Steady-state simulations of homogeneous vapor to liquid nucleation in the grand canonical ensemble "by the intervention of intelligent beings"

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In supersaturated vapors near the spinodal line, nanoscopic liquid droplets are formed at an extremely high rate, rendering the experimental study of these metastable states difficult. Molecular simulation methods are an attractive option for investigating the processes at such states, as the formation of droplets is well within the accessible time and length scale [1 - 4]. However, a major problem in both cases is the fact that nucleation is an instationary process, where the thermodynamic conditions vary rapidly.

The present work proposes a new method to investigate vapor to liquid nucleation by molecular dynamics (MD) simulation in the steady state, where the supersaturation is specified and maintained. Therefore, grand canonical molecular dynamics (GCMD) is combined with a variant of Maxwell's demon which was introduced by McDonald [5]. This demon removes all droplets exceeding a specified size, so that the nucleation rate and further properties of the nucleating system can be sampled over an arbitrary number of time steps.

A series of GCMD simulations with McDonald's demon was carried out for the truncated and shifted Lennard-Jones fluid. Systems with up to ten million particles were simulated with a massively parallel MD program, obtaining nucleation rates down to the order of $10^{23}/(cm^3\ s)$ by direct brute-force simulation. The results are compared to the widely used method by Yasuoka and Matsumoto [1]. Furthermore, various cluster criteria were compared with the objective of minimizing fluctuations and optimizing the precision with which droplets are detected. The results confirm that the classical nucleation theory underpredicts the nucleation rate for high supersaturations.

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