Steady-state simulation of homogeneous vapor-liquid nucleation “by the intervention of intelligent beings“

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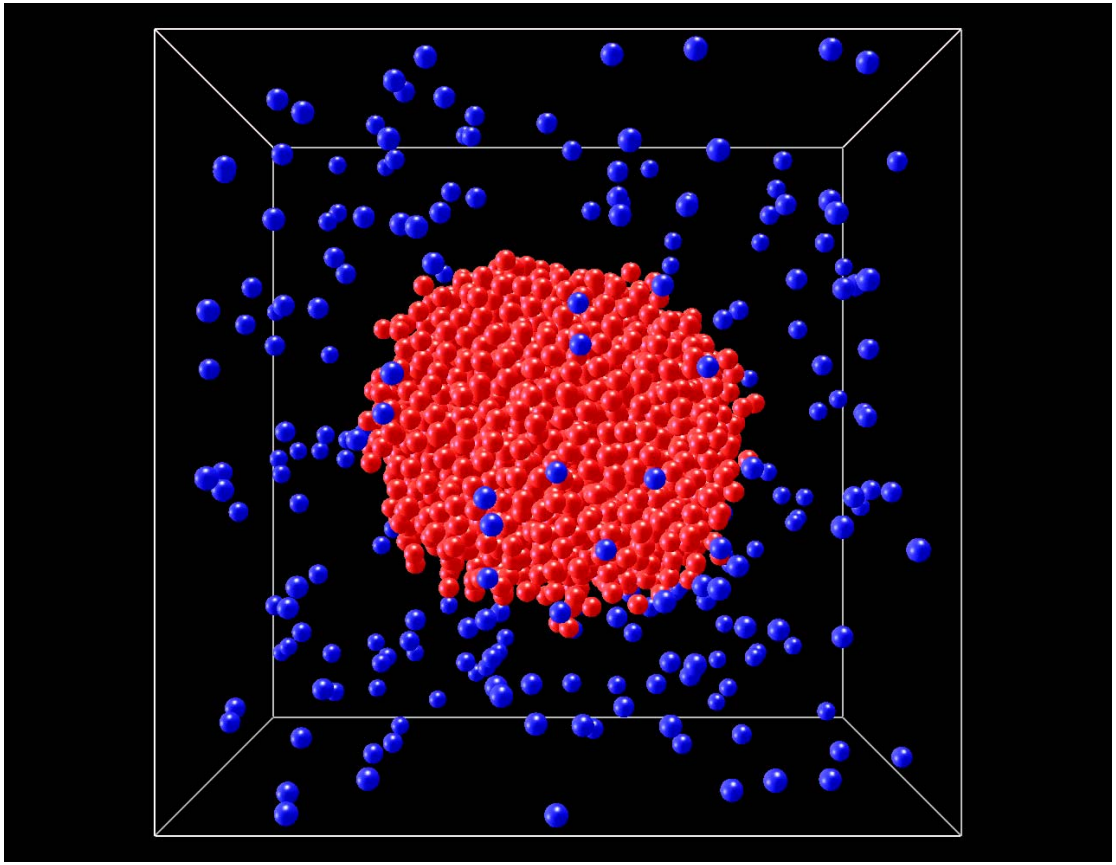
MD simulation of a single droplet

- 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)

Single droplet in non-equilibrium

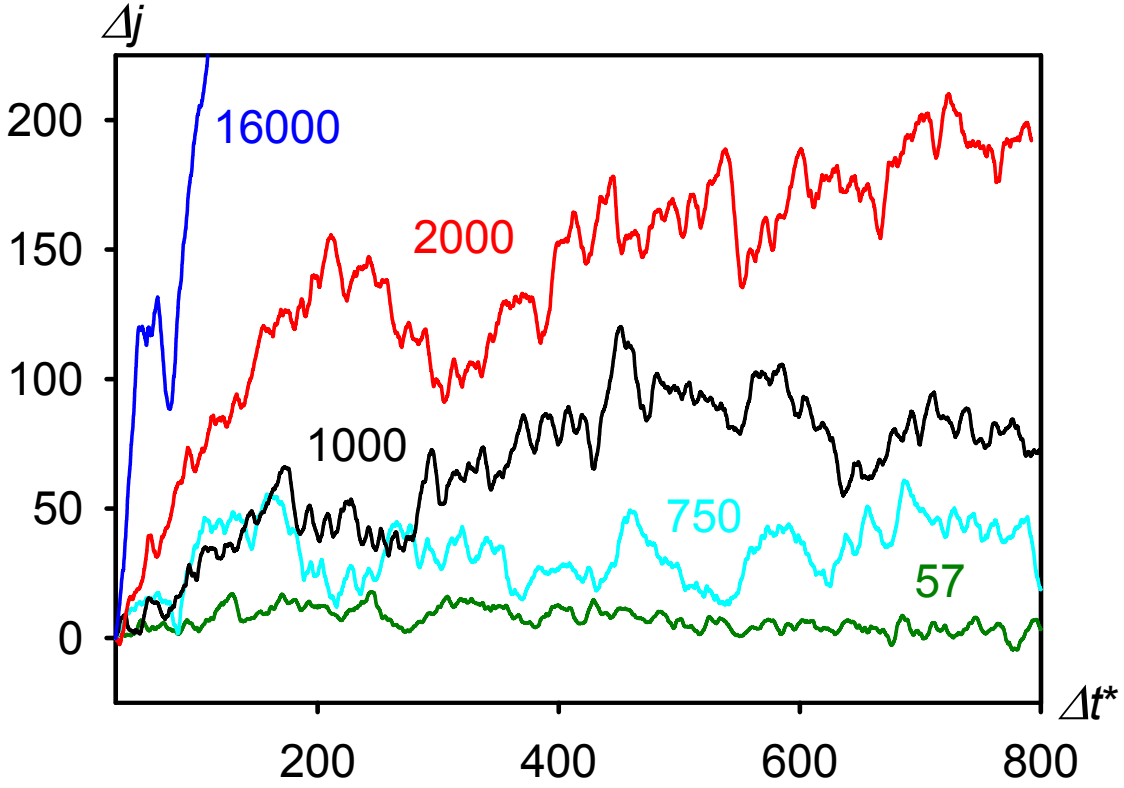
t-s-LJ fluid

Vapor properties:

N = 130,000
ρ = 0.0268 / σ^3
T = 0.80 ε/k

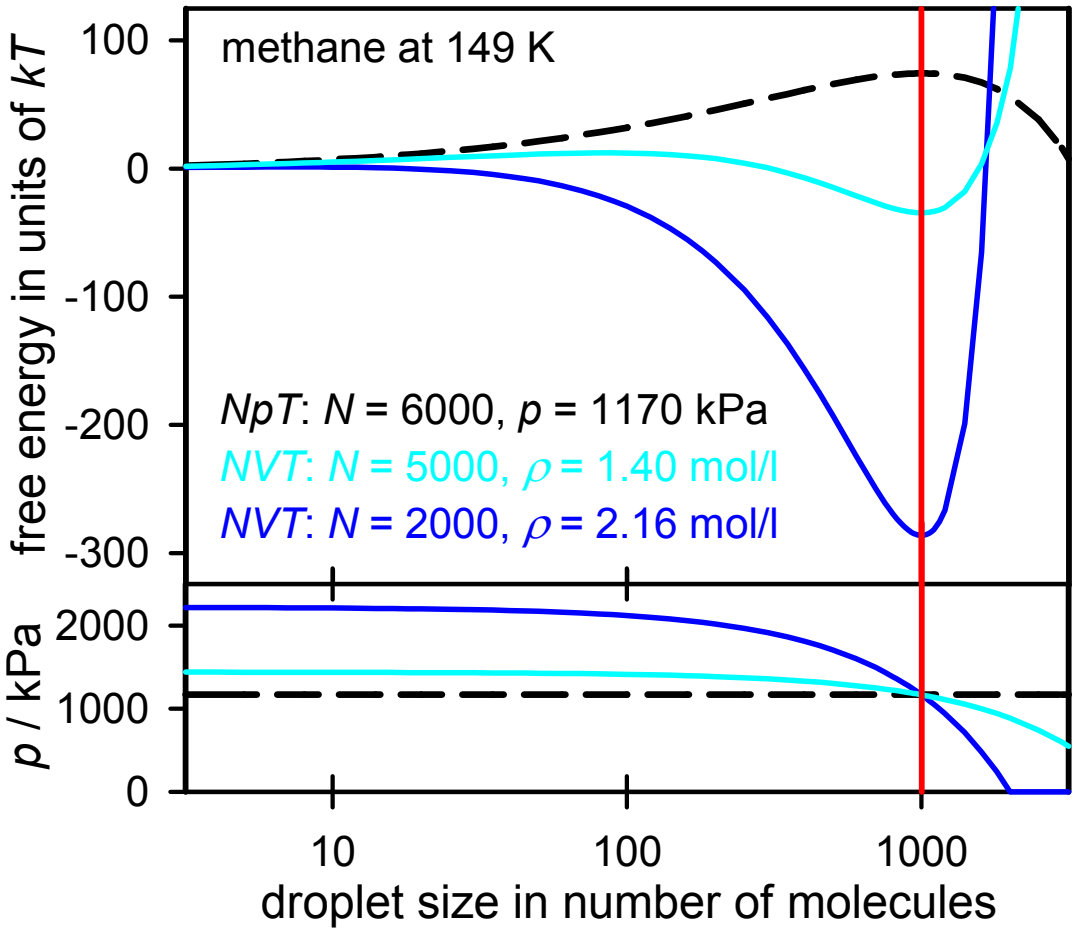
Time interval ≈ 1 ns

Classical theory: j^* = 850



The critical nucleus size cannot be clearly detected by non-equilibrium simulation

Equilibrium vapor pressure



Equilibrium condition for a droplet containing j molecules:

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

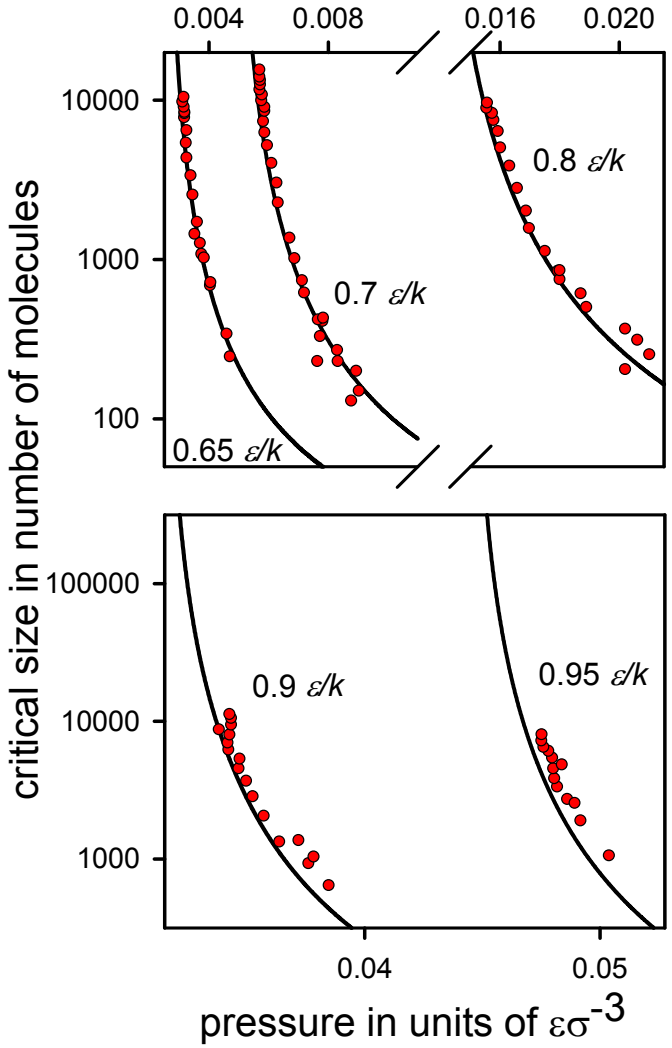
ΔG at constant p and T:

1 unstable equilibrium

ΔF at constant V and T:

1 unstable equilibrium
1 stable equilibrium

Critical nucleus from equilibrium MD simulation



Kelvin equation:

$$j^* = \left(\frac{2\gamma A_1}{3\Delta\mu} \right)^3$$

- present simulation data
- classical theory

- Good prediction of the critical size for low temperatures
- Above 0.8 T_c, significant deviations are present

Nucleation from MD in the *NVT* ensemble

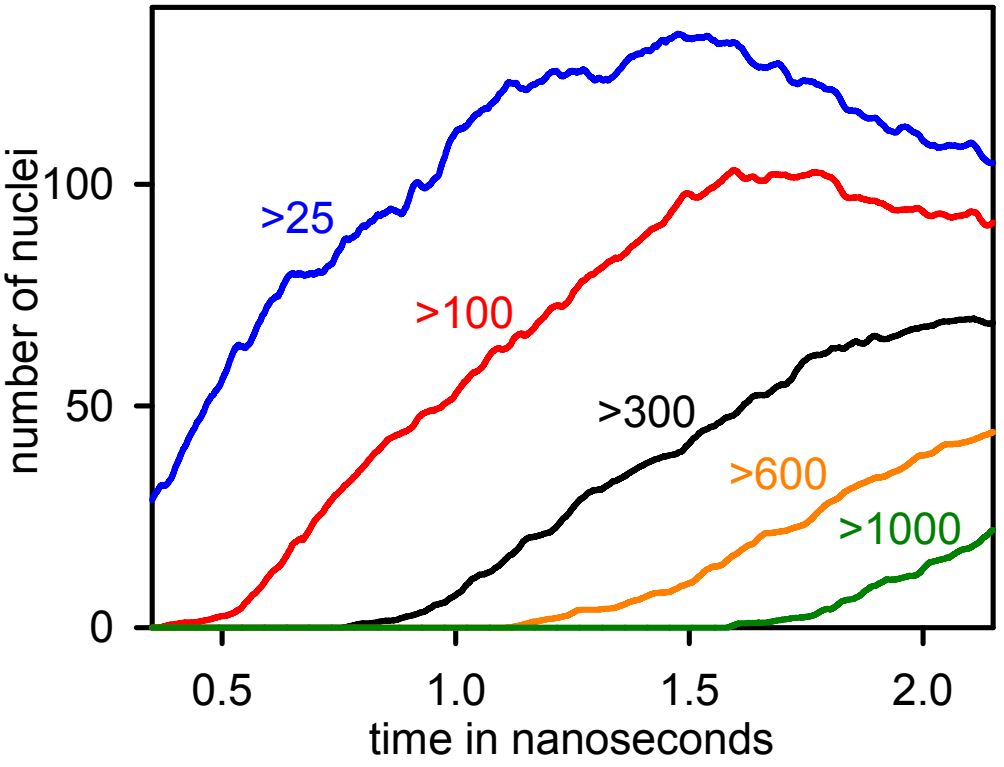
Yasuoka and Matsumoto (1998):

Number of emerging nuclei with >*j* molecules per volume and time

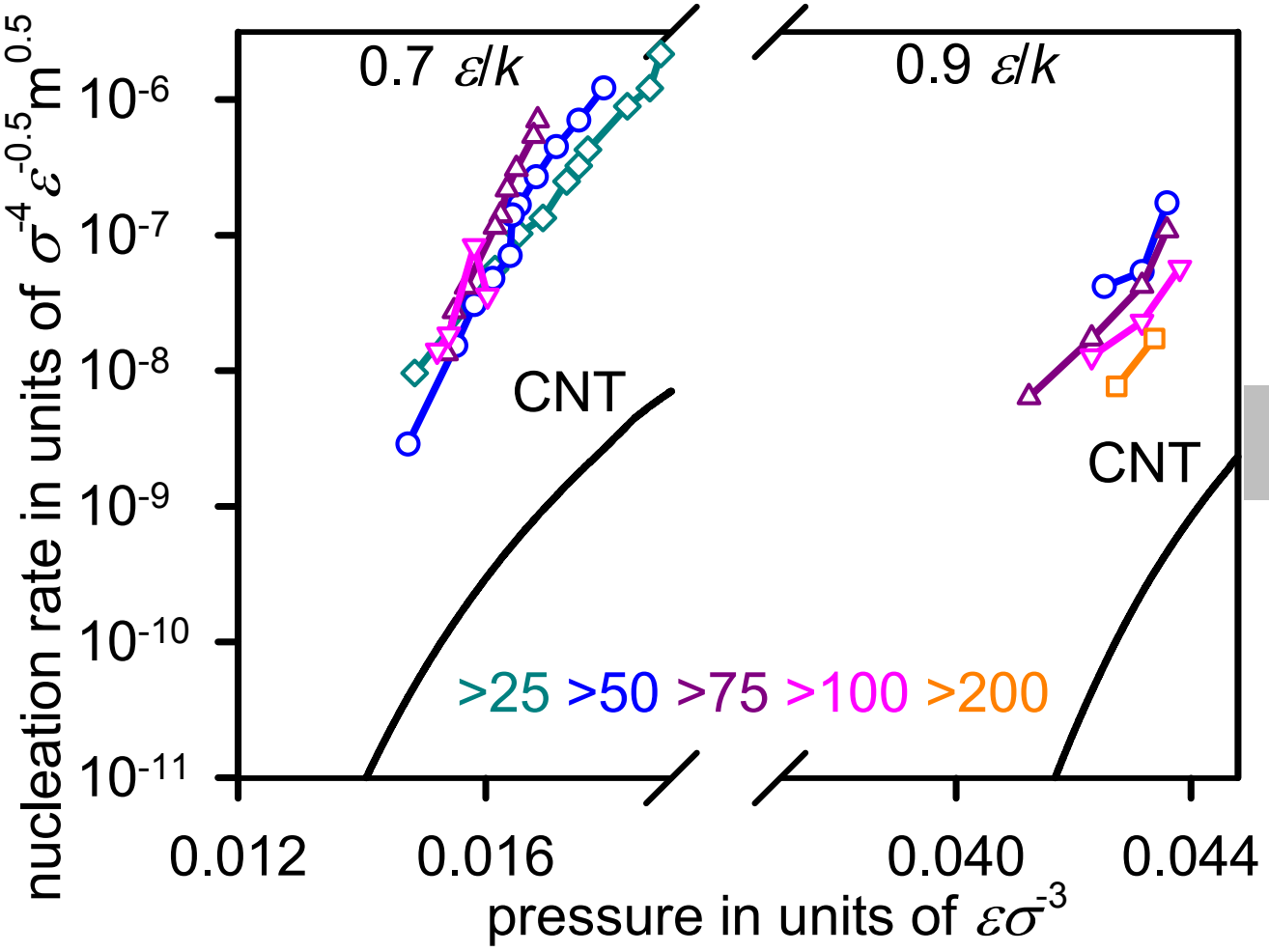
Typical approach:

determine the nucleation rate for various *j* values

250,000 methane molecules at 130 K and 1.606 mol/l (full LJ potential)



Nucleation rate following Yasuoka & Matsumoto



t-s-LJ fluid

Grand canonical MD

Algorithm: MC insertion/deletion steps alternating with MD steps

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

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

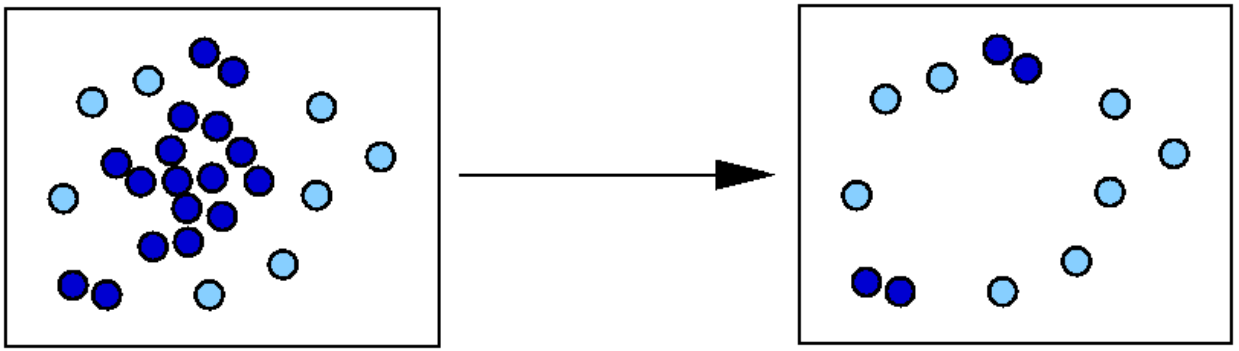
- test deletion of a random molecule

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

- equal number of insertions and deletions ($10^{-6}N$ to $10^{-3}N$ / step)

→ Thermodynamic conditions of supersaturated state are maintained

McDonald‘s demon



McDONALD®

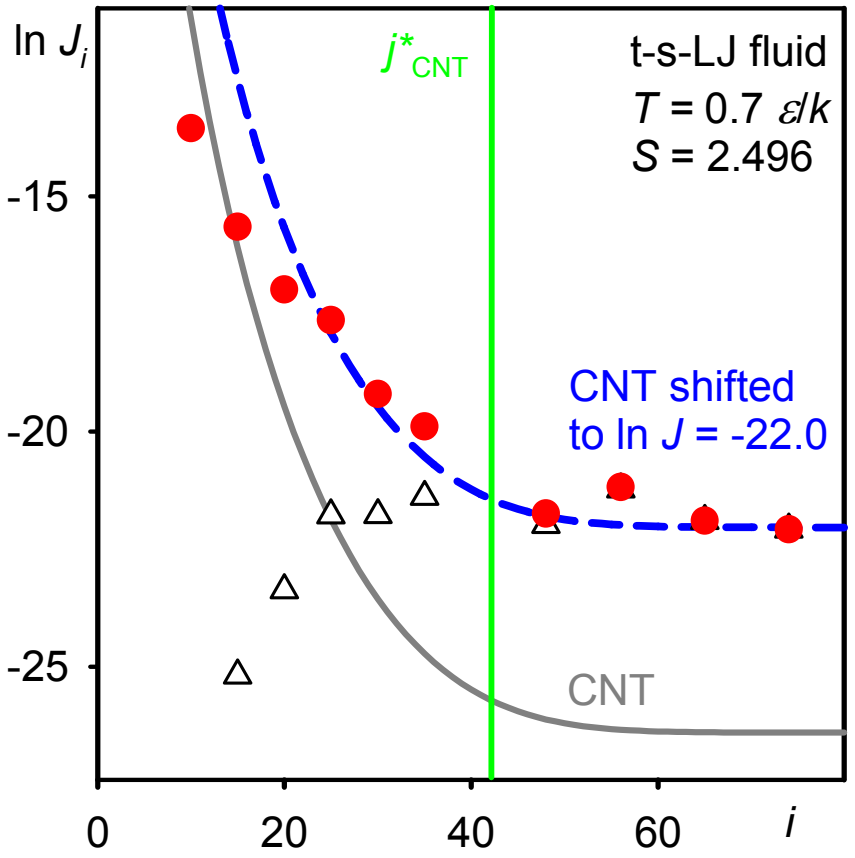
Intervention rate as a function of the threshold size

$$J_i = J/q_i$$

Probability for a nucleus of growing from size *i* to infinite size:

$$q_i = \frac{\int_1^i \exp(2\beta\Omega)\ dj}{\int_1^\infty \exp(2\beta\Omega)\ dj},$$

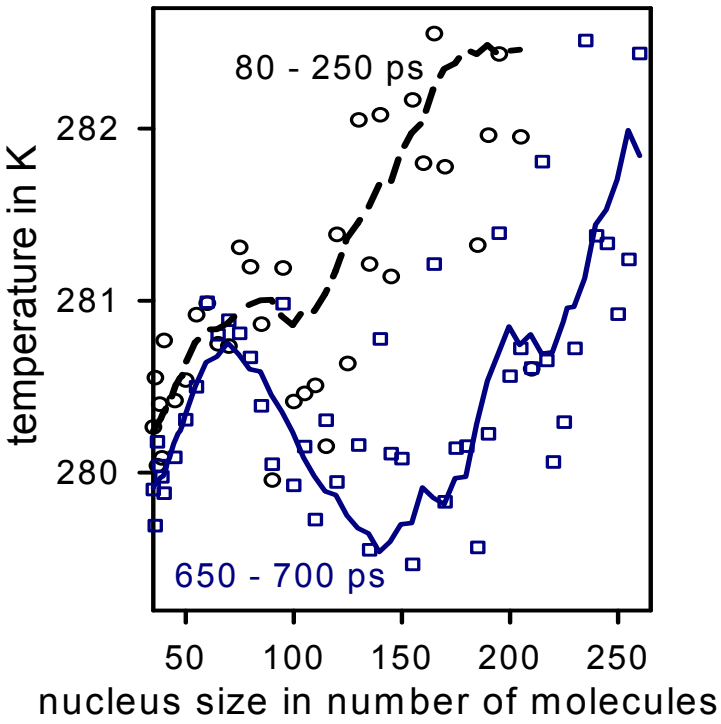
and in particular: $q_{j^*} \approx \frac{1}{2}$



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

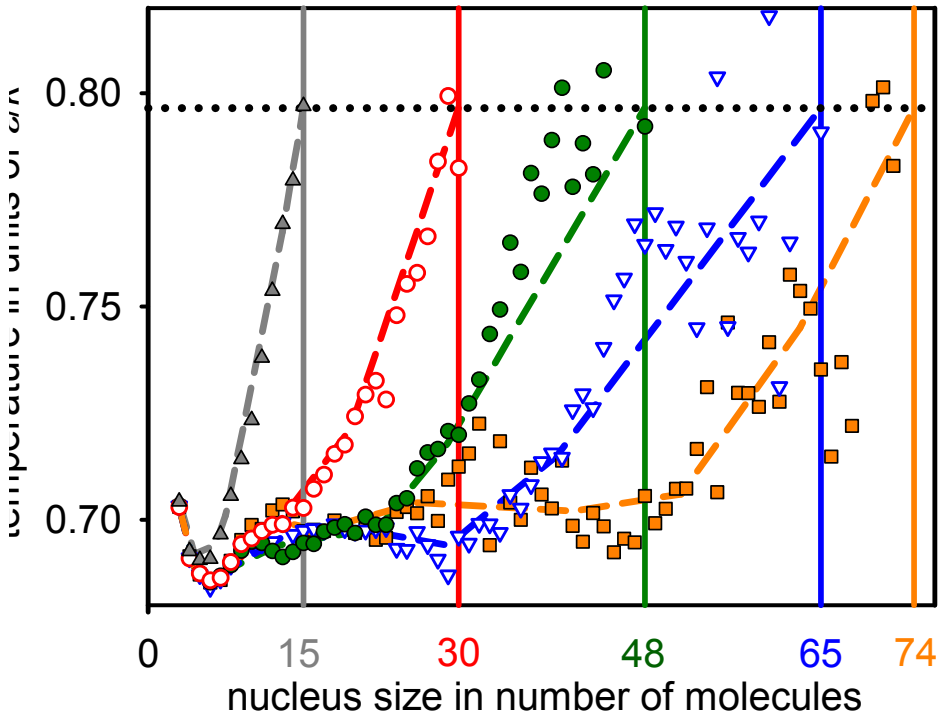
Maximal overheating of growing nuclei

Ethane: 280 K, 2.80 mol/l, *NVT*



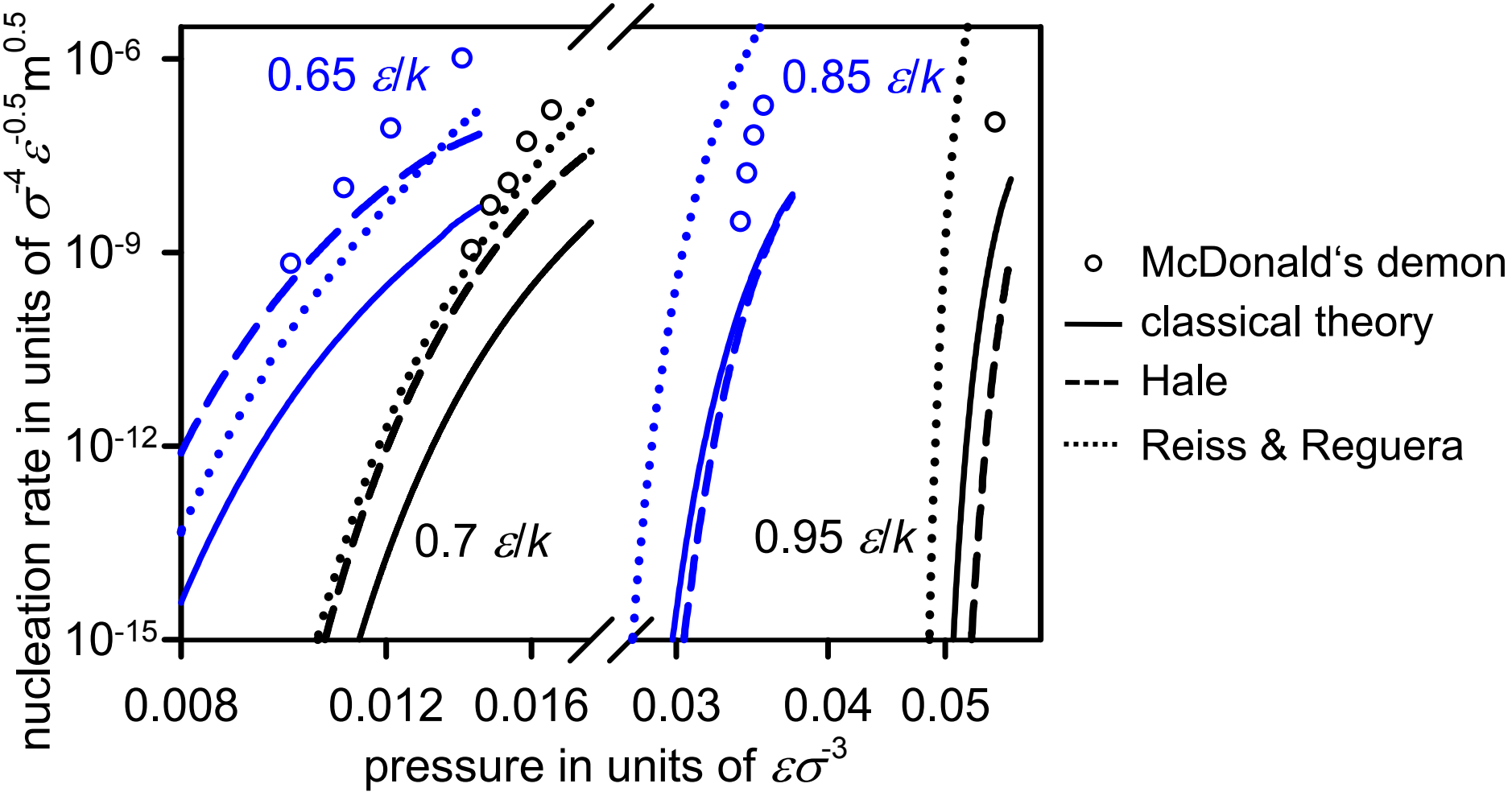
$$(\Delta T)_{j=j^*=78}^{\mathrm{CNT}} = \frac{2 f_Z}{\beta \Delta h^{\mathrm{v}}} T = 1.4\,\mathrm{K}$$

t-s-LJ fluid: 0.7 ε/k, μVT:
supercooled by ΔT = -0.0965 ε/k



$$(\Delta T)_{j \to i} \gg (\Delta T)_{j=j^*=41}^{\mathrm{CNT}} = 0.00608\ \varepsilon/k$$

GCMD simulation of nucleation: Results



Conclusion

- MD simulation of **steady states** 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**
- **Classical nucleation theory** leads to acceptable results for the t-s-LJ fluid