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].

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.

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 $\gamma$ is equal to the tension of the planar vapor-liquid interface.

From equilibrium MD simulation, however, values of $\gamma$ as low as 0.4 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 homogeneous vapor to liquid nucleation in the grand canonical ensemble “by the intervention of intelligent beings”

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The critical nucleus

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 super-saturation 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).

References