Molecular dynamics based analysis of nucleation and surface energy of droplets in supersaturated vapors

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Session 2 – 4: Drops and bubbles in fluidics

Outline

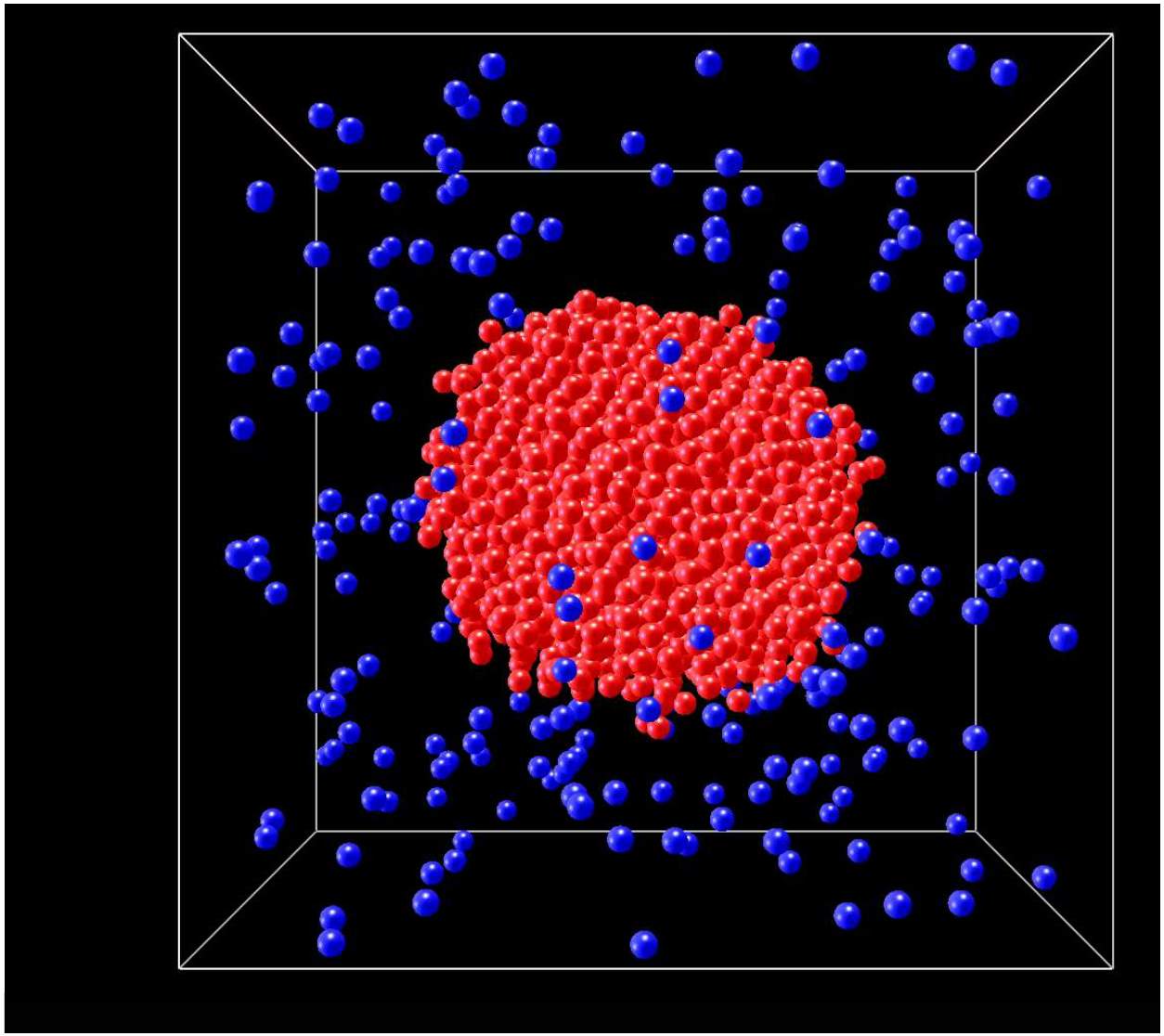
- Simulation of nano-scale droplets in equilibrium with a vapor
  - Surface tension of small droplets
  - Critical nucleus size during condensation
  - Considered fluid: methane

- Direct simulation of nucleation in a supersaturated vapor
  - Nucleation rates along isotherms
  - Considered fluids: methane, ethane and carbon dioxide

MD simulation of single droplets

Nano-scale droplets in equilibrium with a vapor

- Separate equilibration of vapor and liquid
- Insertion of a small droplet, i.e. $100 < N < 10000$, into vapor
- Vapor phase not much larger than the droplet
- Droplet cannot evaporate completely due to increasing supersaturation
- Equilibrium within nanoseconds



Single droplets in equilibrium – normal pressure

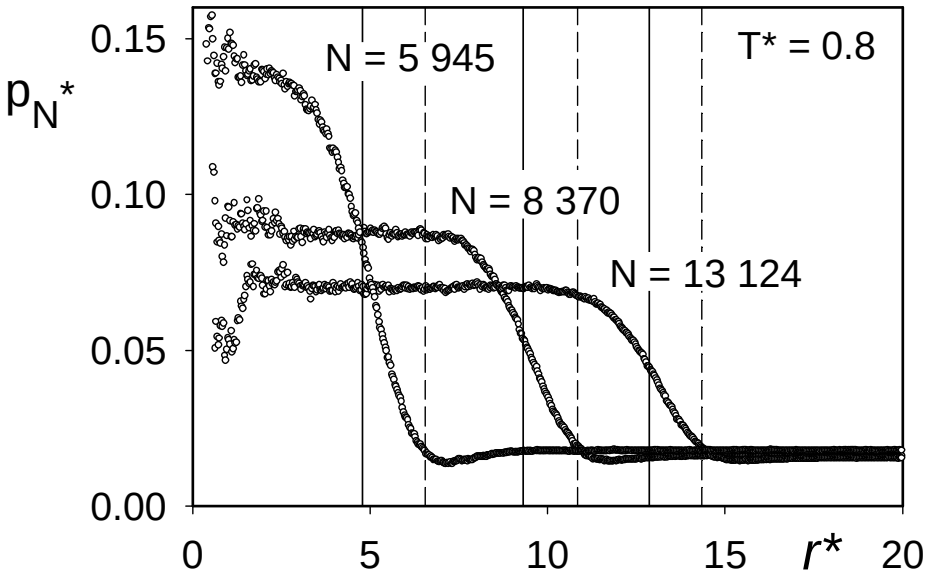
Pressure element perpendicular to the interface

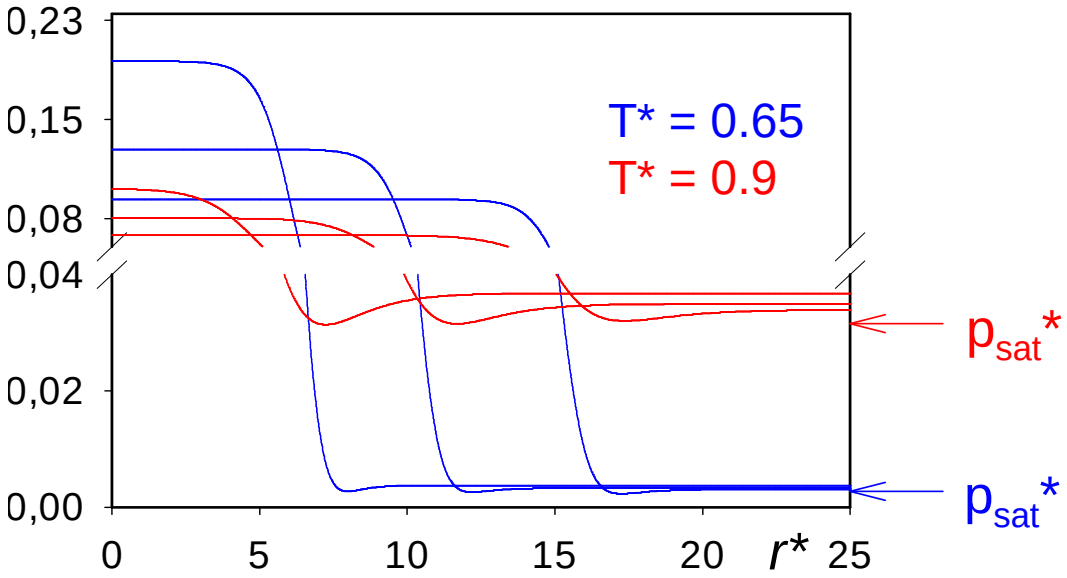
- - - Gibbs absorption radius

—— Laplace radius

$$p_N^*(r^*) = \frac{1}{2}\cdot(p_l^* + p_v^*) - \frac{1}{2}\cdot(p_l^* + p_0^*)\tanh\left(\frac{2}{D_l^*}(r^* - r_l^*)\right)$$

$$+\frac{1}{2}\cdot(p_v^* - p_0^*)\tanh\left(\frac{2}{D_v^*}(r^* - r_v^*)\right)$$





Lennard-Jones fluid, truncated and shifted at $r_c = 2.5\sigma$, in reduced units

Surface tension from the normal pressure profile

Integration of the $p_N(r)$ profile:

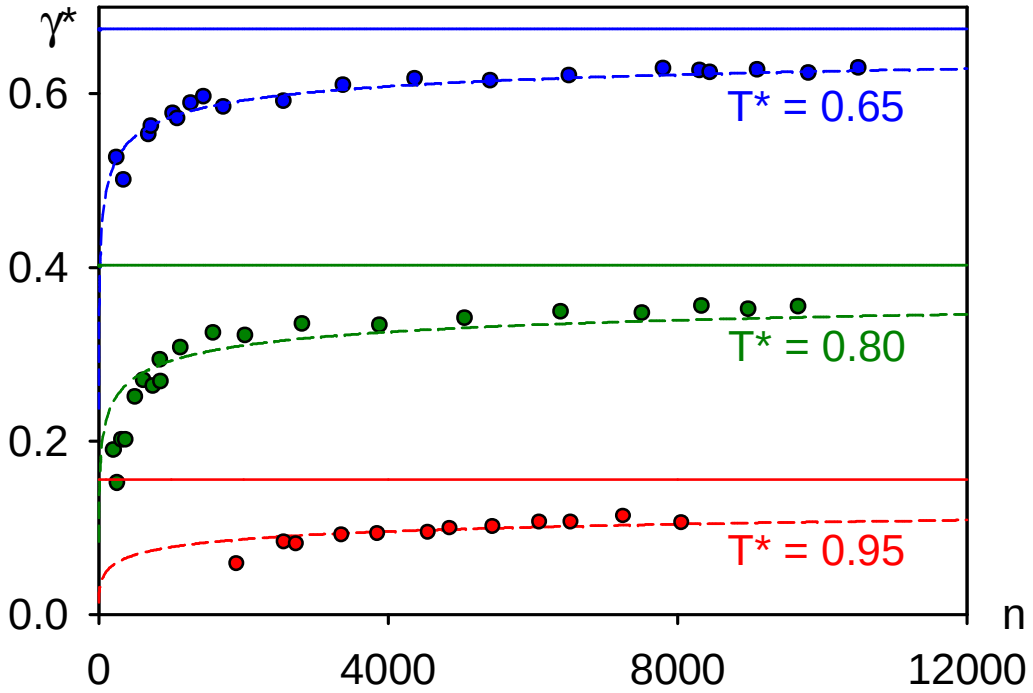
$$(\gamma_n^*)^3 = \frac{-(p_l^* - p_v^*)^2}{8} \int_0^\infty r^{*3} \frac{dp_N^*(r^*)}{dr^*} dr^*$$

Size dependence (Tolman, 1949):

$$\gamma_n^* = \frac{\gamma_\infty^*}{1 + c(T) n^{-1/3}}$$

New correlation from simulation data for $T^* = 0.65, 0.70, \ldots 0.95$:

$$c(T) = \frac{1.531}{T_c^* - T^*} - 1.715$$

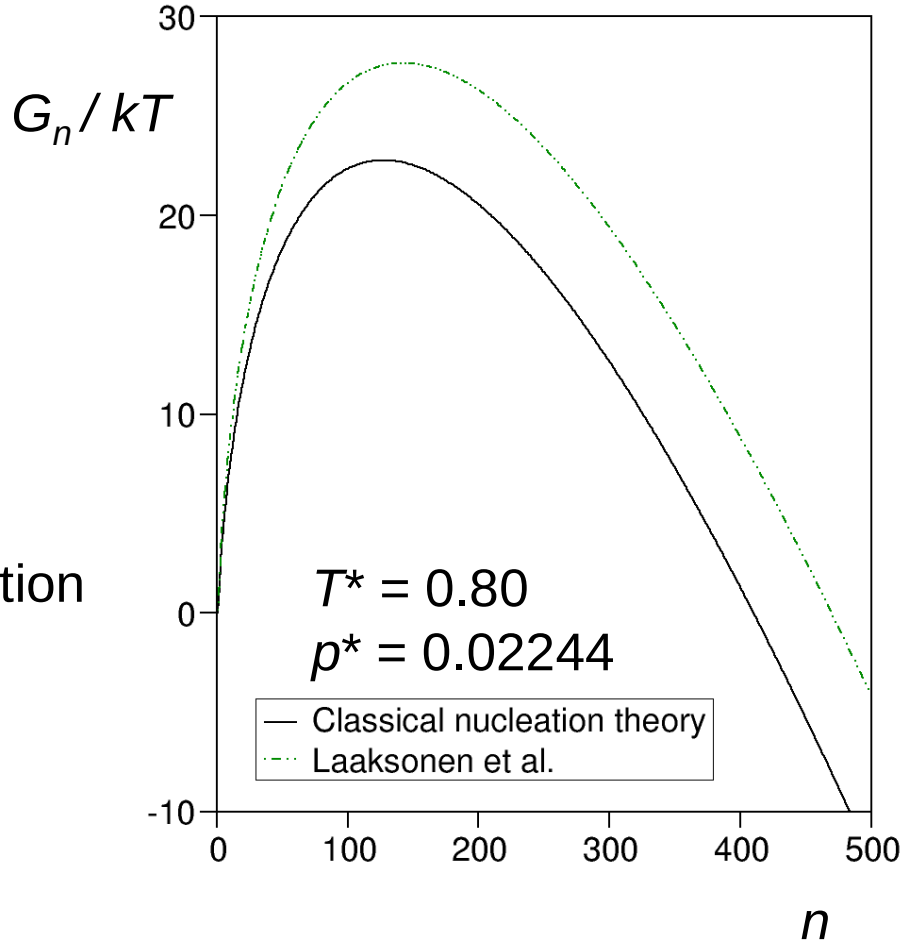


- simulation
- planar interface
- - - new correlation

Gibbs energy of droplet formation

Gibbs energy of droplet formation in a supersaturated ($\mu > \mu_\sigma$) vapor:

$$G_n = n(\mu_\sigma - \mu) + \zeta_n$$



G_n is maximal at the critical size n^*

For critical nuclei: condensation = evaporation

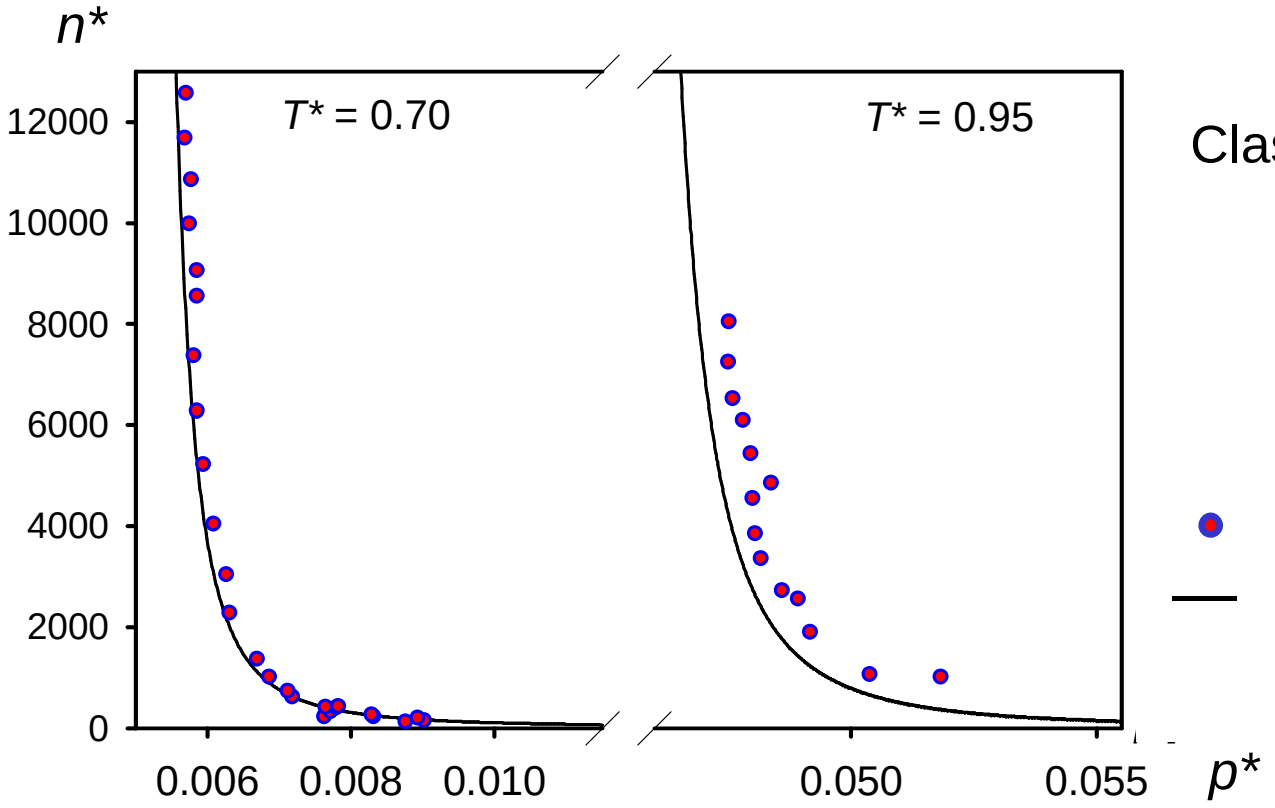
Positive surface energy ζ_n

Classical nucleation theory: $\zeta_n = A_n \gamma_\infty$

Laaksonen et al. (1994): $\zeta_n = A_n \gamma_\infty (1 + \alpha_1 n^{-1/3} + \alpha_2 n^{-2/3})$

Critical nucleus size

Droplets in equilibrium with a vapor are critical nuclei!



Classical nucleation theory:

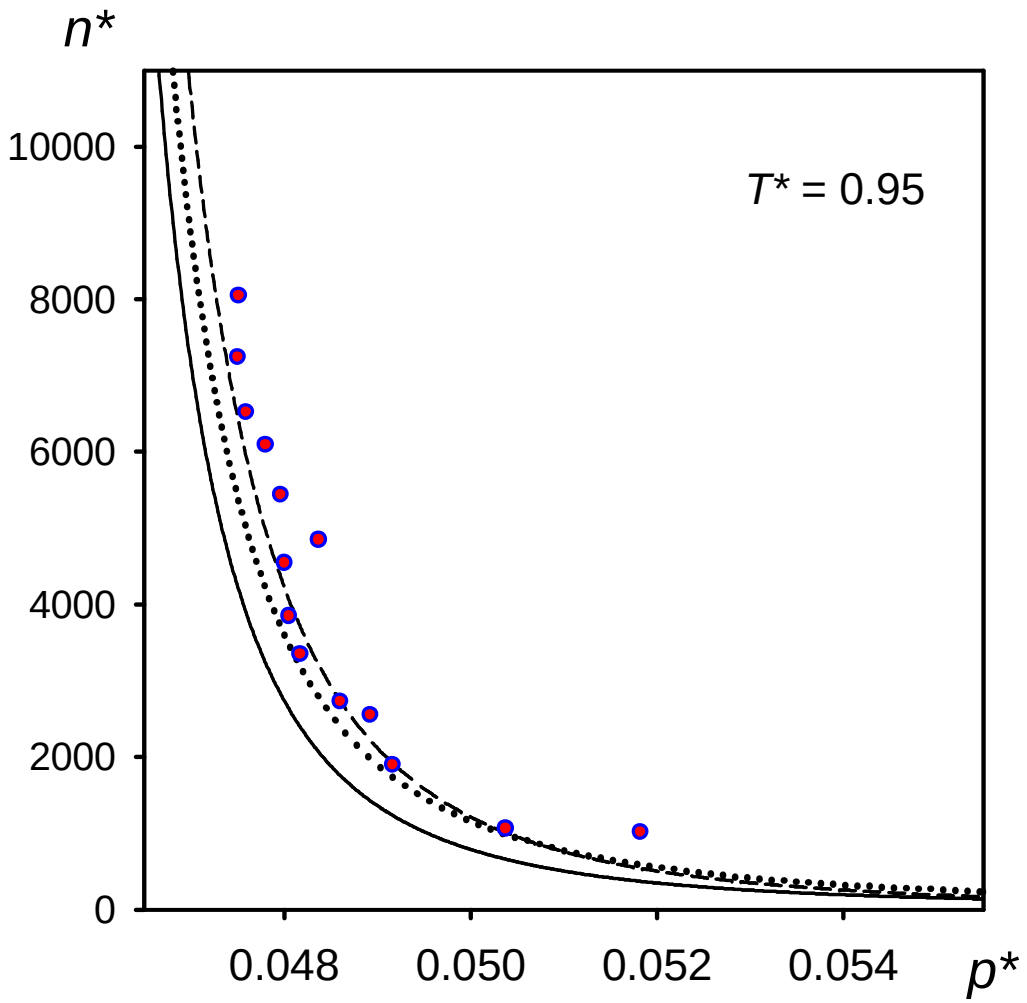
$$n^* = \left(\frac{2\zeta_1}{3(\mu - \mu_\sigma)} \right)^3$$

present simulation data

classical nucleation theory

- Good predictions of the critical size for low temperatures
- For low supersaturations, significant deviations are present

Critical nucleus size, new correlation



New correlation, using surface tension data from simulations with

$$\zeta_n = \int_0^n \gamma_n \frac{dA_n}{dn} dn$$

and an effective surface with

$$\frac{A_n}{A_O} = \frac{0.7892(T_c^* - T^*)^{-1} + \sqrt[3]{0.005n}}{1 + \sqrt[3]{0.005n}}$$

- present simulation data
- classical nucleation theory
- ..... Laaksonen et al.
- - - new correlation

Molecular dynamics simulation of nucleation

- Molecular dynamics solves Newton's equations of motion, where the resolution is typically 2 – 5 fs per time step
- A simulation of 1 ns requires $2 – 5 \cdot 10^5$ time steps
- A saturated vapor with a volume of $(0.1\ \mu m)^3$ contains:
  81 000 molecules (methane at 114 K = 0.6 $T_{c,\ CH4}$)
  703 700 molecules (carbon dioxide at 253 K = 0.83 $T_{c,\ CO2}$)
- To obtain meaningful statistics, at least ~10 nuclei have to be detected

#nuclei	/	(volume V	x	time Δt)	=	nucleation rate J
10	/	(10^{-21} m^3	x	10^{-9} s)	=	10^{31} / m^{3}s

Molecular simulation
above 10^{31} / m^{3}s

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

Nucleation rate from nucleus formation statistics

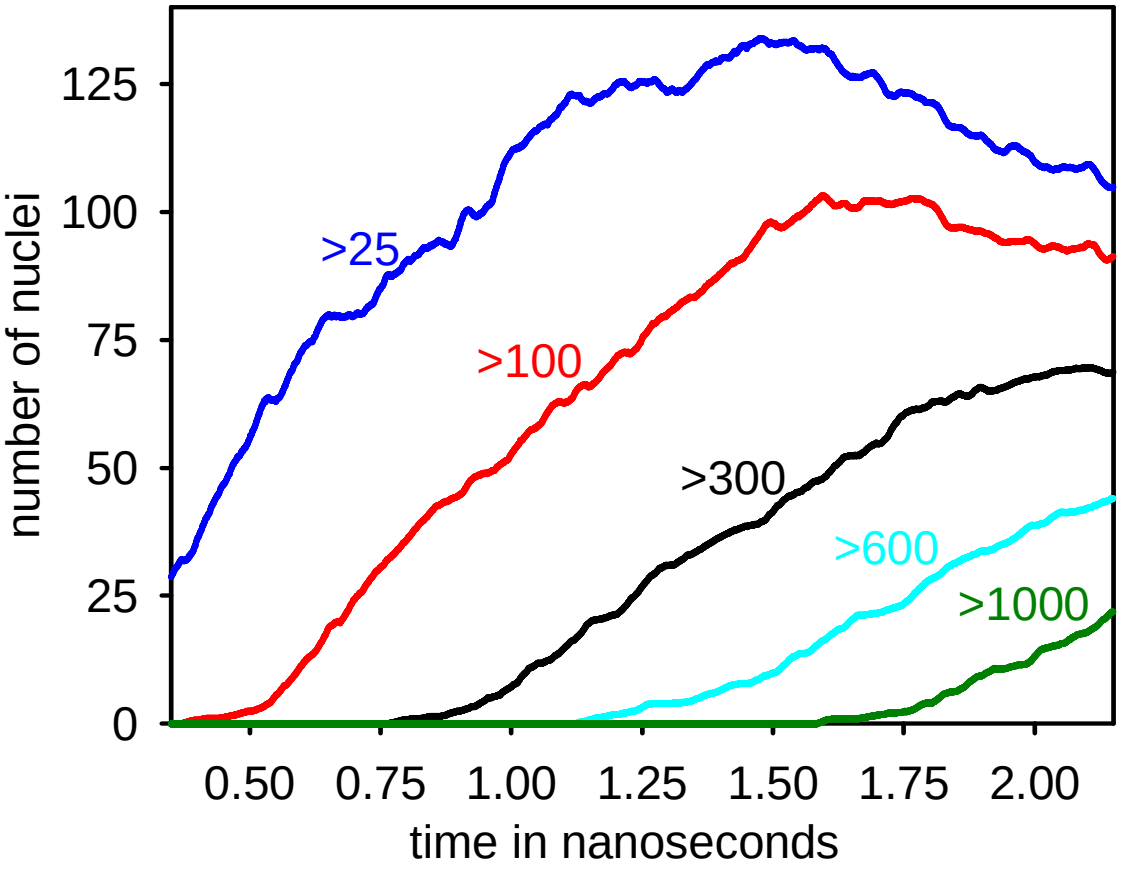
Nucleation rate $J_{\geq n}$ (Yasuoka and Matsumoto, 1998):

number of nuclei with ≥*n* molecules formed per $V\Delta t$, after an initial delay

Approach:

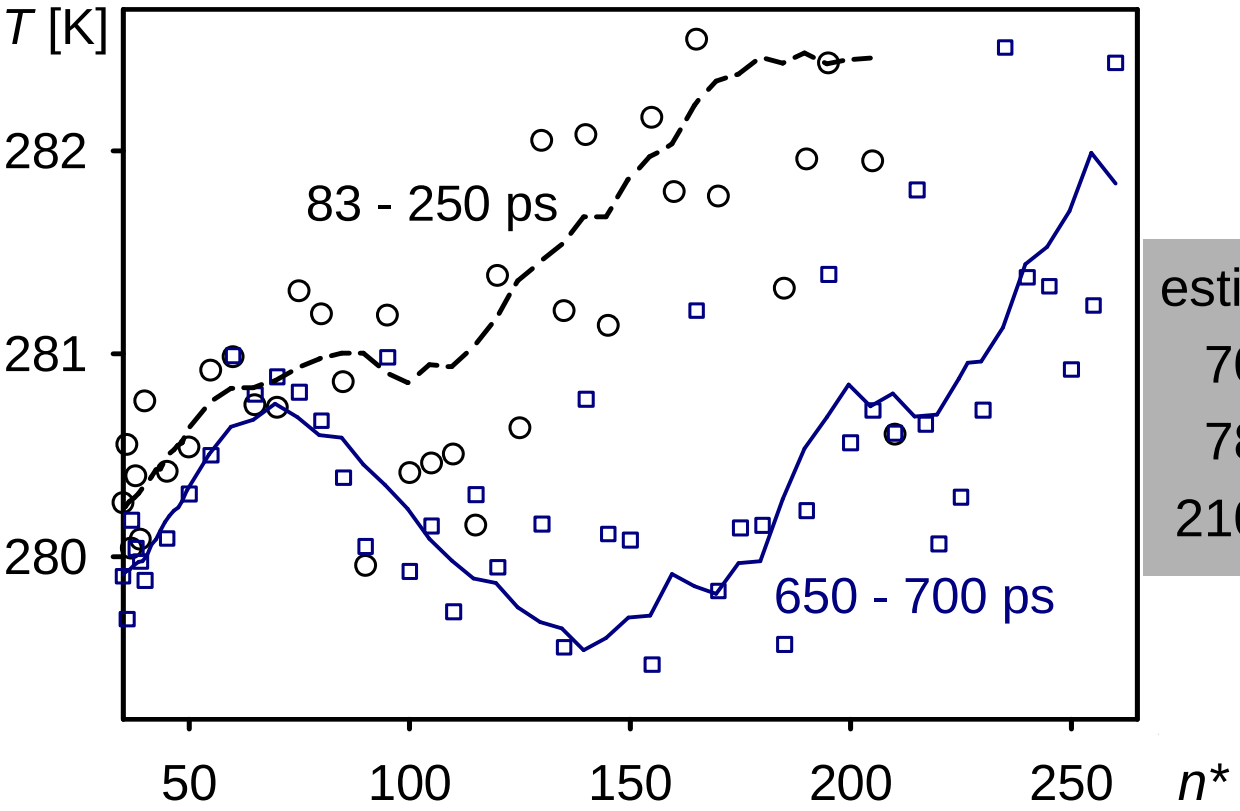
Evaluate $J_{\geq n}$ for different *n*

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



Thermal non-accommodation due to size fluctuations

nucleation in a vapor of 670 000 ethane molecules at 280 K and 2.80 mol/l



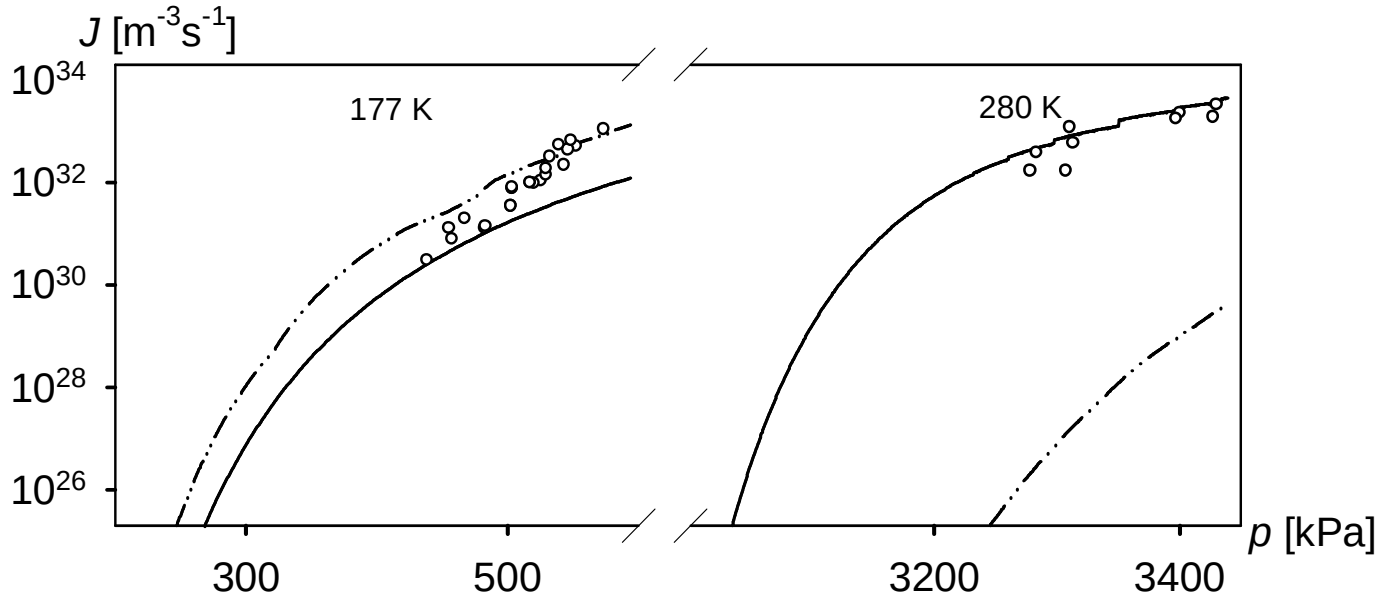
estimates for the critical size:
- 70 (from temperature profile)
- 78 (classical theory)
- 210 (Laaksonen et al.)

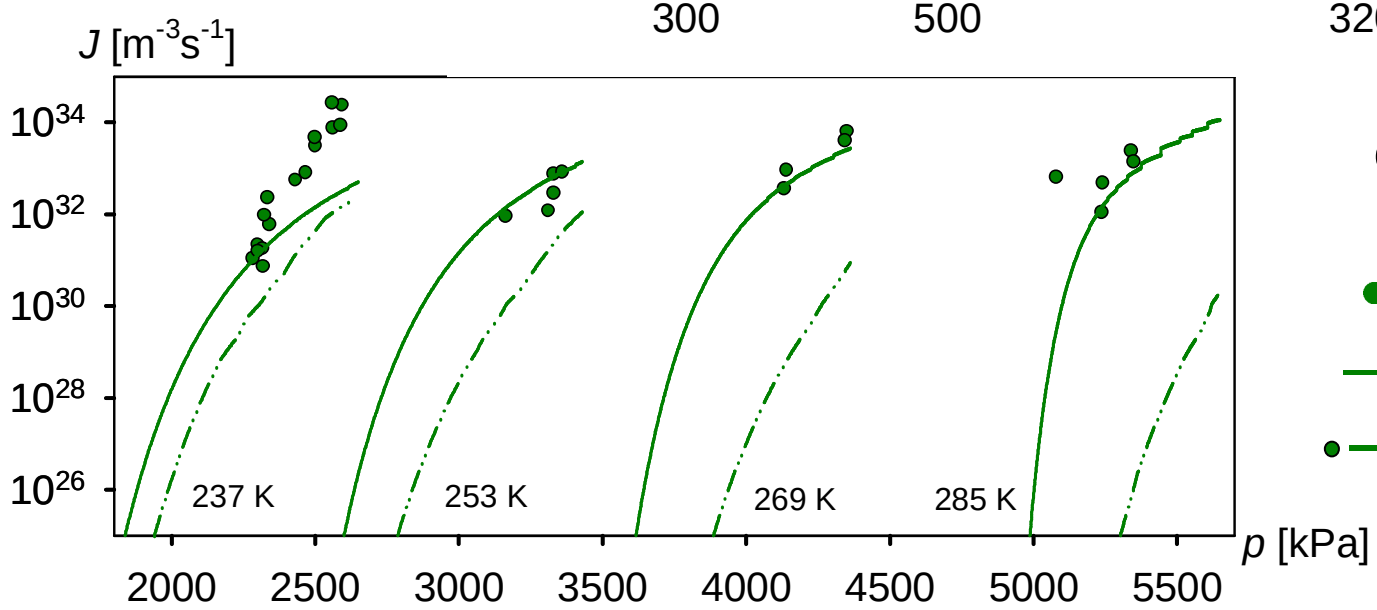
classical expression $(\Delta T)_{n=n^*} = \frac{2kT^2Z}{\Delta h}$ yields 0.72 K in the present case

Nucleation rates for ethane and carbon dioxide

ethane

- simulation
- classical theory
- Laaksonen et al.

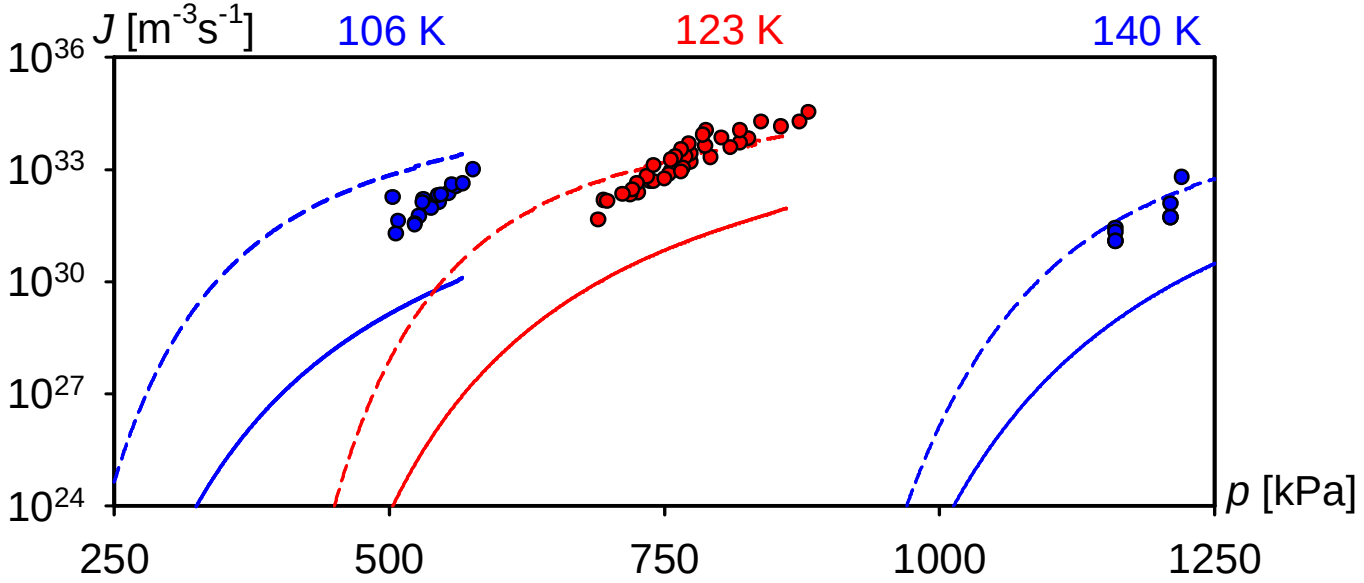


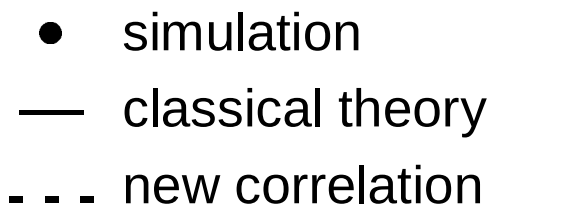


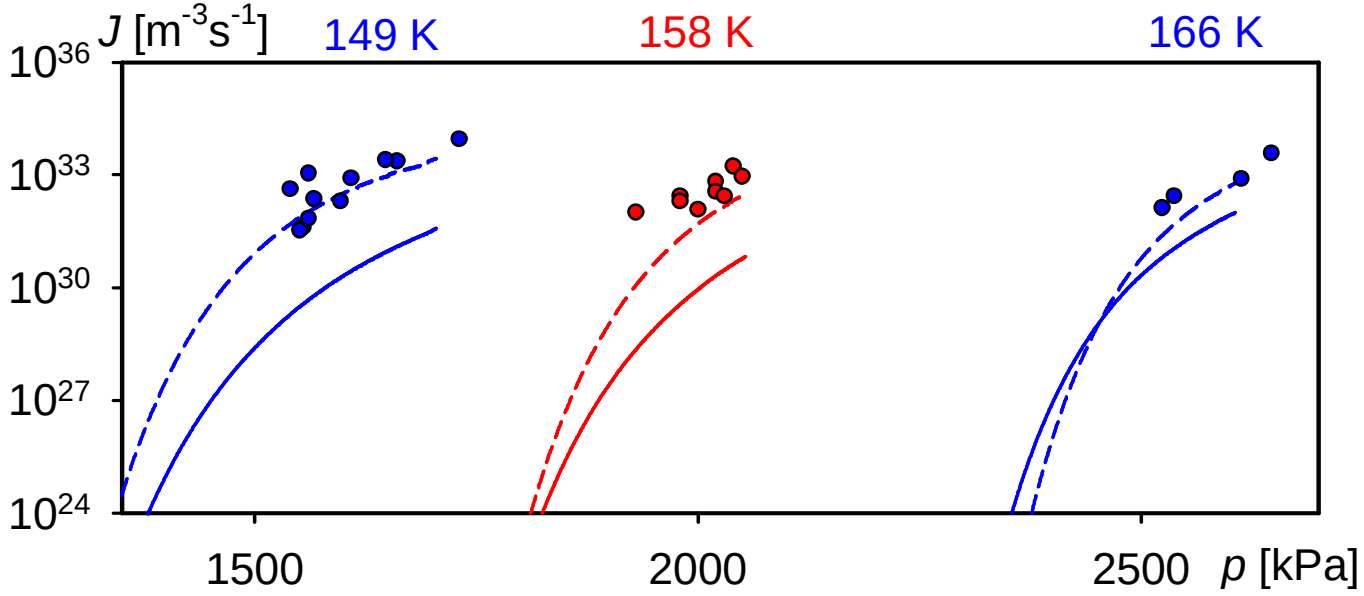
carbon dioxide

- simulation
- classical theory
- Laaksonen et al.

Nucleation rates for methane







Summary

- Dependence of surface tension on droplet size was determined
- Large molecule ensembles are needed for more realistic nucleation regimes
- Simulation results compare reasonably well to the classical nucleation theory
- A new unified correlation was proposed:
  surface tension, critical nucleus size and nucleation rate