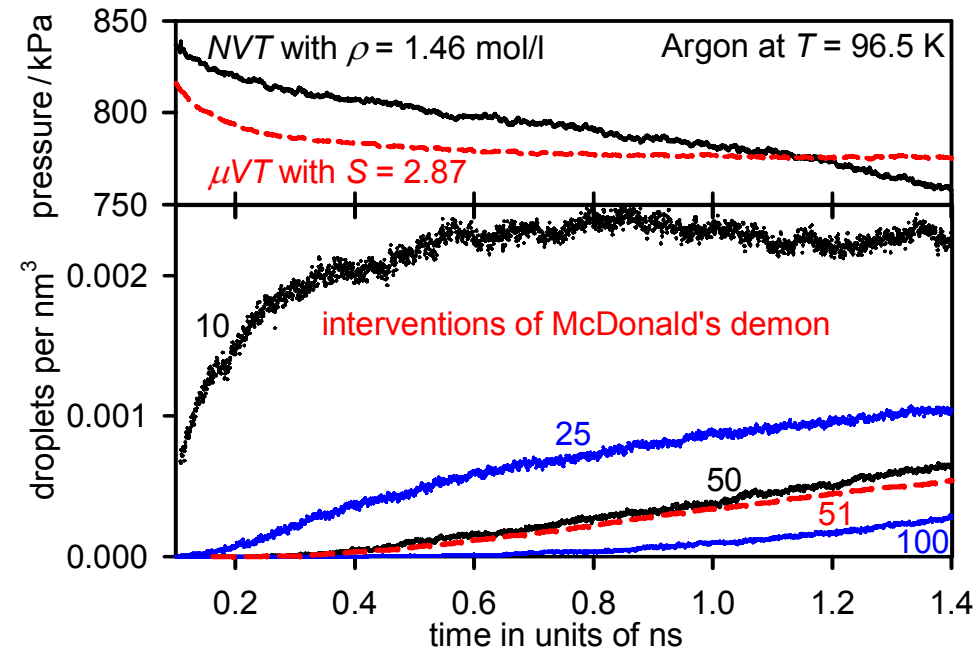
Industrial associates:



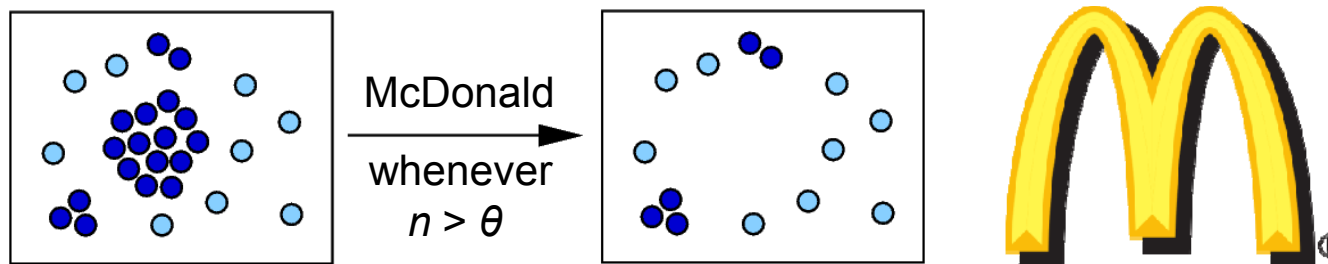
Direct MD simulation of nucleation

Yasuoka-Matsumoto method:

- Canonical MD simulation
- Limited time interval for nucleation
- **Conditions change over time**

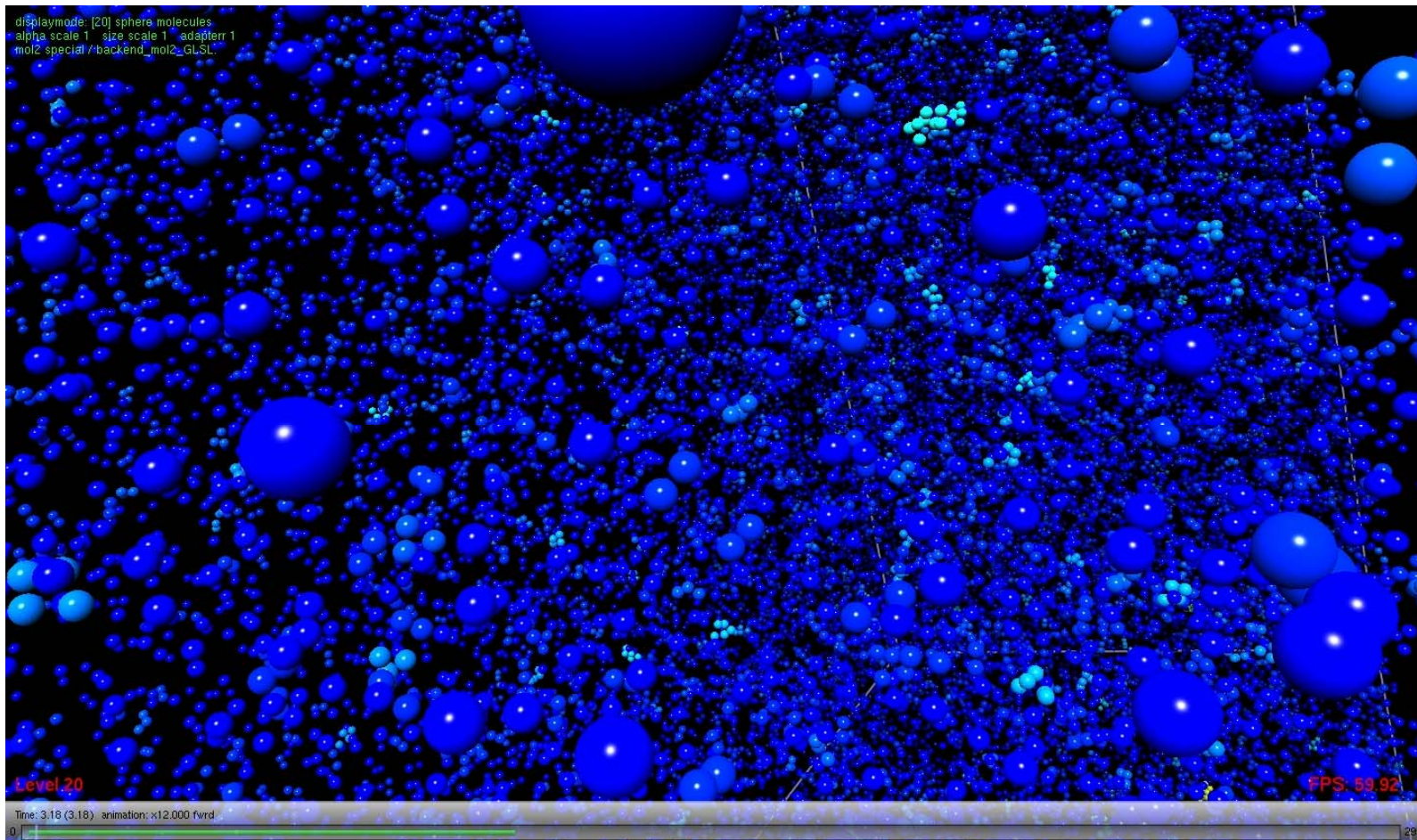


GCMD, i.e. MD steps alternating with GCMC insertion/deletion steps

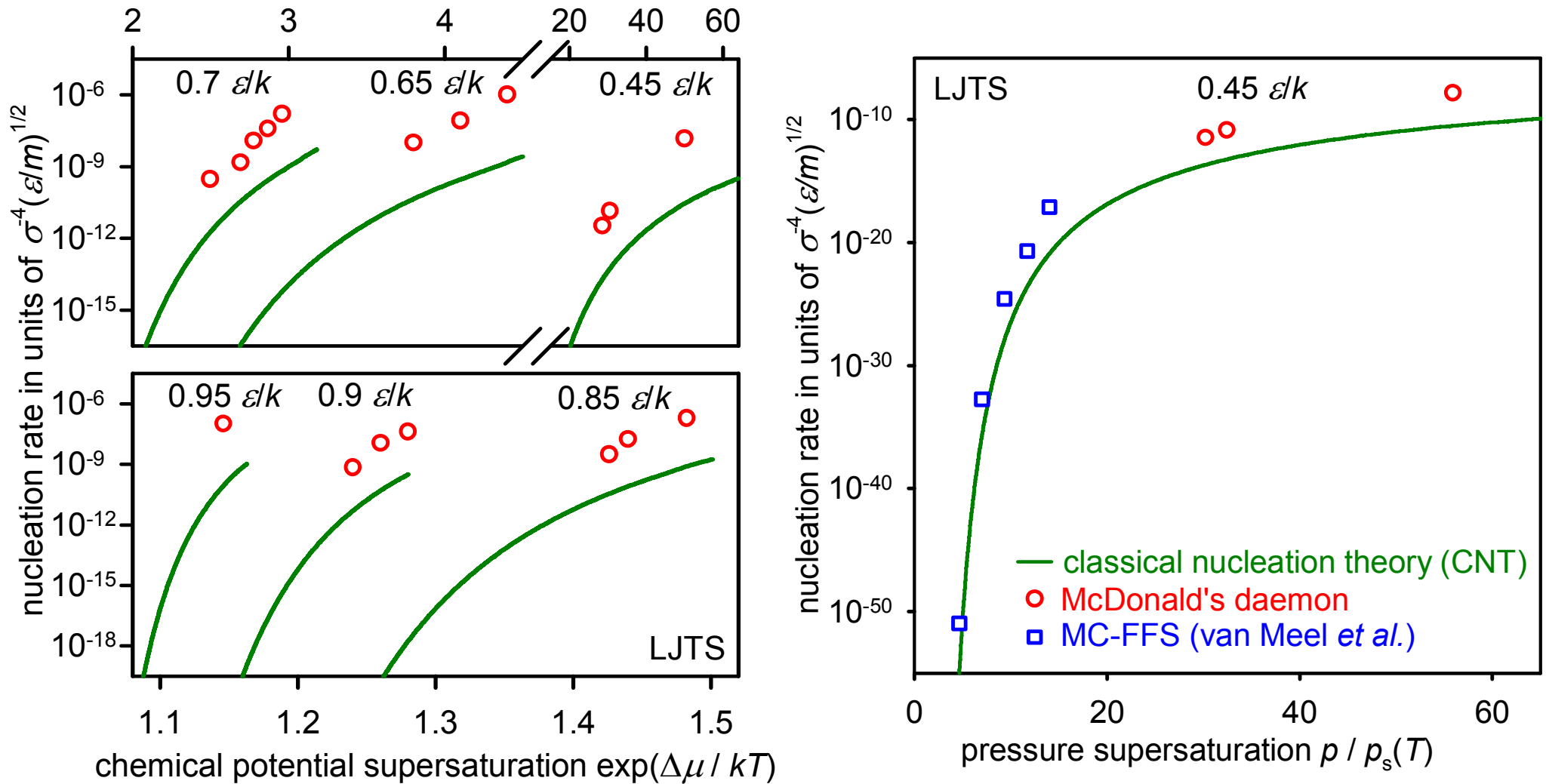


→ **Thermodynamic conditions of the supersaturated state are maintained**

Video: McDONALD`s dæmon



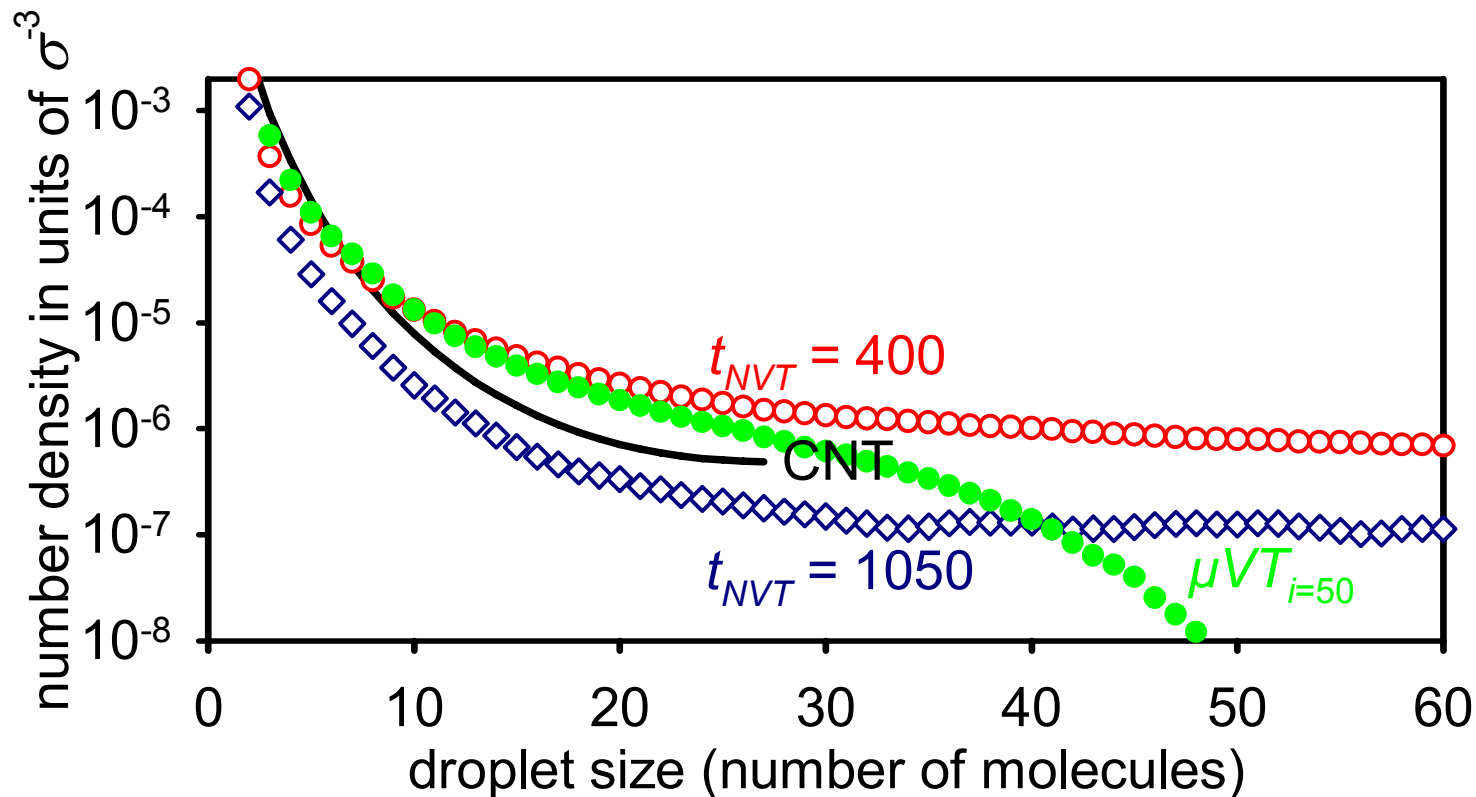
Nucleation rates from GCMD + McDonald's daemon



J. Chem. Phys. **131**: 184104 (2009).

Nucleus size distribution

LJTS fluid at $T = 0.7 \varepsilon/k$:
 μVT ($S_\mu = 2.866$) and NVT ($\rho = 0.004044 \sigma^3$) simulation



Good agreement with CNT for n^* and the number of small nuclei.

Surface property corrected CNT

Equilibrium condition for critical droplets yields $2 dV = R dA$ and hence

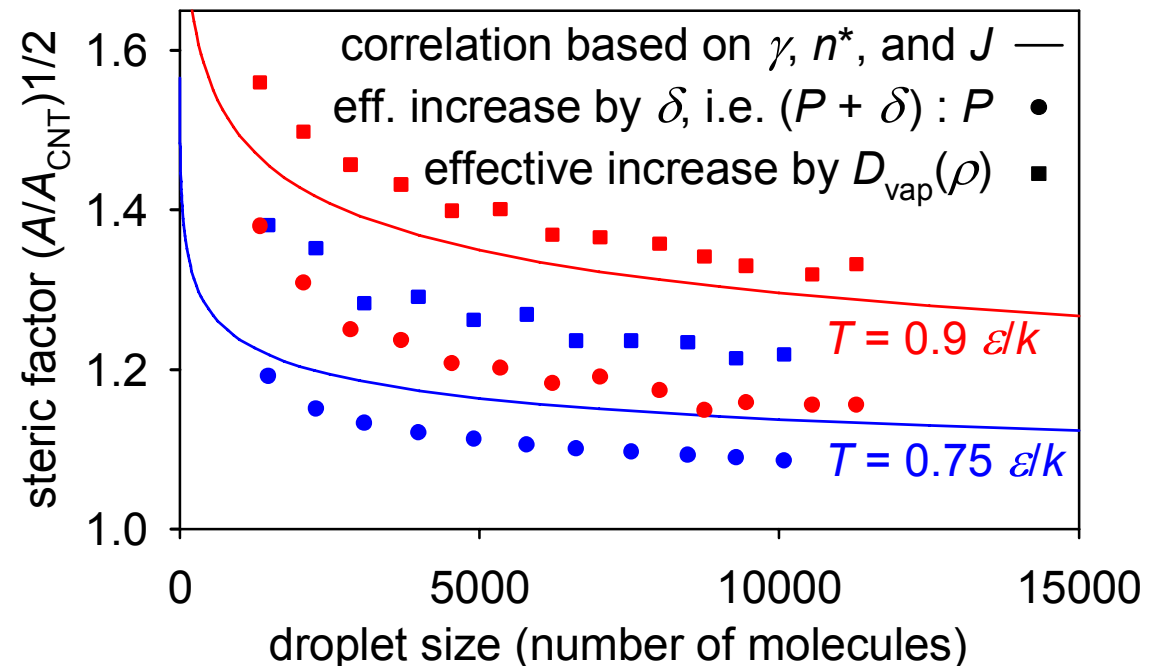
$$dA = \frac{2dV}{R} \approx \frac{8\pi Q^2}{Q - \delta} dQ.$$

δ is positive \longrightarrow dA is larger than according to capillarity approximation.

Correlated surface area

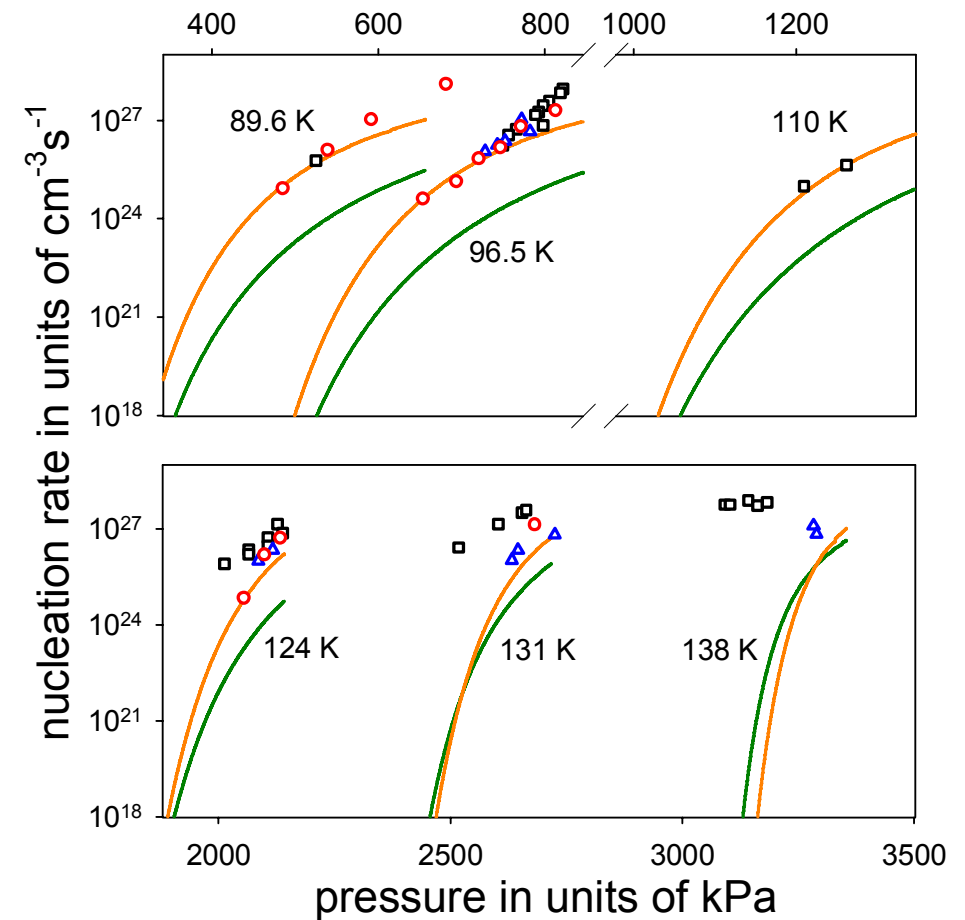
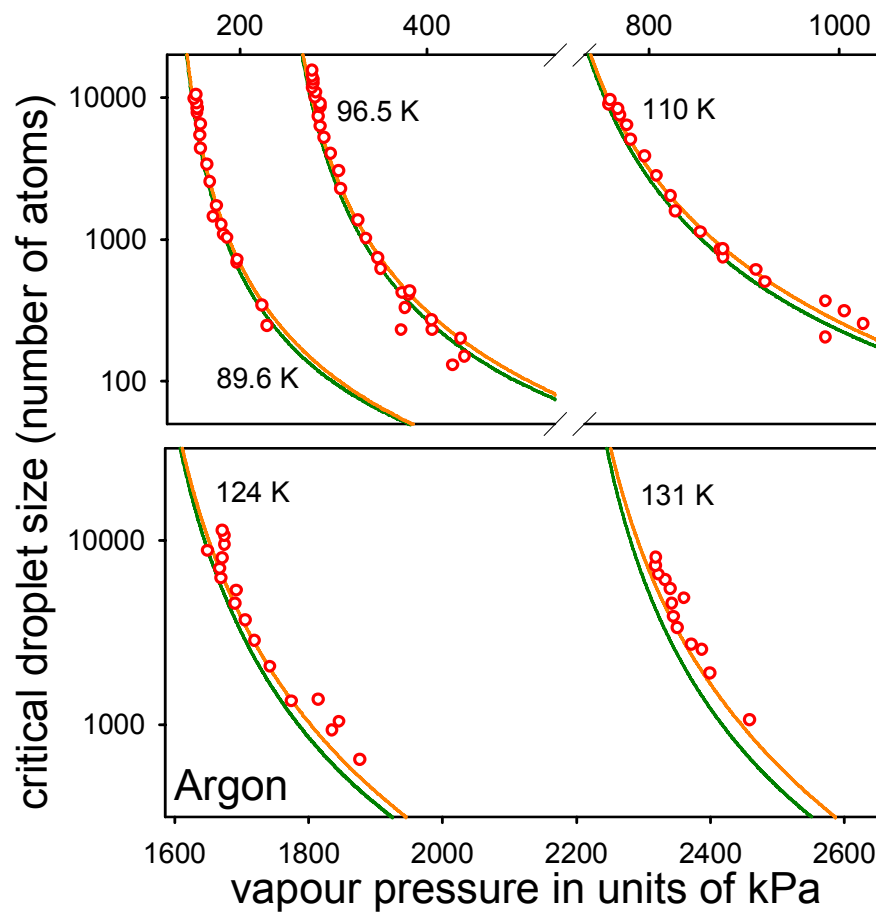
$$A - A_{\text{CNT}} = \frac{0.85(1 - T/T_c)^{-1} - 1}{(n/75)^{1/3} + 1} A_{\text{CNT}}$$

Phys. Rev. E 78: 011603 (2008).



Surface property corrected nucleation theory

Effect: A larger surface area compensates the lower surface tension.



○ steady-state simulation

□ △ YM simulation

— SPC

— CNT

Conclusion

- **MD simulation of equilibria** allows sampling over an arbitrary time interval, eventually leading to the desired level of accuracy.
- **Single droplets** can be stabilized in the **canonical** ensemble.
- A **supersaturated vapour** near the spinodal line can be stabilized by grand canonical simulation with **McDonald's dæmon**.
- The **classical theory** leads to acceptable results for the LJTS fluid. However, it does not take into account curvature effects on the surface tension.
- A consistent description is given by postulating an **increased surface of tension**.