Thermodynamics 2009

Steady state molecular dynamics simulation of vapour to liquid nucleation

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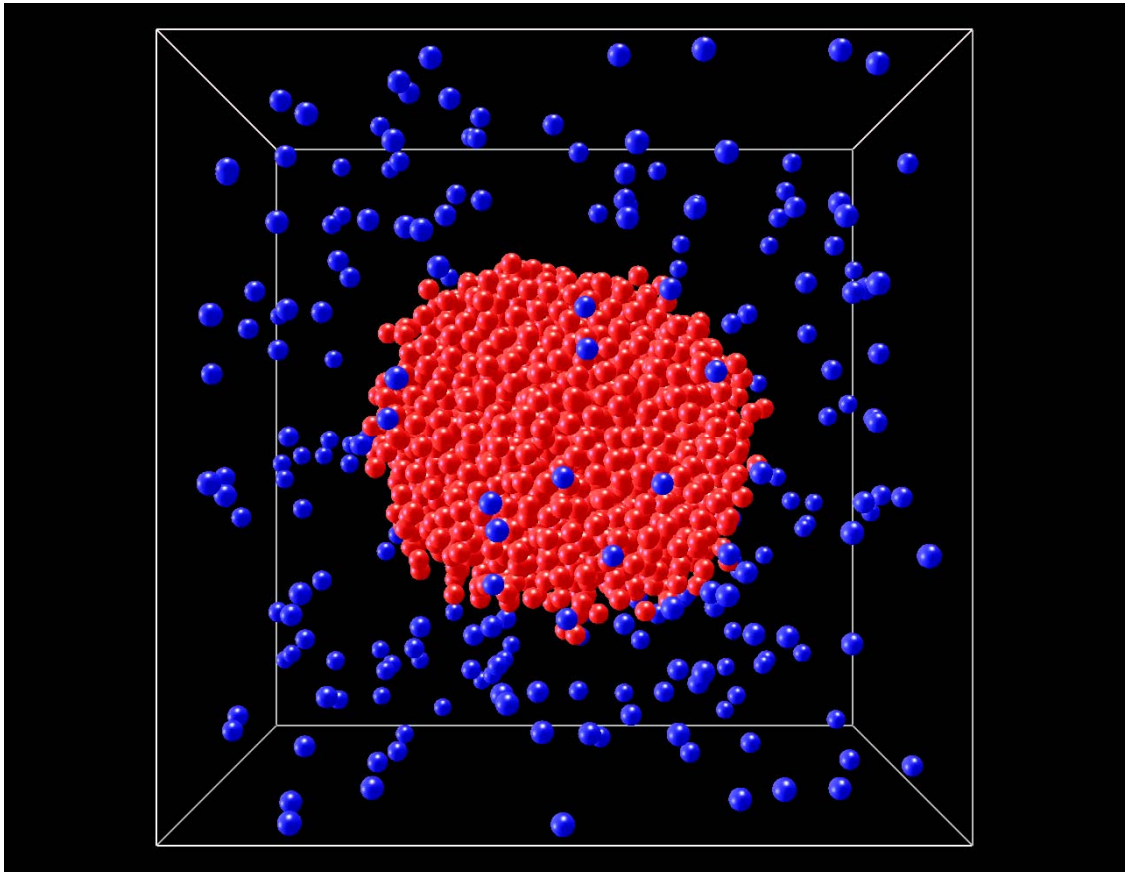
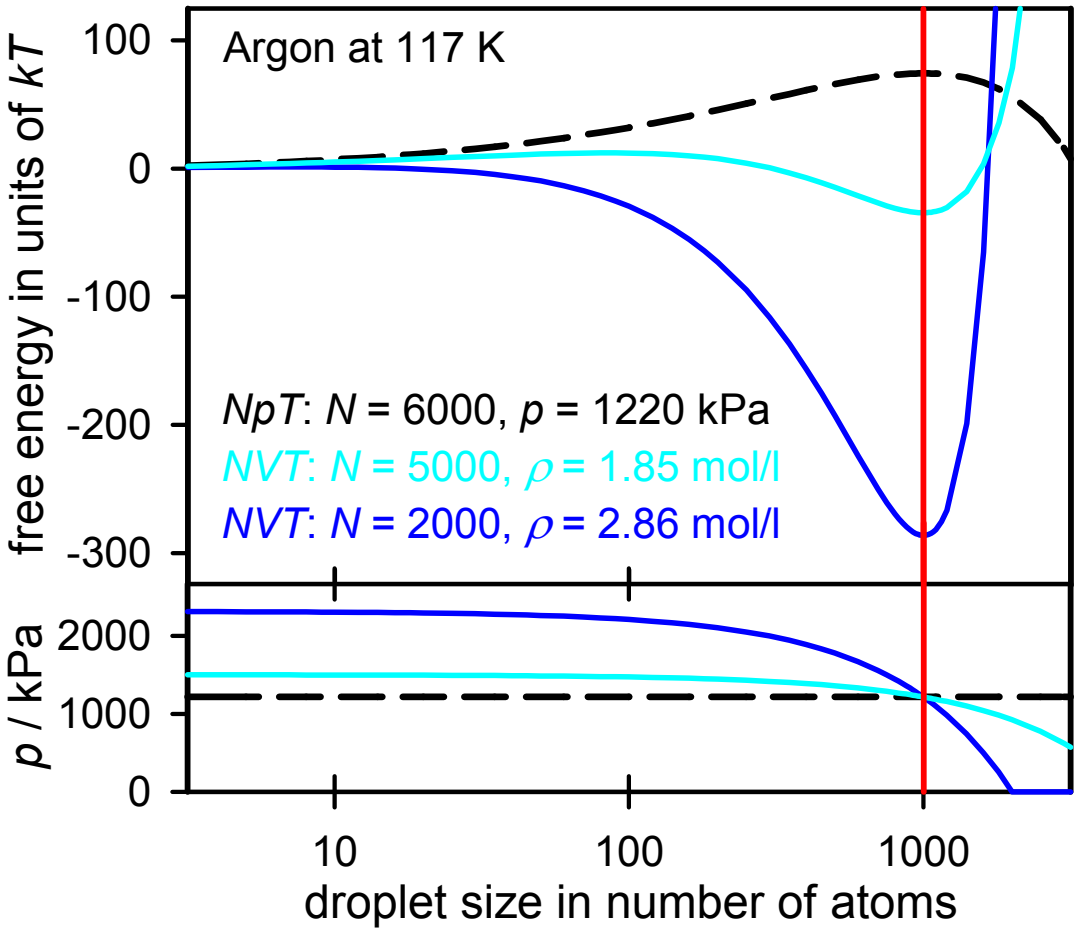
MD simulation of a single droplet

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



truncated-shifted LJ fluid (r_c = 2.5)

Equilibrium vapour pressure



Equilibrium condition for a droplet containing N_ℓ atoms:

$$p = p(T, N_\ell)$$

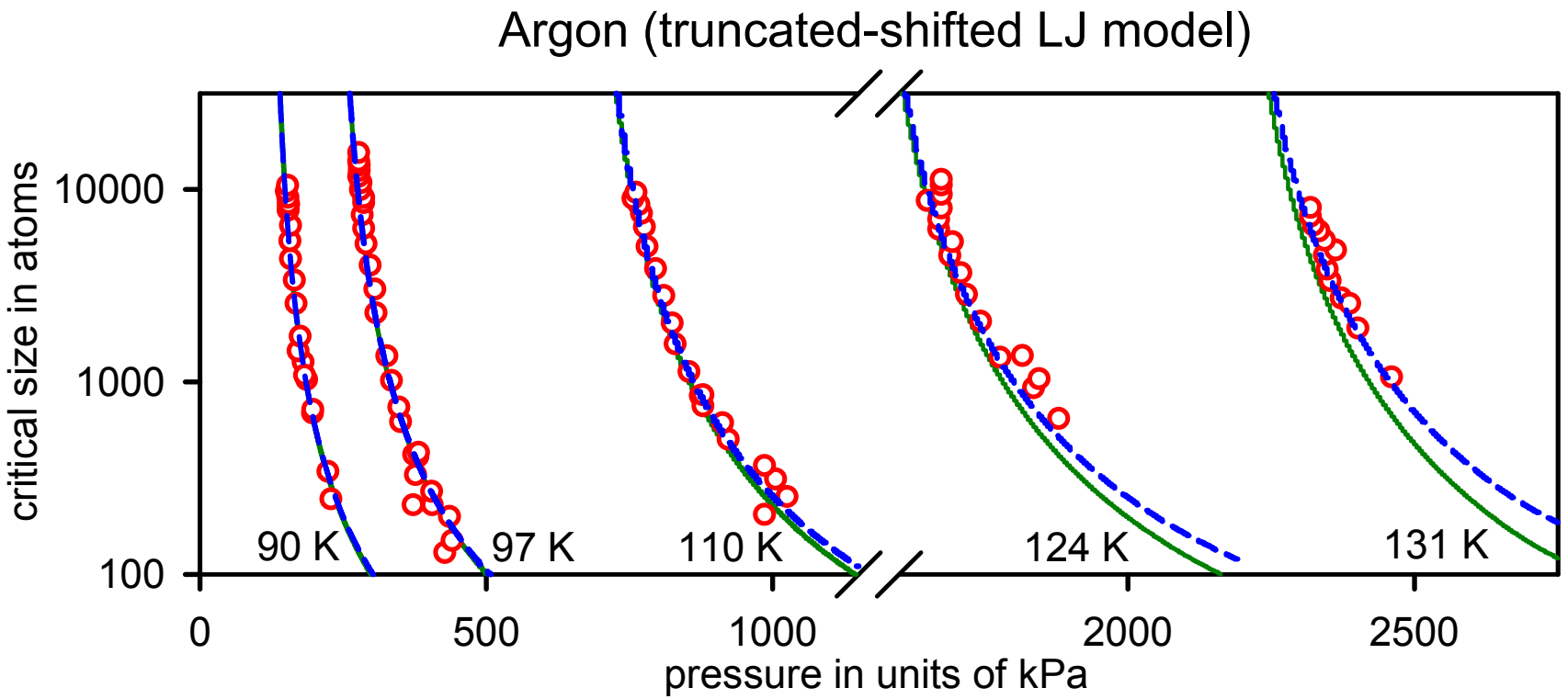
ΔG at constant p and T:

1 unstable equilibrium

ΔF at constant V and T:

1 unstable equilibrium
1 stable equilibrium

Single droplet in equilibrium



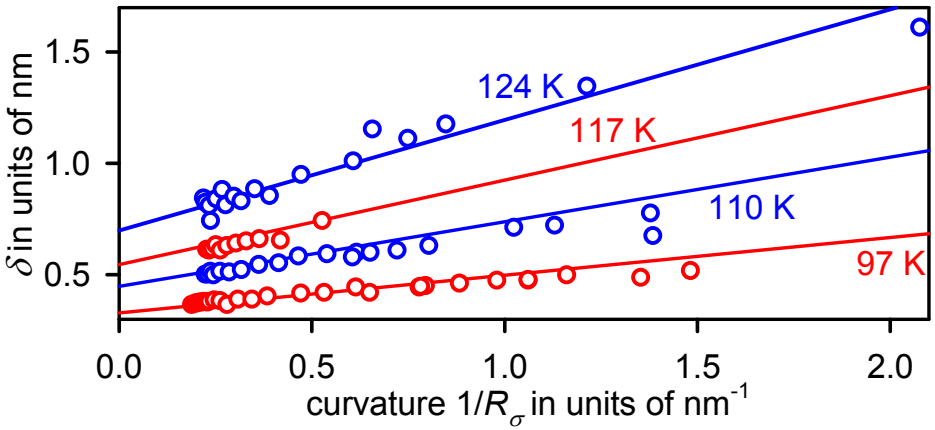
"standard" classical theory

$$N^* = \left(\frac{2\sigma a}{3\Delta\mu}\right)^3$$

classical theory with "pressure effect"

$$N^* = \left(\frac{2\sigma a}{3[\Delta\mu - v'(p - p_s)]}\right)^3$$

Droplet surface tension



For small droplets, the TOLMAN length

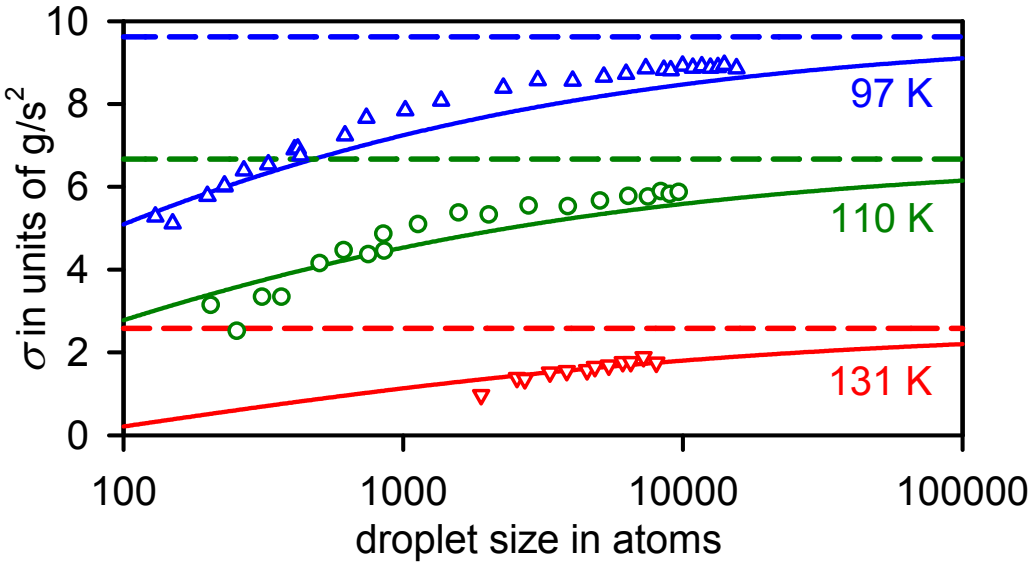
$$\delta = R_e - R_\sigma$$

is significantly elevated.

TOLMAN equation:

$$\frac{\sigma_\infty}{\sigma} \approx \frac{R_e + \delta_\infty}{R_e - \delta_\infty}$$

- simulation
- — TOLMAN equation
- - - planar interface



Grand canonical MD

Algorithm: MC insertion/deletion steps alternating with MD steps

- 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

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

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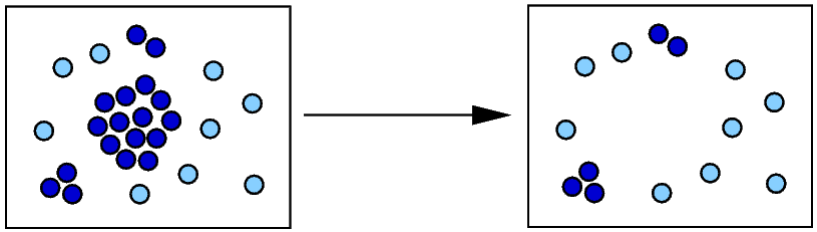

Thermodynamic conditions of supersaturated state are maintained

Grand canonical MD with McDONALD's dæmon

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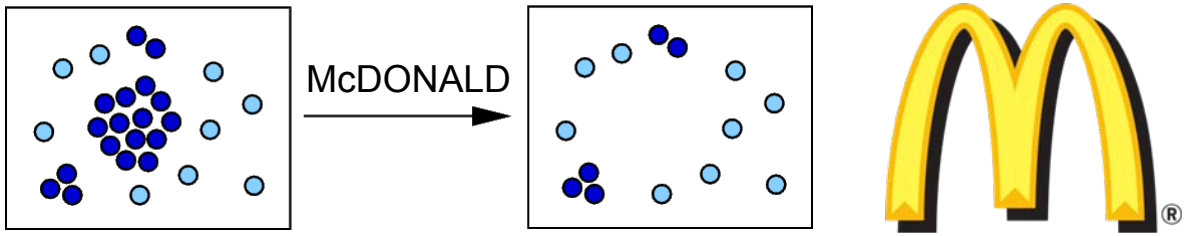
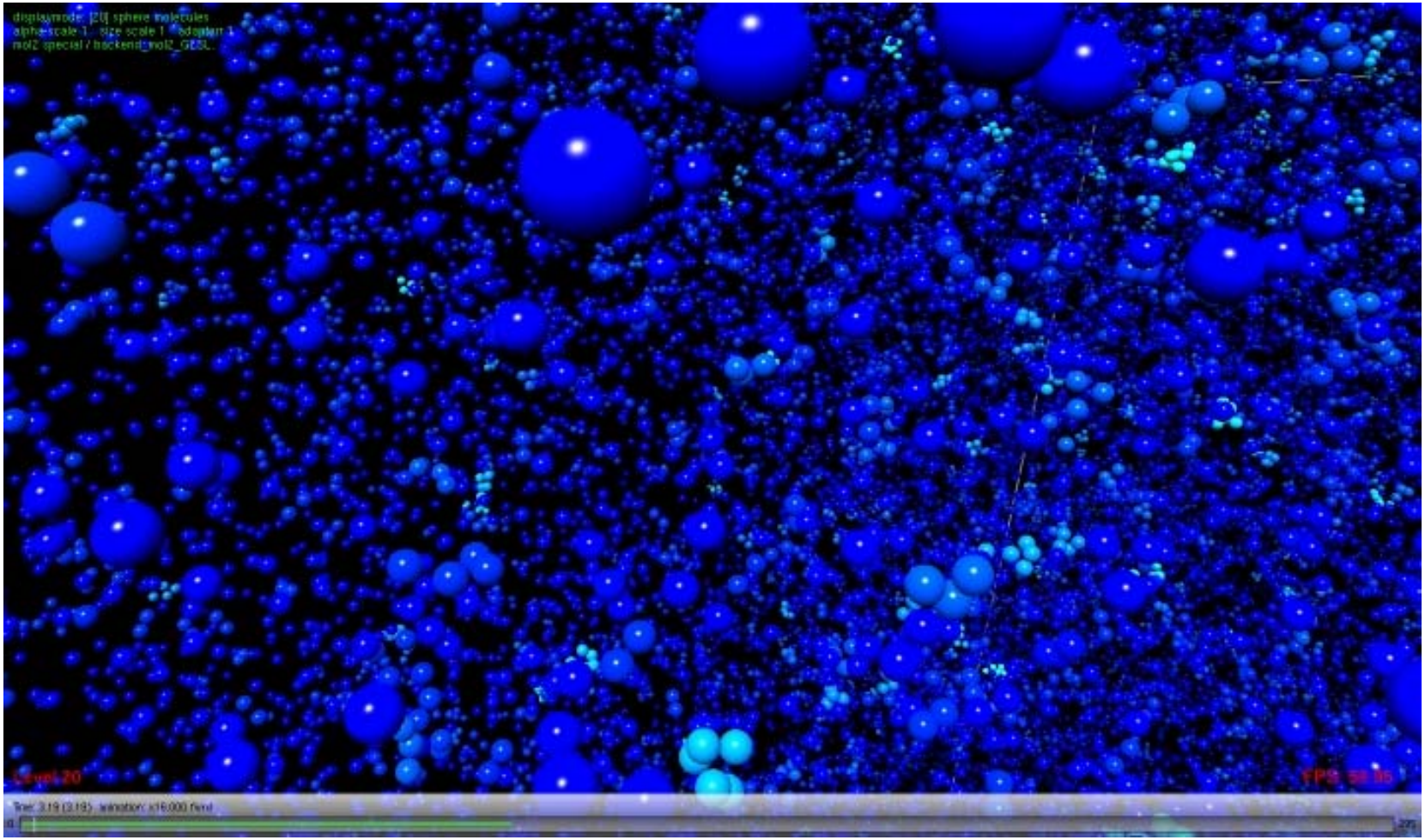


→ Thermodynamic conditions of supersaturated state are maintained

Interactive presentation: McDONALD's dæmon



Intervention rate J_θ and nucleation rate J

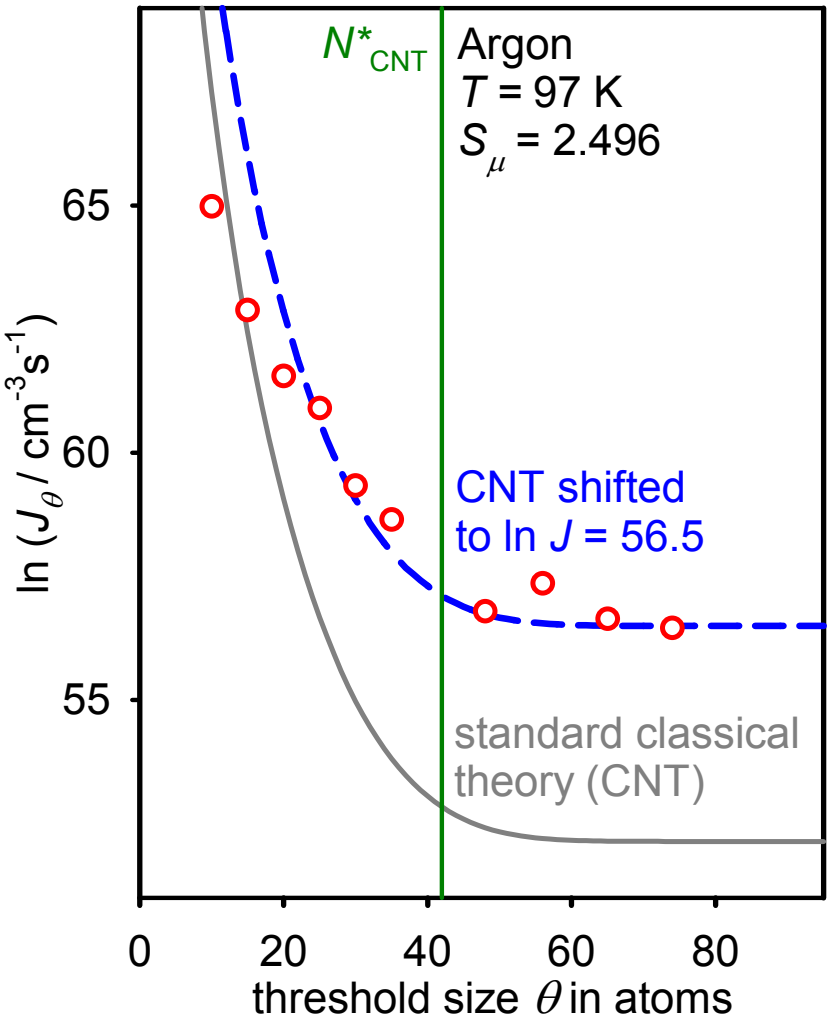
Not all of the removed droplets would eventually reach macroscopic size.

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

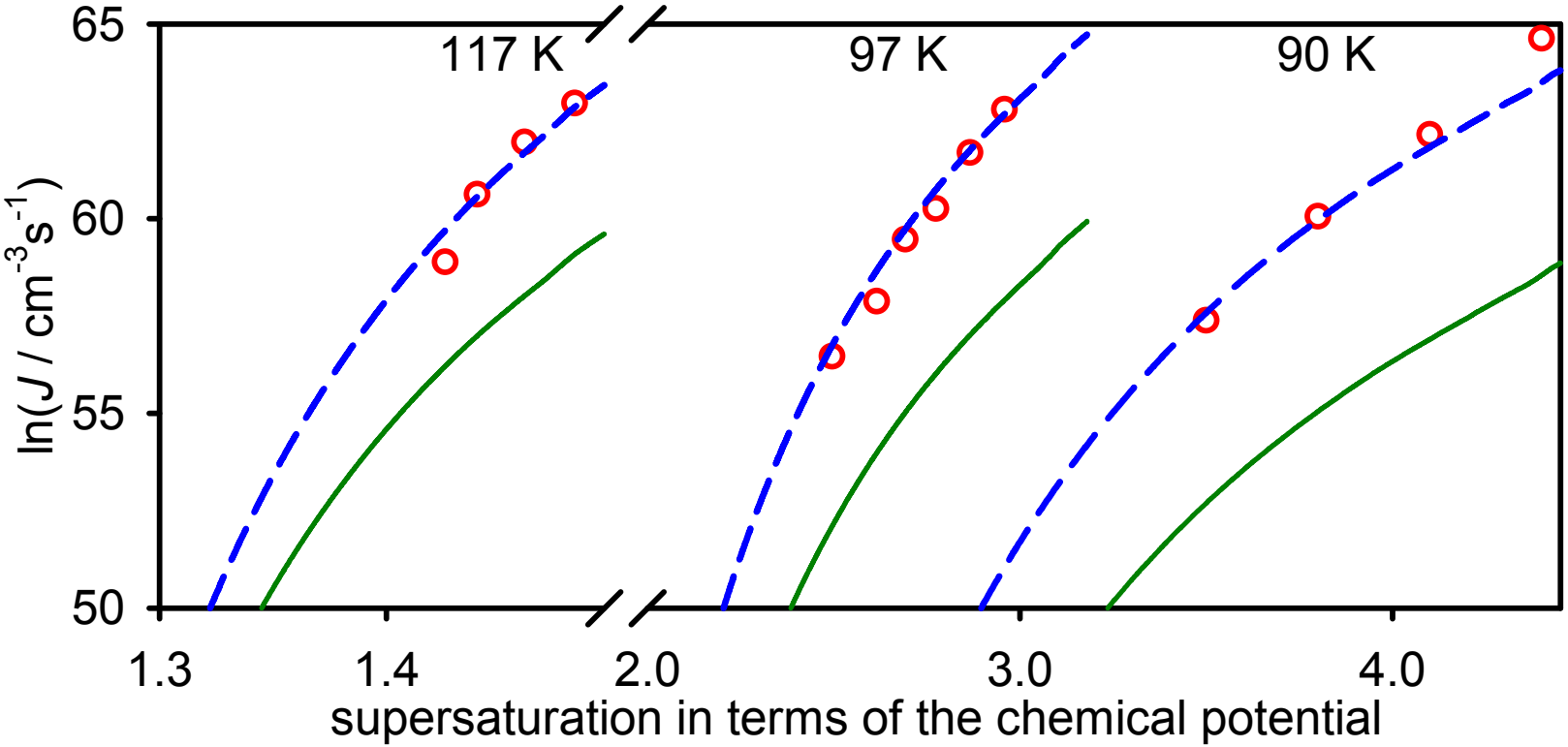
Probability for a droplet of growing from size θ to infinity:

$$q(\theta) = \frac{\int_1^\theta \exp(2\beta F)\, dN_\ell}{\int_1^\infty \exp(2\beta F)\, dN_\ell},$$

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



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** are stable in the **canonical** ensemble and yield the critical droplet size
- A **supersaturated vapour** near the spinodal line can be stabilized by grand canonical MD simulation with **MCDONALD'S dæmon**
- MCDONALD's dæmon allows to simulate the **instationary nucleation** process in the **steady state**
- The **classical theory** leads to excellent results for argon