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Steady-state simulation of homogeneous vapor to liquid nucleation in the grand canonical ensemble “by the intervention of intelligent beings”

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McDonald’s demon

With adequate molecular dynamics (MD) simulation methods, both the nucleation kinetics and the steady-state properties of near-spinodal supersaturated vapor can be sampled. This is achieved by combining grand canonical MD (GCMD), introduced by Cielinski [1], and an intelligent being that removes all large droplets: McDonald's demon [2].

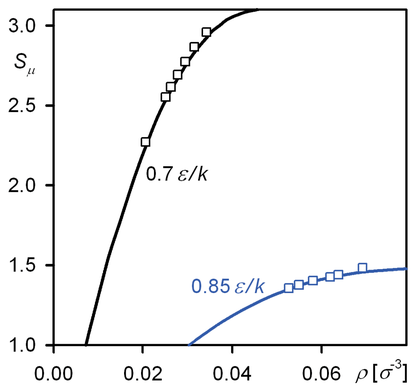


Fig. 1. Chemical potential supersaturation over density for the LJTS fluid, obtained by integration of the Gibbs-Duhem equation, using data from canonical ensemble simulations at T = 0.7 and 0.85 ε/k (solid lines), as well as results of GCMD simulations with McDonald’s demon (squares).

If the intervention threshold size i is large enough, the intervention rate corresponds to the nucleation rate of the supersaturated vapor. For smaller thresholds, however, the intervention rate is significantly elevated (Fig. 2), because smaller nuclei are formed at a higher rate than macroscopic droplets.

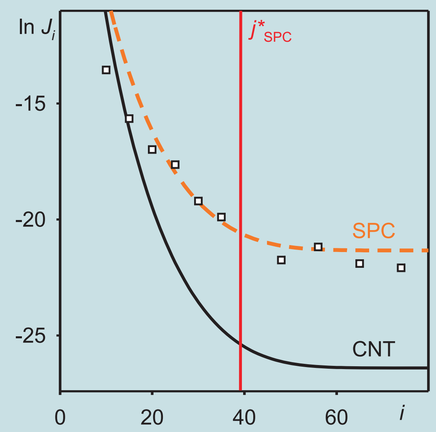


Fig. 2. Intervention rate logarithm in a supersaturated vapor of the LJTS fluid at T = 0.7 ε/k and S_μ = 2.4958 from GCMD simulation with McDonald’s demon (squares) and according to CNT (solid line) as well as the SPC modification (dashed lines). Vertical line: critical size according to the SPC modification of CNT.

The critical nucleus

... can be stabilized by simulating the canonical ensemble.

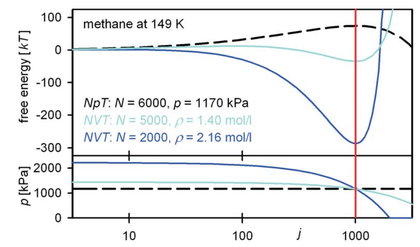


Fig. 3. Top: Gibbs energy of nucleus formation in a supersaturated vapor of methane at constant temperature and pressure (dashed line) and Helmholtz energy of nucleus formation at constant temperature and volume (solid lines), in dependence of the nucleus size. Bottom: supersaturated vapor pressure over nucleus size.

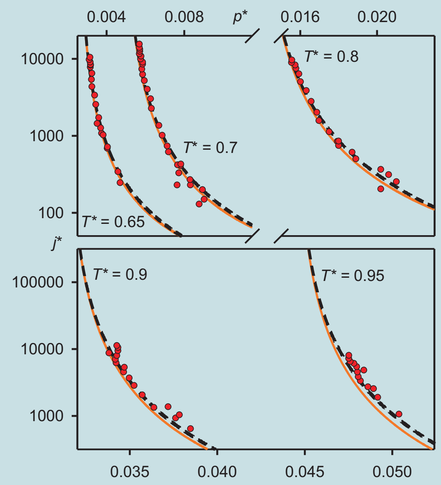


Fig. 4. Critical size in dependence of the supersaturated vapor pressure for the LJTS fluid from equilibrium MD simulation (bullets) and according to CNT (solid lines) as well as the SPC modification (dashed lines).

The classical nucleation theory (CNT) assumes that density and chemical potential are the same for a nucleus and the bulk liquid. The nucleus surface tension γ' is equated with the tension γ of the planar vapor-liquid interface.

From equilibrium MD simulation, however, values of γ' as low as 0.4 γ were found [3]. This leads to a surface property corrected (SPC) modification [4] of CNT, based on the Tolman equation for the surface tension and a term for the surface area that takes interface fluctuations into account.

Steady-state simulation of nucleation

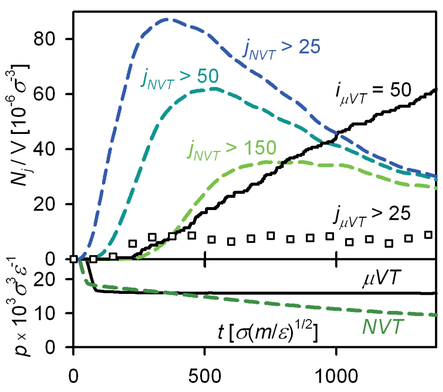


Fig. 5. Top: number density of nuclei containing more than 25, 50, and 150 molecules in a canonical simulation at T = 0.7 ε/k and ρ = 0.004044 σ^{-3} (dashed lines), number density of nuclei with j > 25 in a GCMD simulation with McDonald’s demon at T = 0.7 ε/k, S_μ = 2.8658, and i = 50 (squares), and the number of demon interventions per volume aggregated over simulation time (solid line). Bottom: pressure over time for both MD simulation runs.

For the steady state, the pressure and the demon intervention rate (Fig. 5) as well as the nucleus size distribution (Fig. 6) are constant. In contrast, the supersaturation and the number of nuclei can decrease significantly over simulation time for the canonical ensemble.

With McDonald's demon, the impact of thermalization on nucleation can be studied. Nucleus growth stops when nucleus overheating countervails the supercooling of the vapor at constant pressure (Fig. 7).

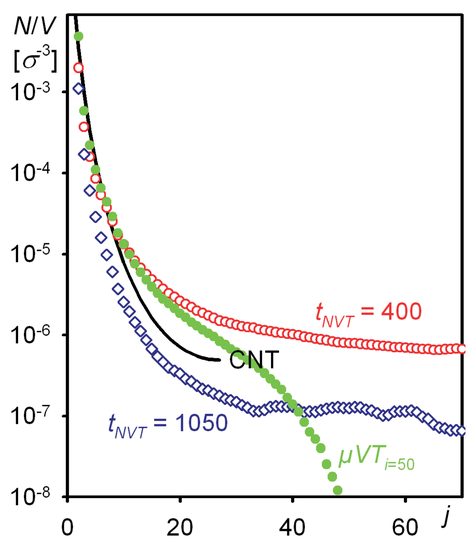
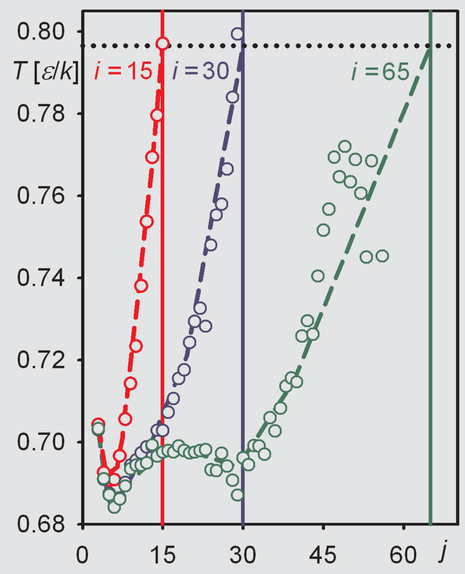


Fig. 6. Number density of nuclei in dependence of nucleus size from MD simulation of the canonical ensemble for sampling intervals of 320 - 480 (circles) and 970 - 1130 (diamonds) time units after simulation onset and for the steady state (bullets) from GCMD simulation with McDonald’s demon (same conditions as Fig. 5). Solid line: prediction based on CNT.

Fig. 7. Circles: nucleus temperature over nucleus size from GCMD simulation with McDonald’s demon for various intervention threshold sizes i (same conditions as Fig. 5); solid lines: threshold size; dotted line: saturation temperature of the vapor; dashed lines: guide to the eye.



Nucleation theory

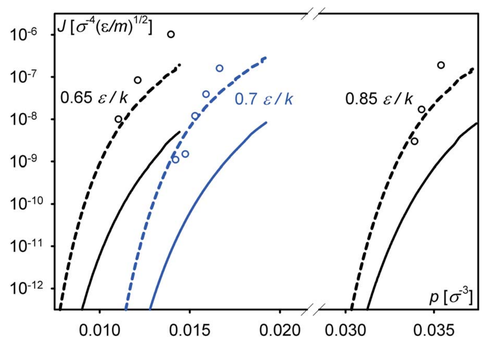


Fig. 8. Nucleation rate over pressure for the LJTS fluid at temperatures of 0.65, 0.7, and 0.85 ε/k according to standard CNT (solid lines) and the SPC modification (dashed lines), in comparison with results from GCMD simulation with McDonald’s daemon (circles).

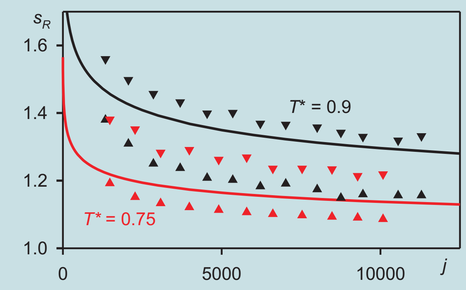
A series of GCMD simulations with McDonald's demon was carried out for the truncated and shifted Lennard-Jones (LJTS) fluid.

Systems with up to 17 million particles were simulated with a massively parallel MD program, obtaining nucleation rates down to the order of 10^{29} $m^{-3}s^{-1}$ by direct brute-force simulation (Fig. 8).

Due to oscillations of the vapor-liquid interface and their growth velocity, the surface area of nuclei is larger than the area of spheres with the same volume.

The SPC modification of CNT proposes a size dependent steric coefficient. As Fig. 9 shows, this increase is similar in magnitude to physical properties that express the interface thickness.

Fig. 9. Steric radius factor in dependence of the nucleus size at temperatures of 0.75 and 0.9 ε/k (solid lines) in comparison with the nucleus radius extended by the thickness of the vapor-liquid interface in terms of the nucleus radius according to the capillarity approximation. Thereby, the vapor-side density based interface length $D_{\rho,v}$ (triangle down) [3] and the Tolman length (triangle up) are used as a measure of the interface thickness.



Results from GCMD simulation with McDonald's demon confirm the SPC modification. For the LJTS fluid, CNT underestimates the nucleation rate by two orders of magnitude (Fig. 8).

References

[1] Martin M. Cielinski, M. Sc. thesis, University of Maine (1985).
[2] James E. McDonald, *American Journal of Physics* **31**: 31 (1962).
[3] Jadran Vrabec, Gaurav K. Kedia, Guido Fuchs, and Hans Hasse, *Molecular Physics* **104**: 1509 (2006).
[4] Martin Horsch, Jadran Vrabec, and Hans Hasse, *Physical Review E* **78**: 011603 (2008).