Molecular Modeling and Simulation for Industrial Applications:
Physico-Chemical Properties and Processes

Steady state molecular dynamics simulation of nucleation and droplet surface properties in a supersaturated vapor

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Classical nucleation theory

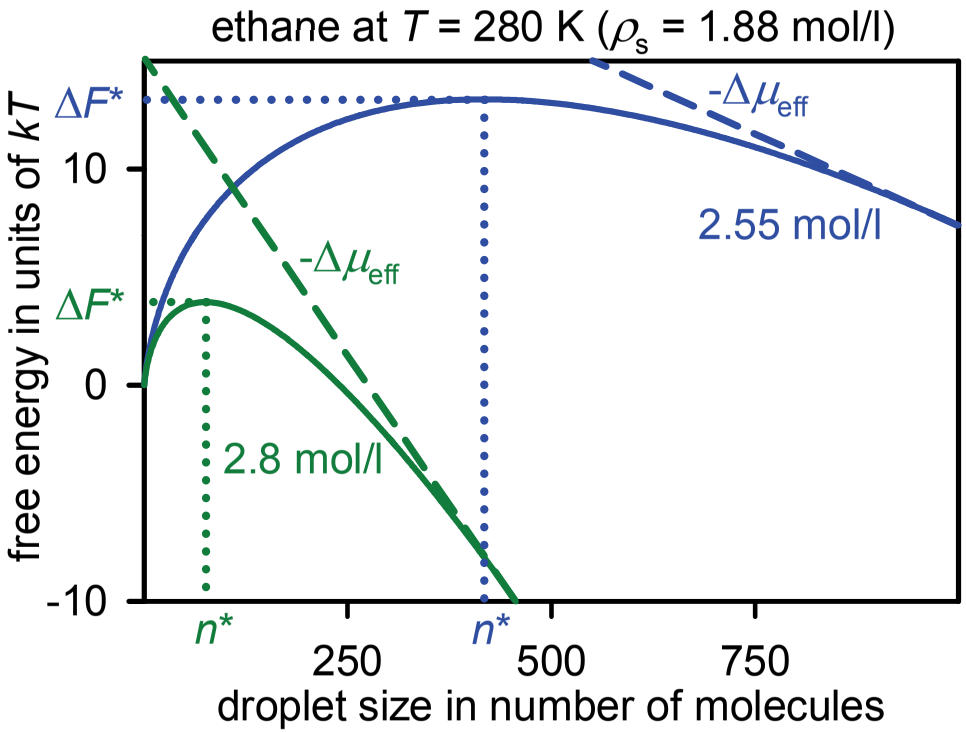
Free energy of formation

Positive surface contribution:

$$\left(\frac{\partial F_A}{\partial A_\gamma}\right)_T = \gamma\left(R_L^{-1}, T\right)$$

Negative bulk contribution:

$$\left(\frac{\partial F_b}{\partial n}\right)_{N,V,T} = \mu^\ell - \mu + \frac{p - p^\ell}{\rho^\ell} = -\Delta\mu_{\text{eff}}$$

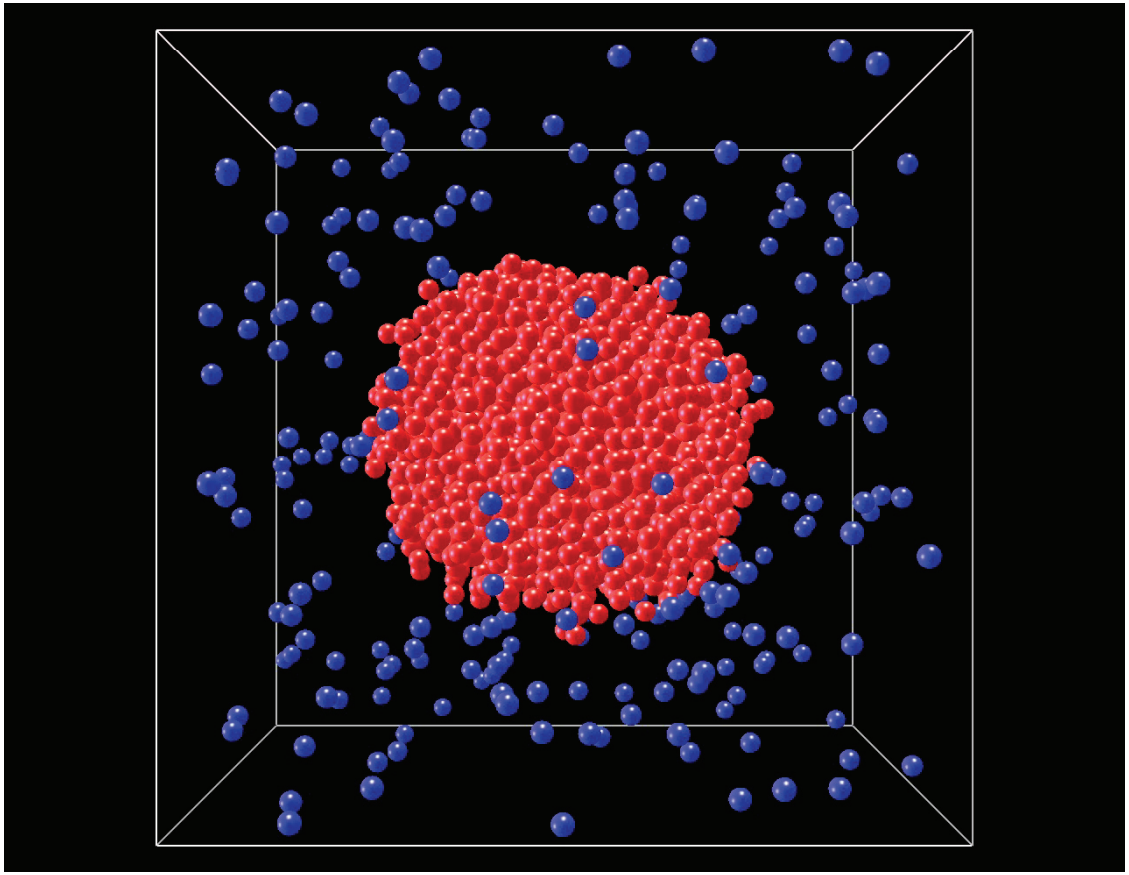


I. The zero-curvature surface tension γ_0 is used instead of γ.

II. The *pressure effect* is neglected, i.e. $\mu - \mu_s$ is used instead of $\Delta\mu_{\text{eff}}$.

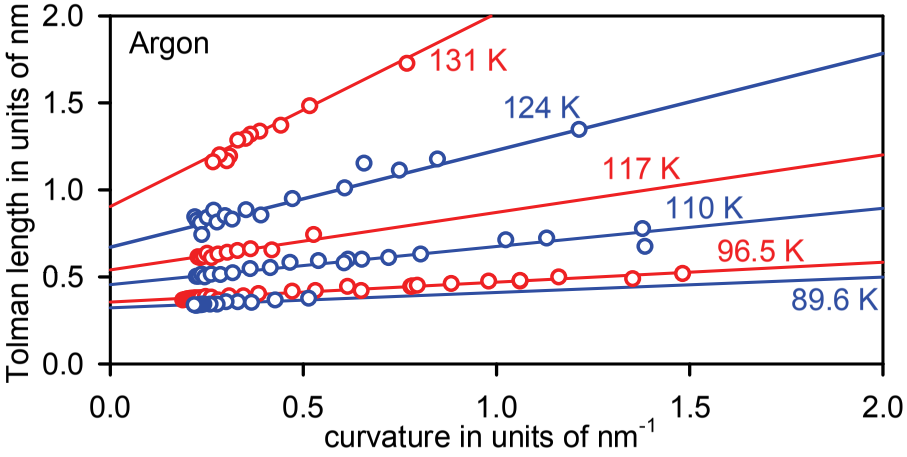
MD simulation of a single droplet

- Vapor and liquid are equilibrated separately
- A small (n < 10 000) droplet is inserted into the vapor
- If the droplet cannot evaporate completely, an equilibrium is established within a few nanoseconds



truncated and shifted LJ potential (r_c = 2.5 σ)

Droplet surface tension



For small droplets, the Tolman length

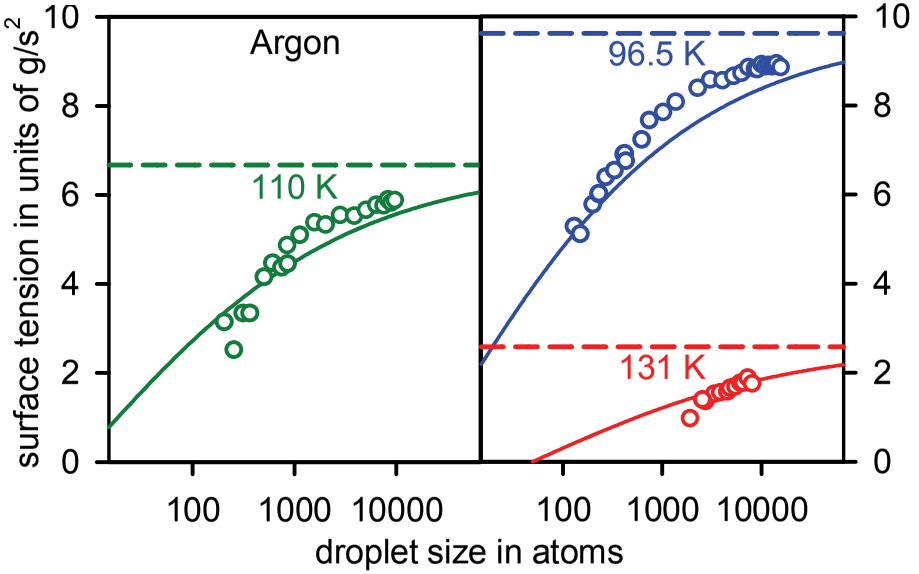
$$\delta = R_e - R_L$$

is significantly elevated.

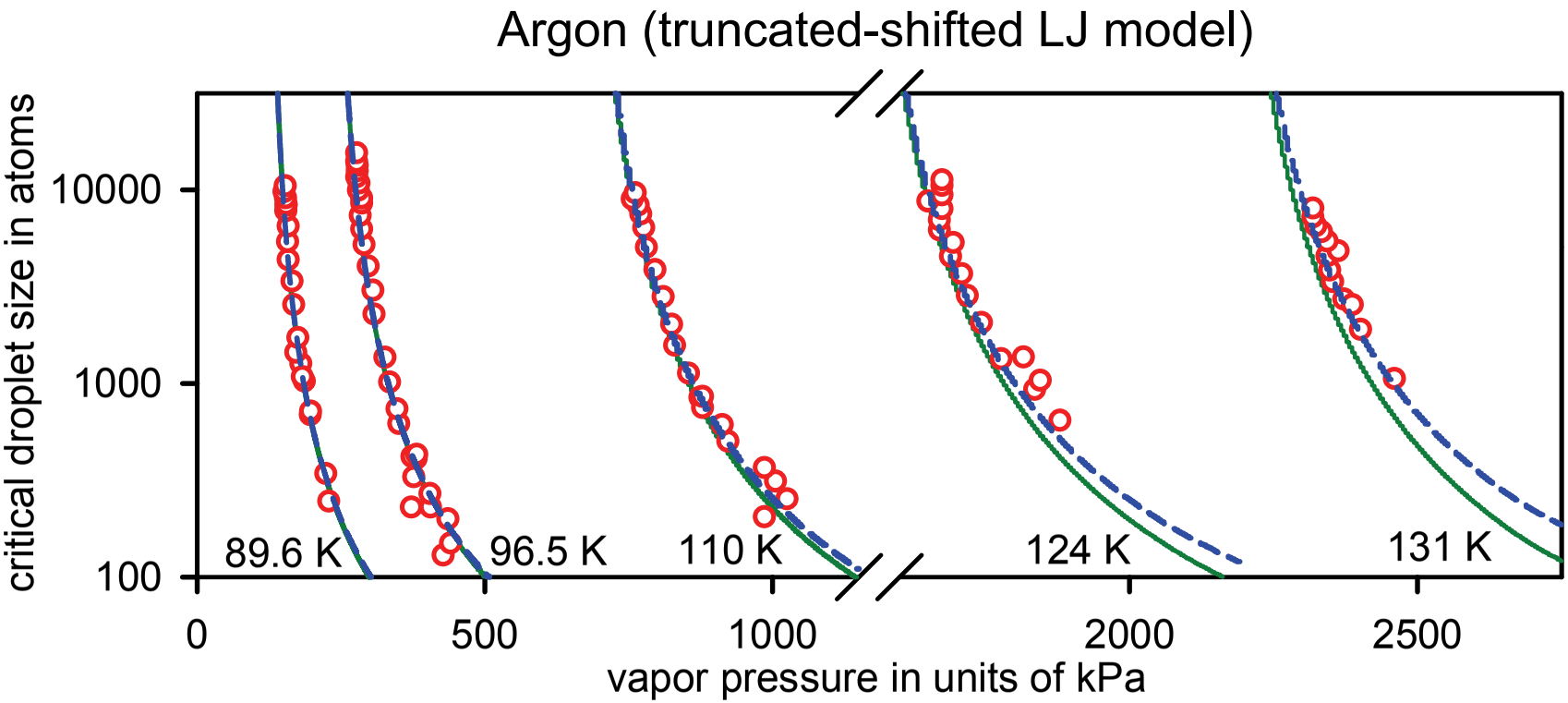
Tolman equation:

$$\frac{\gamma_0(T)}{\gamma} \approx 1 + 2\delta_0(T) R_L^{-1}$$

- MD simulation
— Tolman equation
- - - zero curvature



Single droplet in equilibrium



"standard" CNT

$$n^* = \left(\frac{2\gamma_0 a}{3(\mu - \mu_s)} \right)^3$$

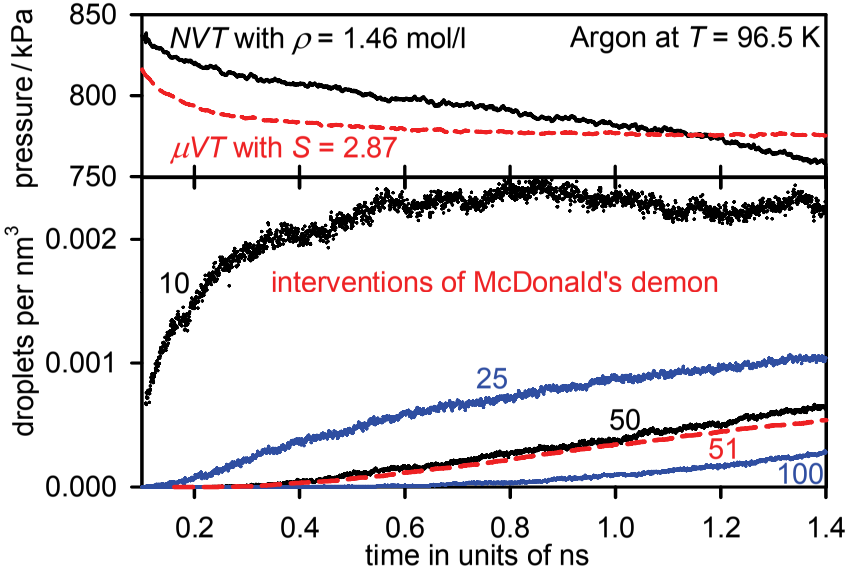
CNT with the pressure effect

$$n^* = \left(\frac{2\gamma_0 a}{3\Delta\mu_{\text{eff}}} \right)^3$$

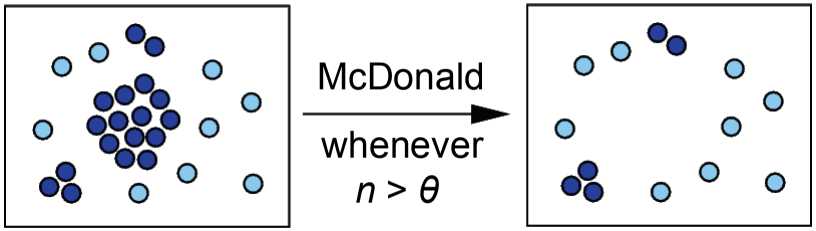
Direct MD simulation of nucleation

Yasuoka-Matsumoto method:

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

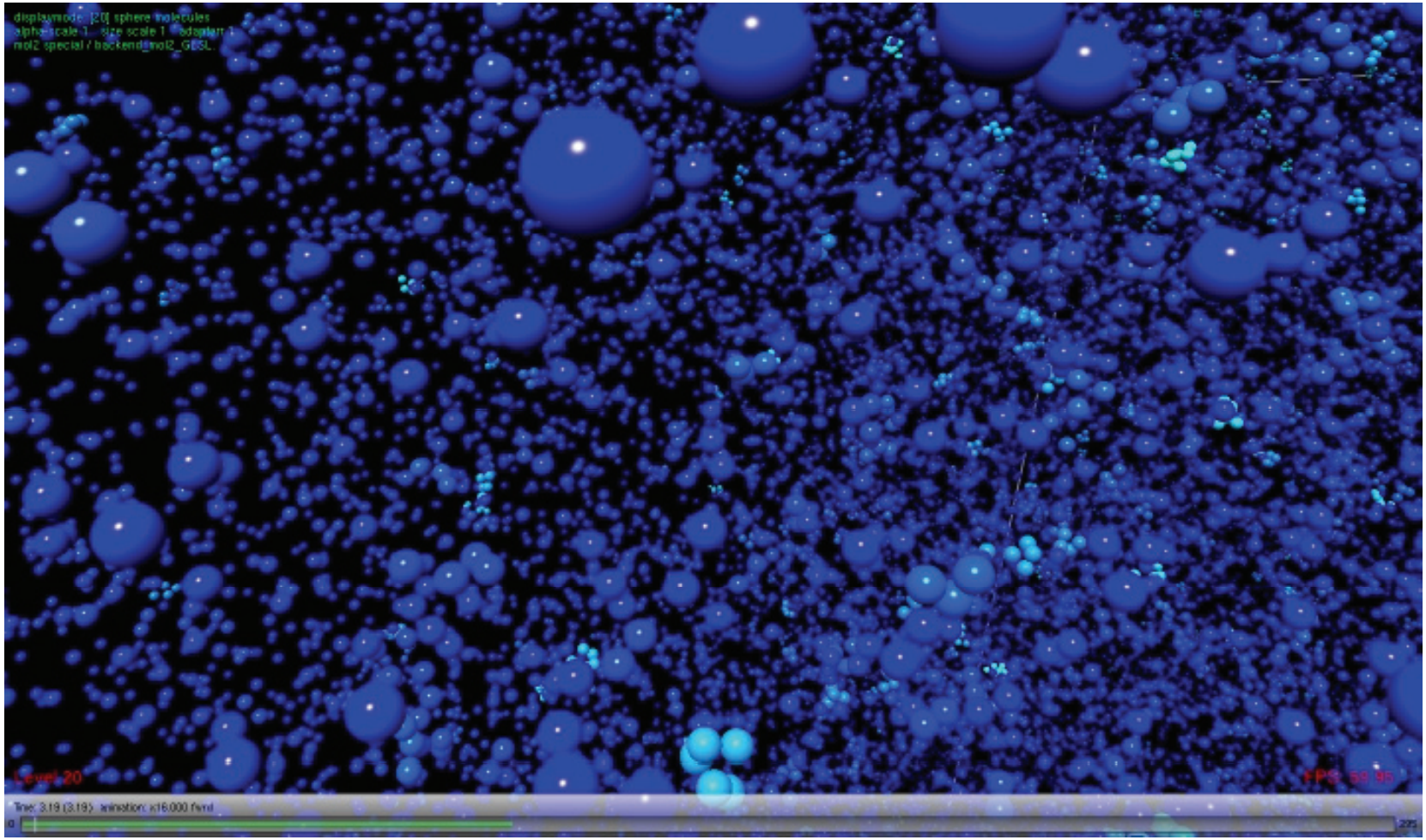


GCMD, i.e. MD steps alternating with GCMC insertion/deletion steps



→ Thermodynamic conditions of the supersaturated state are maintained

Video: McDonald‘s demon



Intervention rate J_θ and nucleation rate J

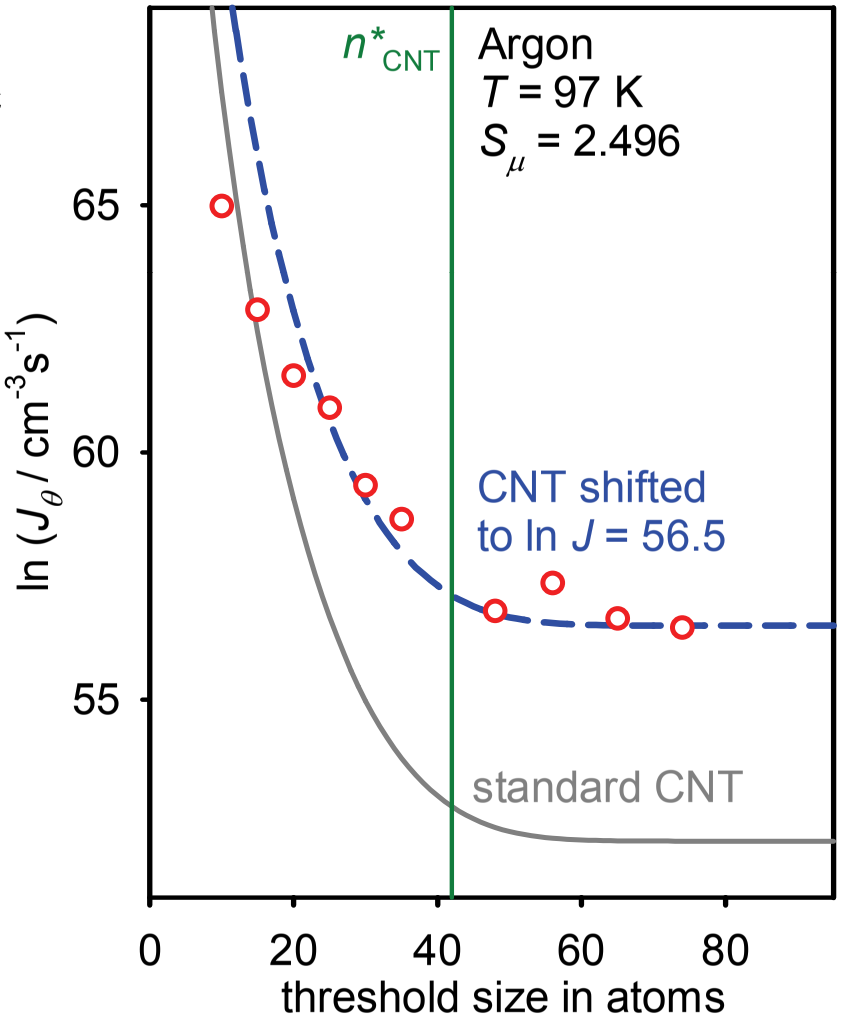
Not all of the removed droplets would eventually reach macroscopic size.

$$J = J_\theta q(\theta)$$

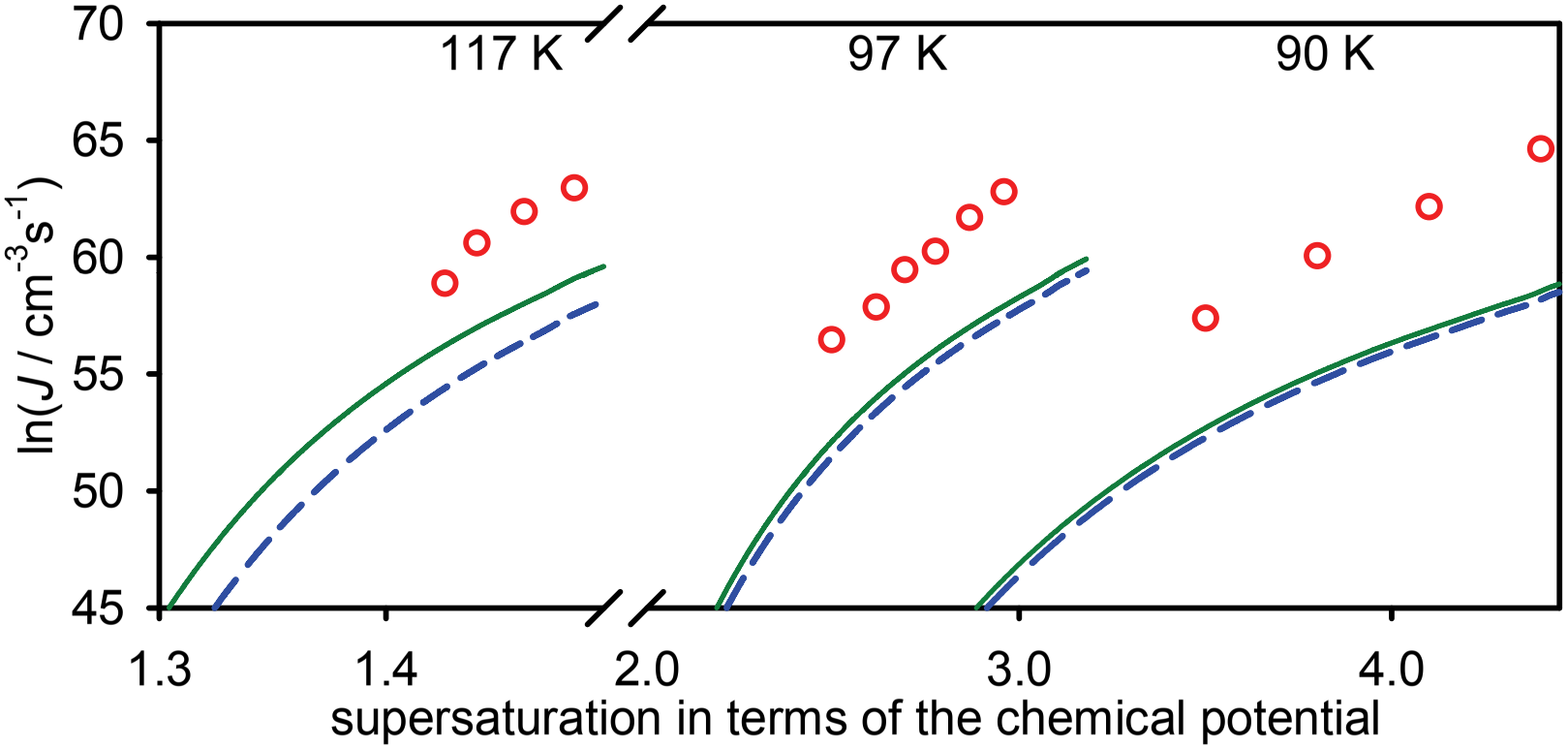
Probability for a droplet of growing from size θ to infinity:

$$q(\theta) = \frac{\int_1^\theta dn \exp(2F/kT)}{\int_1^\infty dn \exp(2F/kT)},$$

and in particular: $q(n^*) \approx 1/2$



GCMD simulation of nucleation: Results



The thermodynamic surface of tension

The *surface tension* γ corresponds to a *surface of tension* A_γ with

$$\gamma = \left(\partial F_A / \partial A\right)_T .$$

Equilibrium condition for critical droplets yields $2\,dV = R_\mathrm{L}\,dA_\gamma$ and hence

$$dA_\gamma = \frac{2dn}{\rho R_\mathrm{L}} \approx \frac{8\pi R_\mathrm{e}^2}{R_\mathrm{e} - \delta} dR_\mathrm{e} .$$

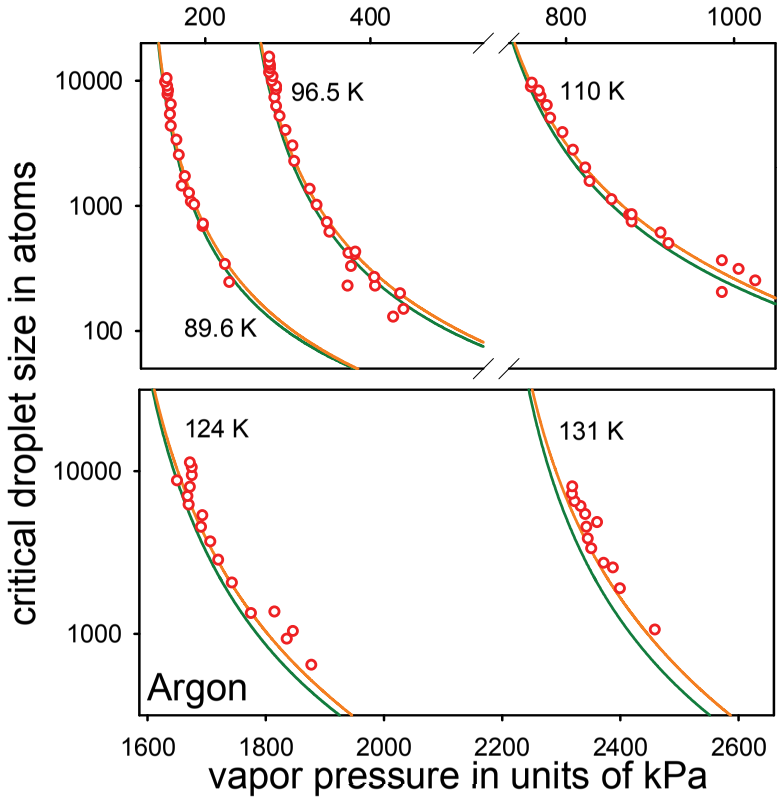
δ is positive ⟶ dA_γ is larger than according to capillarity approximation.

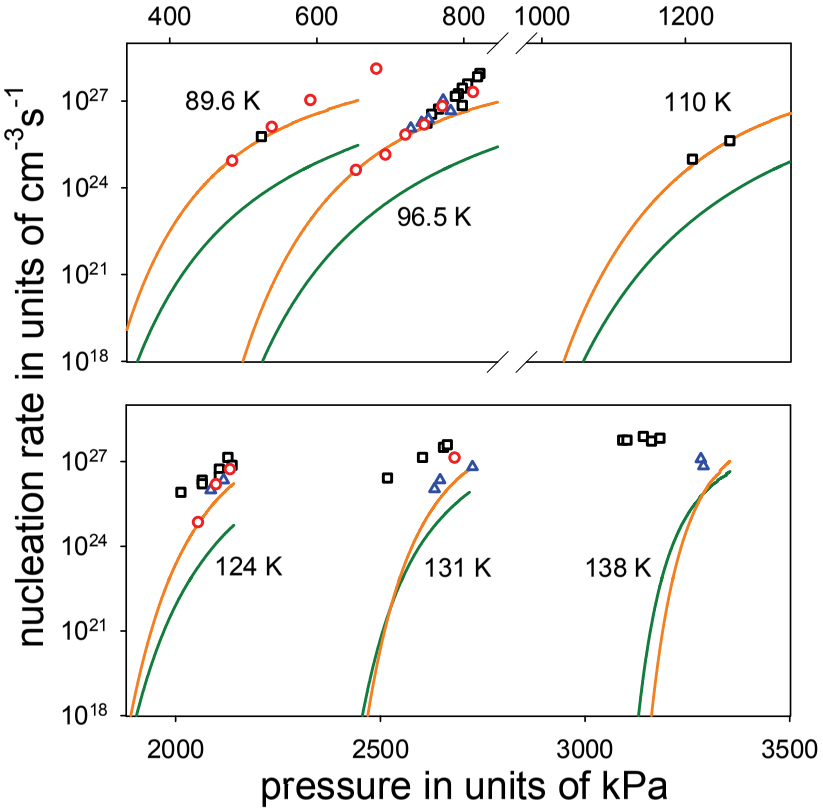
Postulated surface area deviates from the incompressible spherical case by

$$A - A_\mathrm{cap} = \frac{0.85\left(1 - T/T_\mathrm{c}\right)^{-1} - 1}{\left(n/75\right)^{1/3} + 1} A_\mathrm{cap} .$$

Surface property corrected nucleation theory

Hypothesis: 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 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 argon/LJ. However, it does not take into account curvature effects on the surface tension.
- Explanation: an **increased surface area** compensates the reduction of the surface tension due to curvature effects.