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

\[ p_N^*(r^*) = \frac{1}{2} \left( (p_i^* + p_v^*) - \frac{1}{2} \cdot (p_i^* + p_0^*) \tanh \left( \frac{2}{D_i^*} (r^* - r_i^*) \right) \right) + \frac{1}{2} \cdot (p_v^* - p_0^*) \tanh \left( \frac{2}{D_v^*} (r^* - r_v^*) \right) \]

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:

$$\left(\gamma_n^*\right)^3 = -\frac{(p_1^* - p_v^*)^2}{8} \int_0^\infty r^3 \frac{dp_N^*(r^*)}{dr^*} dr^*$$

Size dependence (Tolman, 1949):

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

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

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

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:

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

- 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

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

and an effective surface with

\[ \frac{A_n}{A_0} = \frac{0.7892(T_c^* - T^*)^{-1} + \sqrt[3]{0.005n}}{1 + \sqrt[3]{0.005n}} \]

- 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 · 10⁵ time steps.

- A saturated vapor with a volume of (0.1 μm)³ contains:
  - 81 000 molecules (methane at 114 K = 0.6 \( T_c,\text{CH}_4 \))
  - 703 700 molecules (carbon dioxide at 253 K = 0.83 \( T_c,\text{CO}_2 \))

- To obtain meaningful statistics, at least ~10 nuclei have to be detected.

\[
\text{#nuclei} / (\text{volume} \ V \times \text{time} \ \Delta t) = \text{nucleation rate} \ J
\]

\[
10 \ / \ (10^{-21} \ m^3 \times 10^{-9} \ s) = 10^{31} / \ m^3s
\]

Molecular simulation above \( 10^{31} / \ m^3s \) Experiment up to \( 10^{23} / \ m^3s \)
Nucleation rate from nucleus formation statistics

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

number of nuclei with $\geq n$ 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

classical expression

\[
(\Delta T)_{n=n^*} = \frac{2kT^2Z}{\Delta h}
\]

yields 0.72 K in the present case

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

![Graph showing nucleation rates for methane with simulations and correlations.](image-url)
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