BCNucleation-Aggregation Workshop

Grand canonical molecular dynamics simulation of homogeneous nucleation

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Molecular simulation of nucleation

Indirect simulation:

Transition path sampling
Determination of the critical size
… by observing single droplets in non-equilibrium
… by observing single droplets in equilibrium

Direct simulation:

… of a metastable state far from the spinodal line
… of nucleation at a high supersaturation, decreasing over time

… of a metastable state near the spinodal line
… of nucleation at a constantly high supersaturation

The critical nucleus

… is defined by a *stable* or *unstable* equilibrium with the vapor.

Free energy of formation

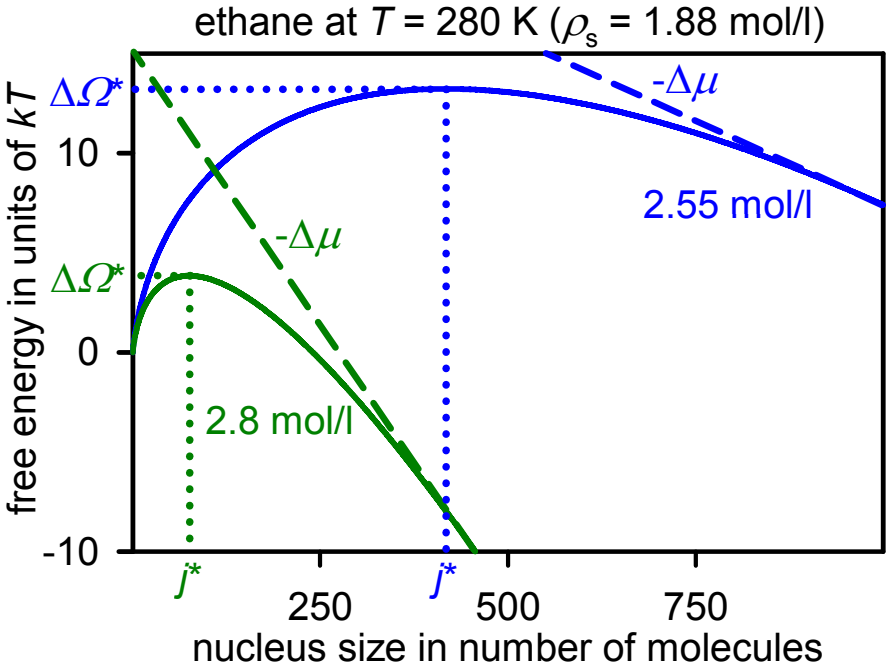
Positive surface contribution:

$$d\Omega_A / dA = \gamma_j$$

Negative volume contribution:

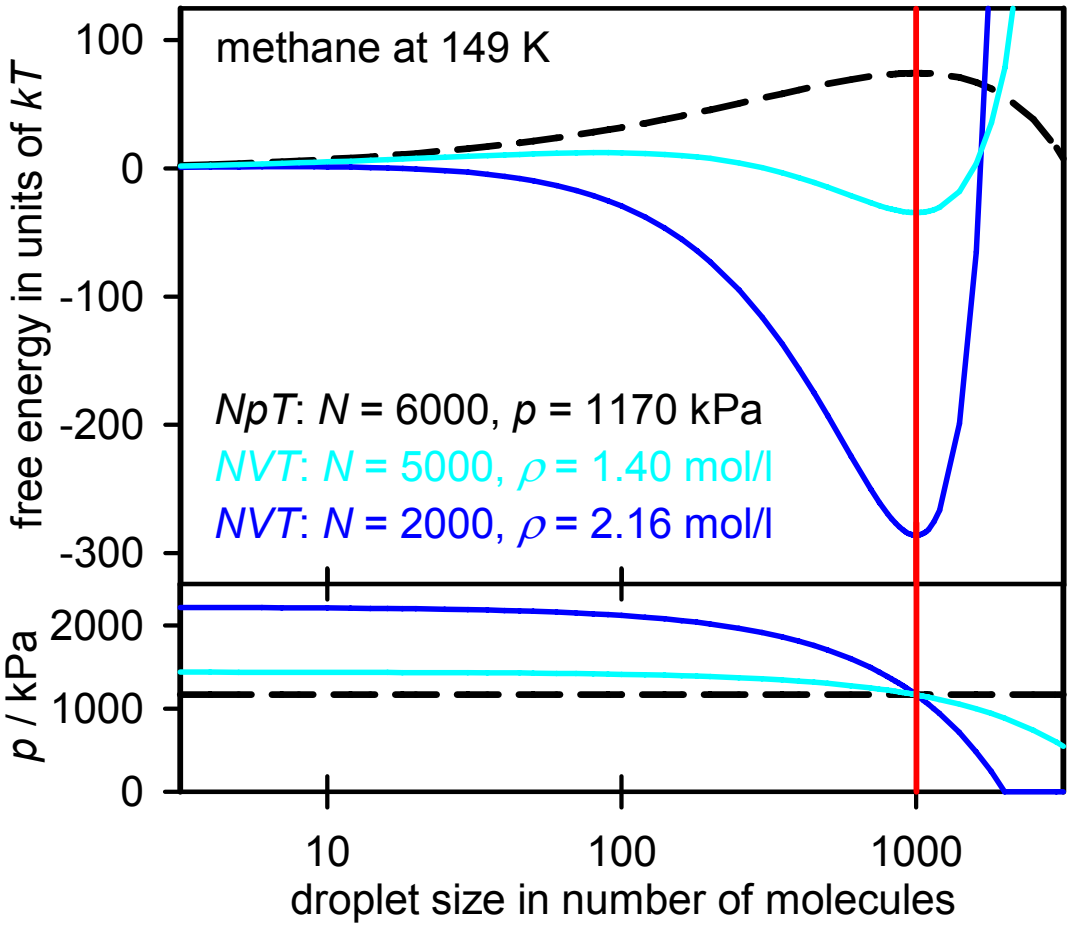
$$d\Omega_V / dj = \mu_j^{\mathrm{liq}} - \mu$$

$$\lim_{j \to \infty} \mu_j^{\mathrm{liq}} = \mu_s$$



It is essential to know the supersaturation in terms of $\Delta\mu$.

Equilibrium vapor pressure



Equilibrium condition for a droplet containing j molecules:

$$p = p(T, j)$$

ΔG at constant p and T:

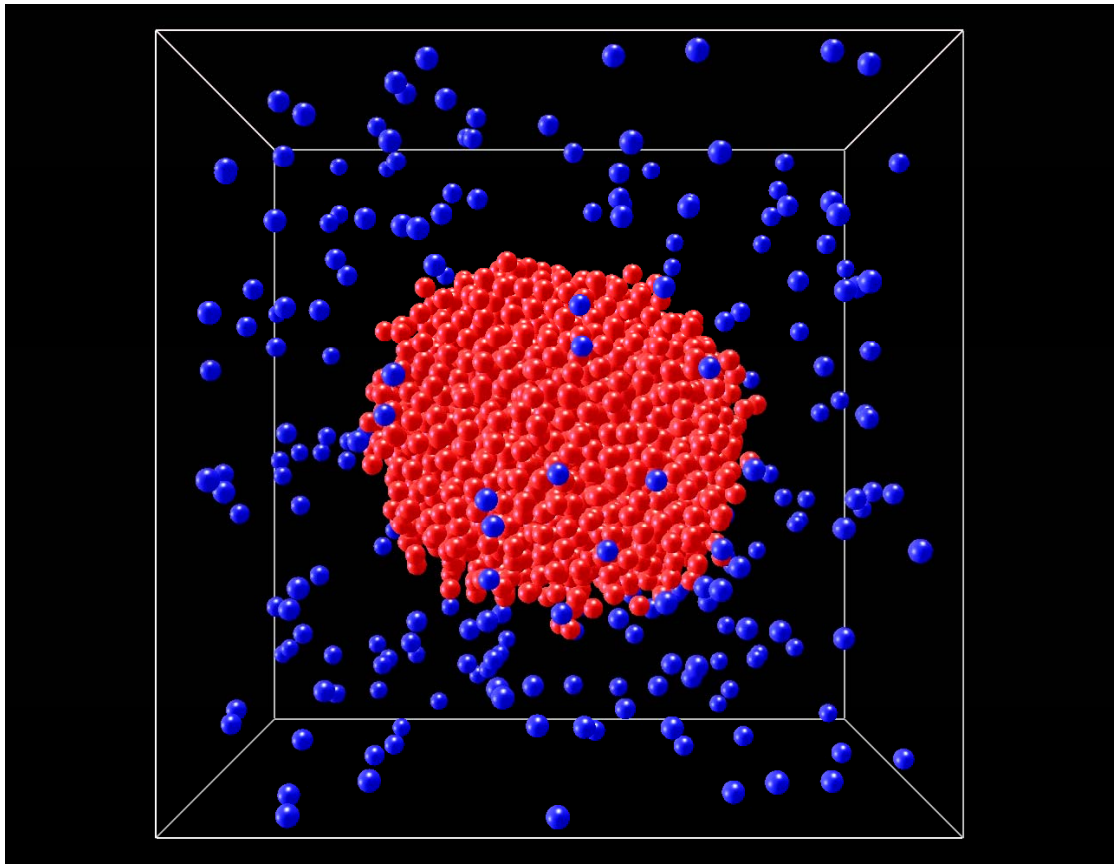
1 unstable equilibrium

ΔF at constant V and T:

1 unstable equilibrium
1 stable equilibrium

Systems containing a single droplet

- Vapor and liquid are equilibrated separately.
- A small (j < 10000) droplet is inserted into the vapor.
- If the droplet cannot evaporate completely, an equilibrium is established within a few nanoseconds.



t-s-LJ fluid (r_c = 2.5 σ)

Surface tension

Integration of the $p_N(r)$ profile:

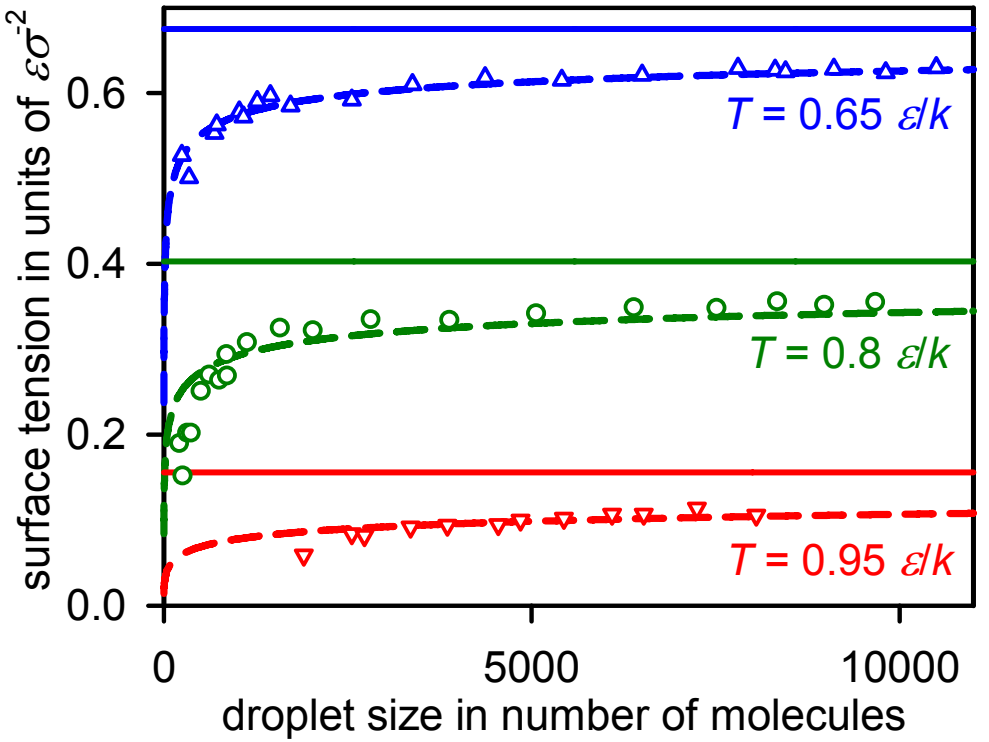
$$\gamma^{-3} = \frac{-(p_l - p)^2}{8} \int_0^\infty r^3 \left[\frac{dp_N(r)}{dr} \right] dr$$

Size dependence (Tolman):

$$\frac{\gamma_\infty}{\gamma} = 1 + \frac{2\delta_T}{R_\gamma} + O\left(R_\gamma^{-2}\right)$$

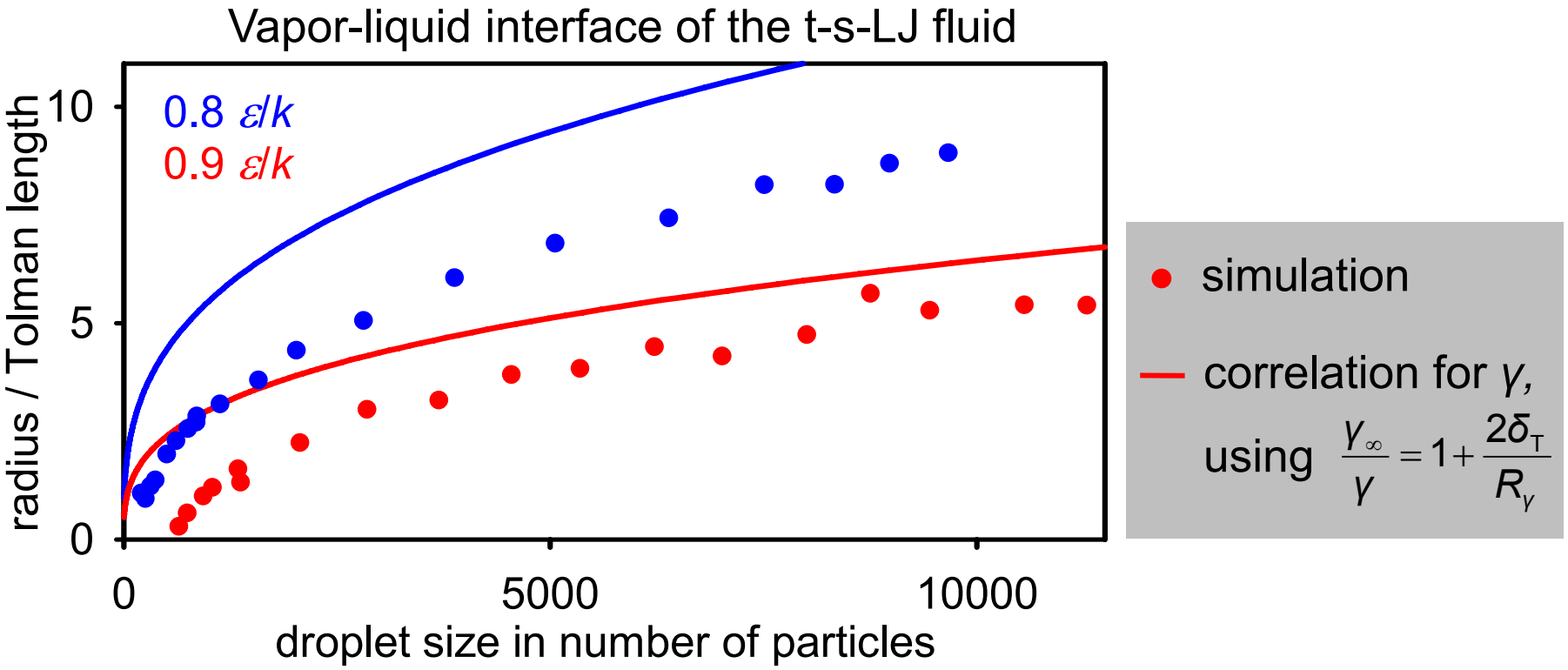
Correlation from simulation data for T = 0.65, 0.70, … 0.95 ε/k:

$$\frac{\delta_T}{R_\gamma} = \left(\frac{0.7}{1 - T/T_c} - 0.9 \right) j^{-1/3}$$



● simulation
— planar interface
- - - new correlation

Tolman equation



The higher order terms of the Tolman equation should not be neglected.

Direct MD simulation of nucleation

- Integration time step typically between 1 and 5 fs;
  Feasible simulation time: on the order of nanoseconds.
- A saturated vapor with $V = 10^{-20}$ m^3 contains:
  800,000 molecules (methane at 114 K = 0.6 T_c)
  7,000,000 molecules (CO_2 at 253 K = 0.83 T_c)
- Minimal nucleation rate accessible by direct simulation:

#nuclei /	(volume V x	time Δt) =	nucleation rate J
10 /	(10^{-20} m^3 x	10^{-9} s) =	10^{30} / m^{3}s

Direct MD simulation above 10^{30} / m^{3}s ⟷ Experiment up to 10^{23} / m^{3}s

Grand canonical molecular dynamics

Algorithm according to Cielinski:

- fixed values of μ, V und T
- test insertion of a molecule at a random position

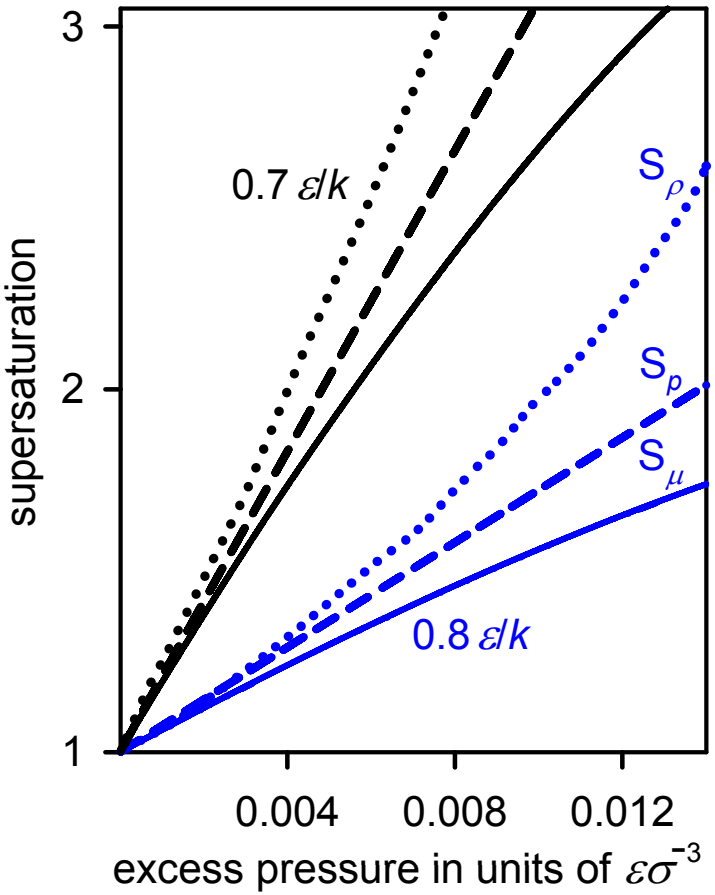
$$P_{\text{ins}} = \max\left[1, \exp\left(\frac{\mu - \Delta U_{\text{ins}}}{kT}\right)\frac{V}{\Lambda^3 (N+1)}\right]$$

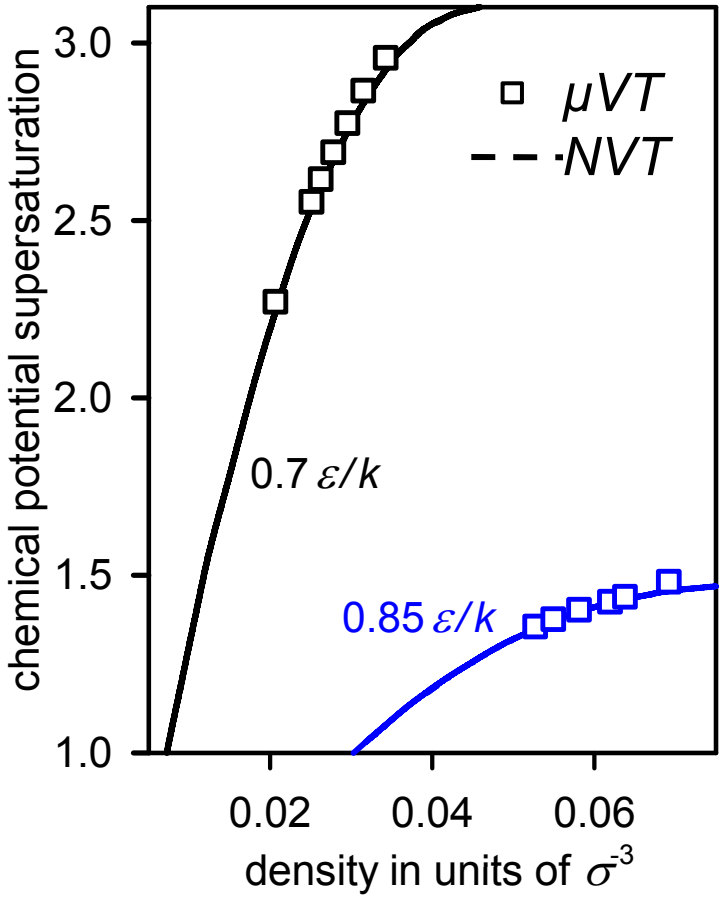
- test deletion of a random molecule

$$P_{\text{del}} = \max\left[1, \exp\left(\frac{-\mu - \Delta U_{\text{ins}}}{kT}\right)\frac{V}{\Lambda^3 N}\right]$$

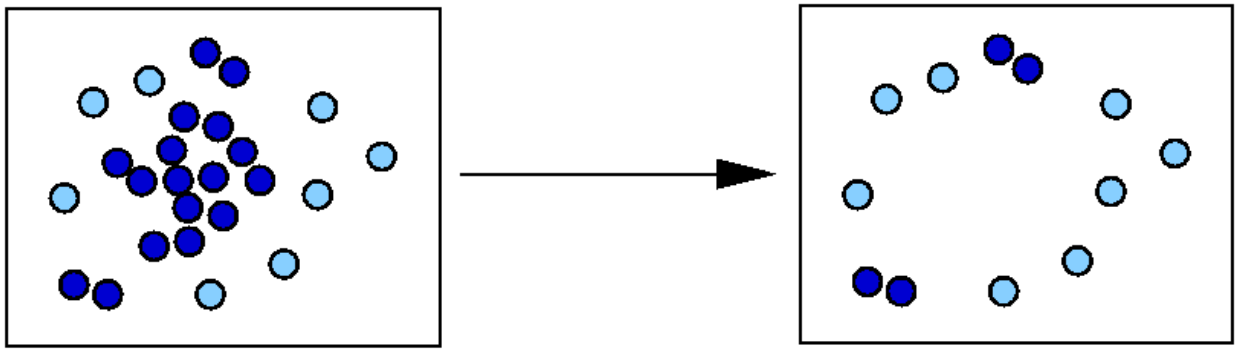
- equal number of test insertions and deletions (10^{-5} – 10^{-3} / step)

Supersaturation from *NVT* and *μVT* simulation



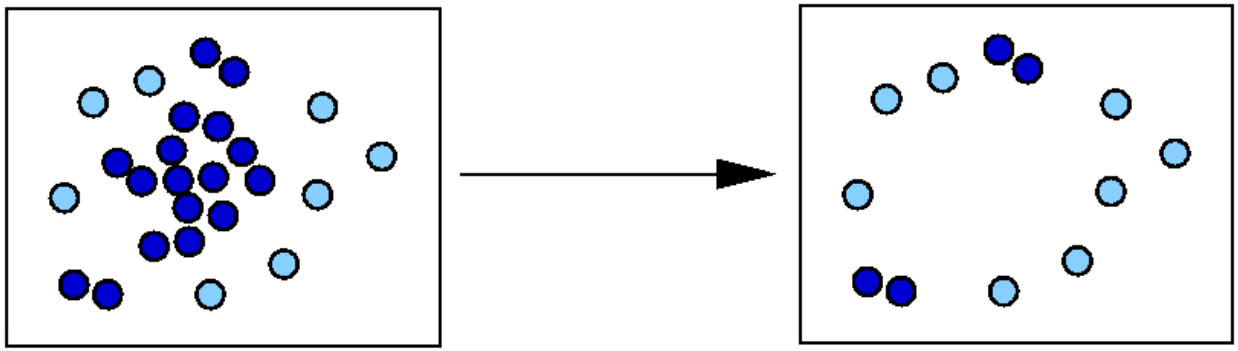


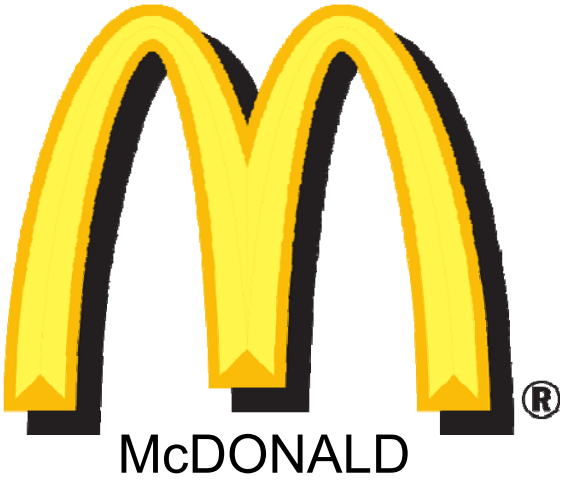
Szilárd‘s demon



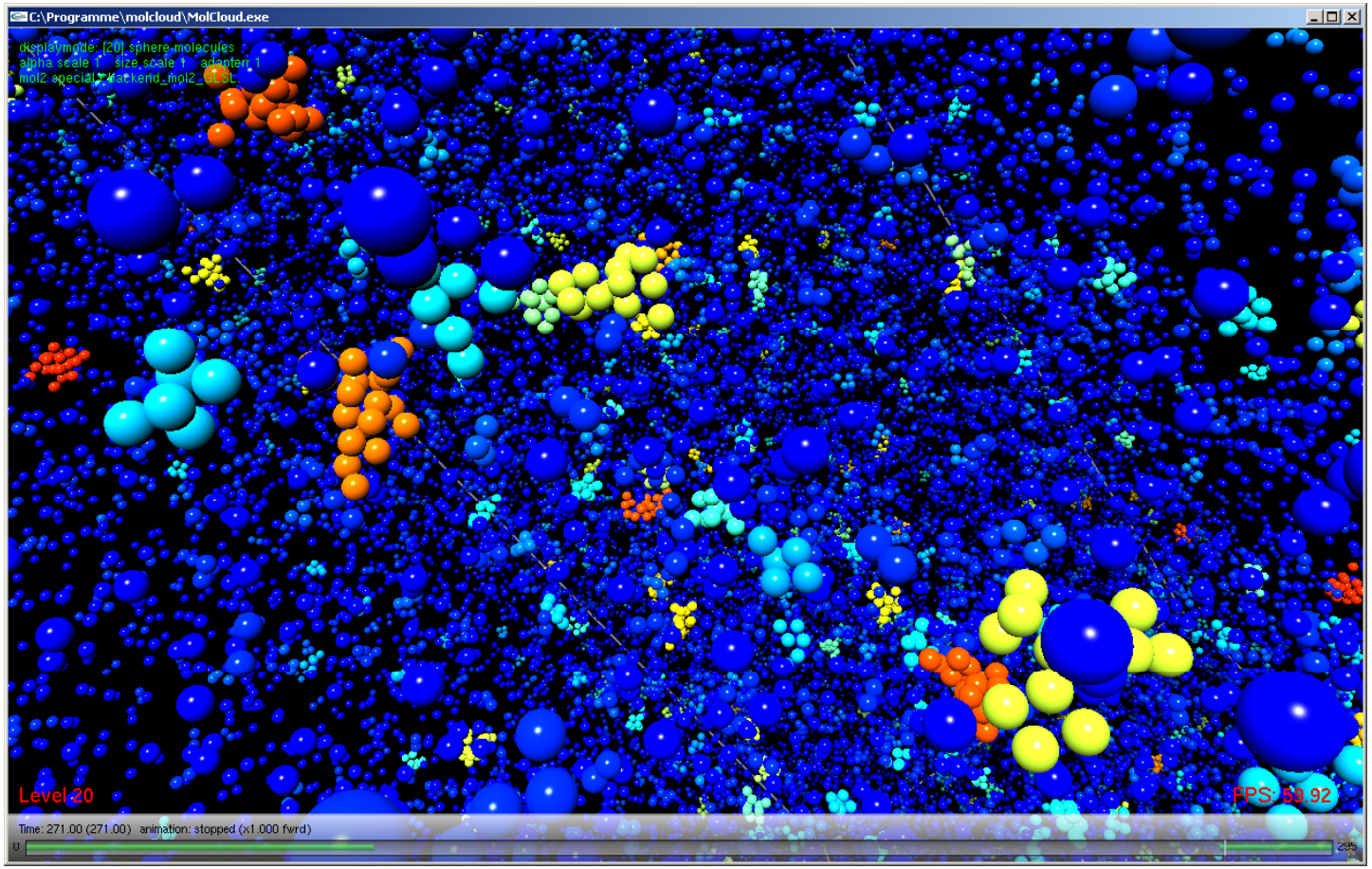
SZILÁRD

McDonald‘s demon

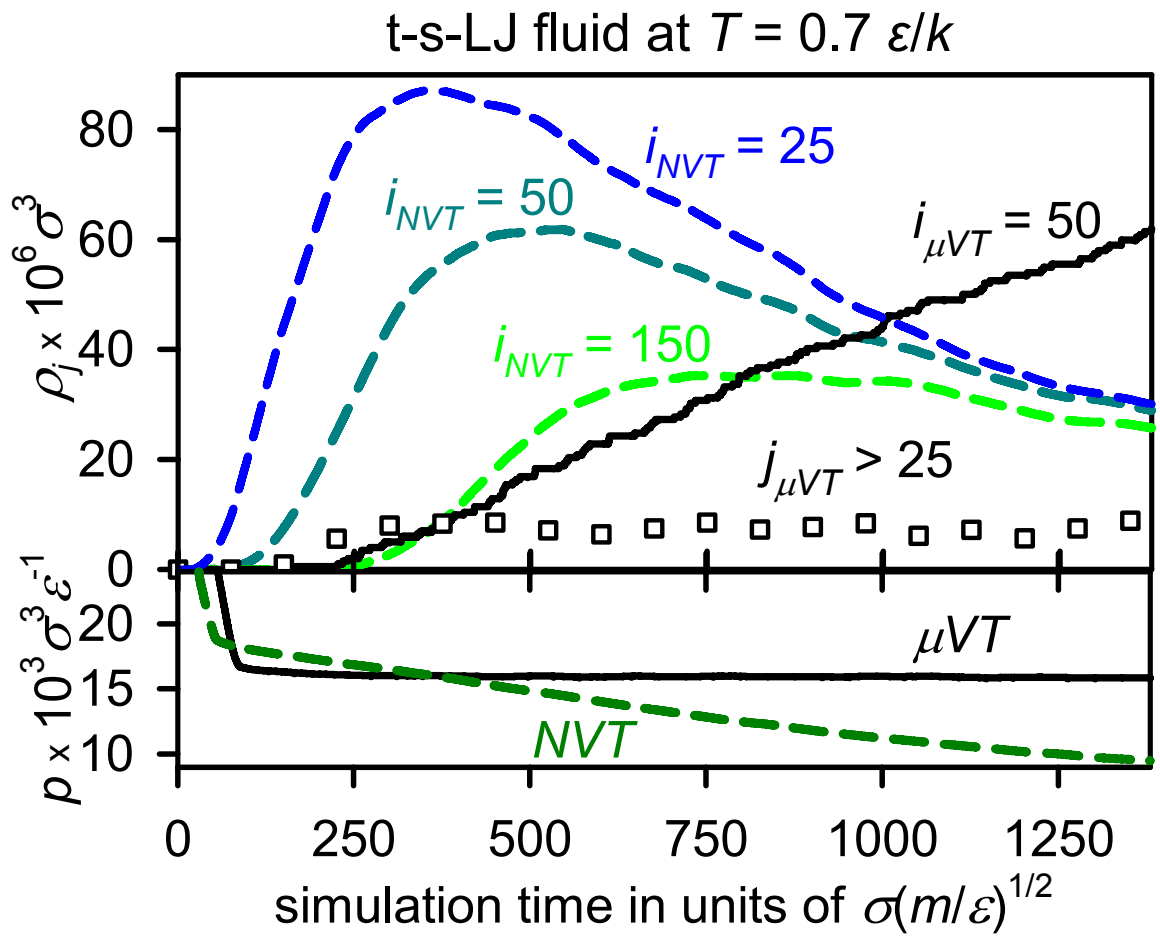




Interactive presentation: McDonald‘s demon



Comparison: *NVT* and *μVT* simulation

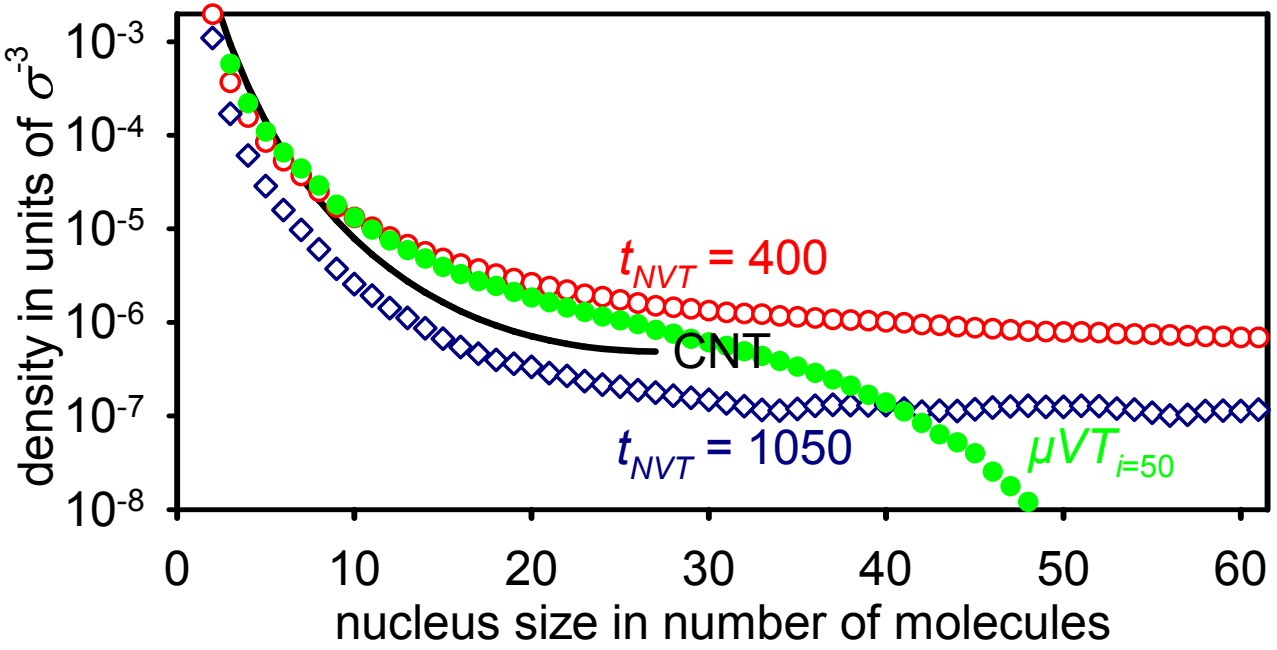


μVT: $S = 2.866$

NVT: $\rho = 0.004044\ \sigma^{-3}$

Nucleus size distribution

t-s-LJ fluid at $T = 0.7\ \varepsilon/k$:
μVT ($S = 2.866$) and NVT ($\rho = 0.004044\ \sigma^{-3}$) simulation



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

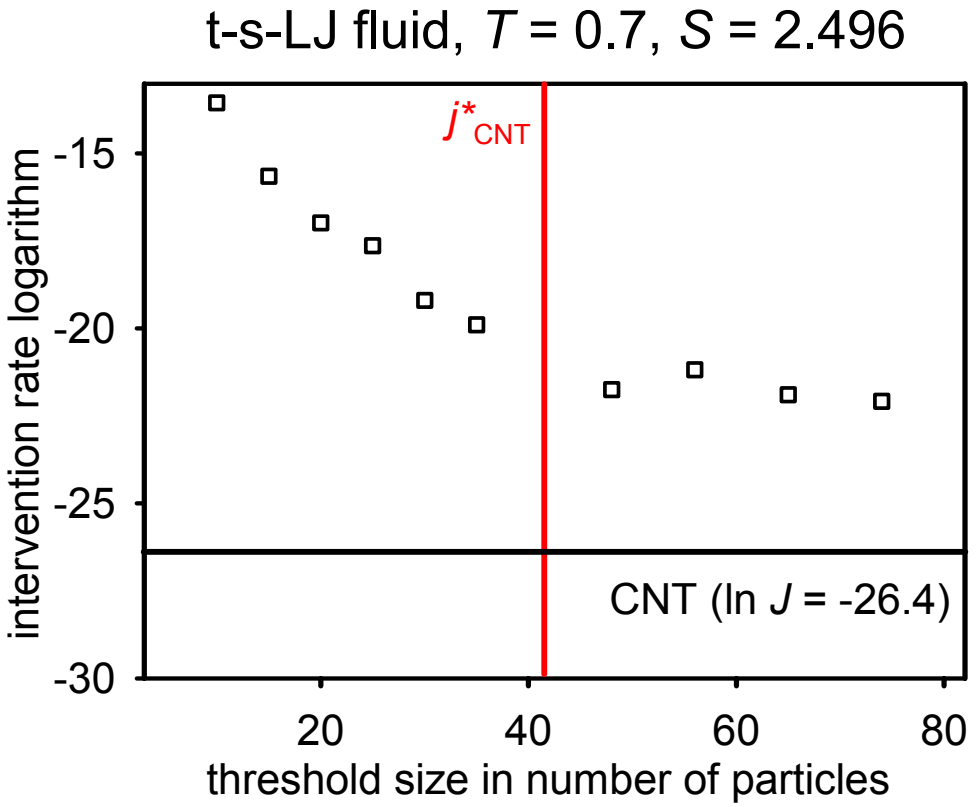
Threshold dependence of the intervention rate

Statistical probability for a nucleus of growing from size j to infinite size:

$$P^{\infty}(j) = 1 - \int_{j}^{\infty} \omega_Z \exp\left(\frac{2\Omega}{kT}\right) dj,$$

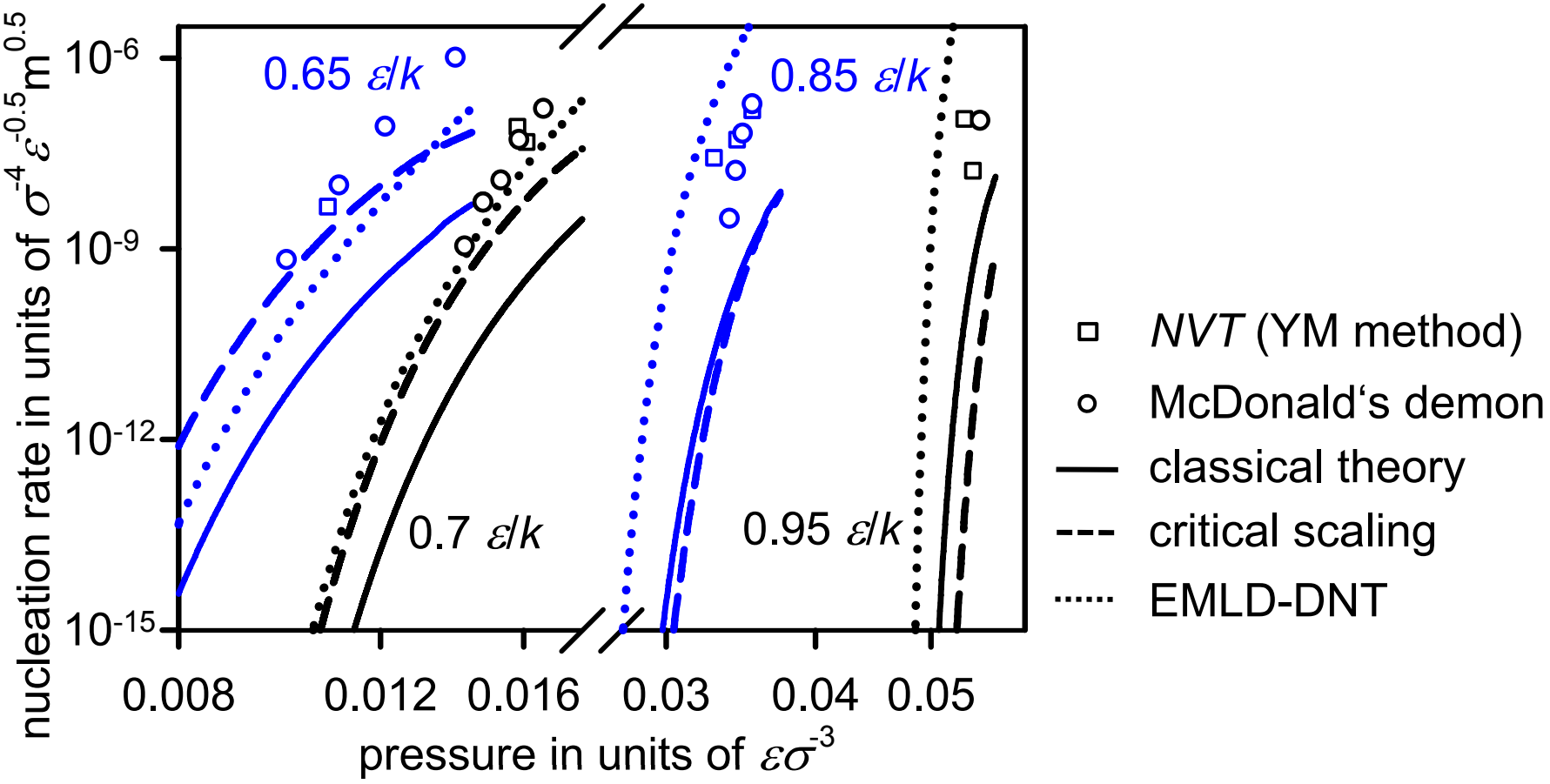
such that

$$P^{\infty}(j^*) = \tfrac{1}{2}$$



CNT predicts an acceptable value for j^* and underestimates J significantly.

GCMD simulation of nucleation: Results



Conclusion

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