Steady-State Simulation Of Homogeneous Vapor-Liquid Nucleation "By The Intervention Of Intelligent Beings"

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Abstract. Grand canonical molecular dynamics (GCMD) is applied to vapor to liquid nucleation. With a variant of Maxwell's demon, proposed by McDonald, all droplets exceeding a certain size are removed so that the nucleation rate and further properties of the process can be sampled in a steady-state simulation over a long time. A series of GCMD simulations with McDonald's demon is carried out for the truncated and shifted Lennard-Jones fluid. The results are in agreement with other simulative methods and confirm that the classical nucleation theory underpredicts the nucleation rate for high supersaturations.

Key Words: phase transition; molecular dynamics; Lennard-Jones fluid; Maxwell's demon

INTRODUCTION

Significant shortcomings of the classical nucleation theory (CNT) are known for a long time. Among them is the assumption that in many respects, emerging droplets have the same thermodynamic properties as the saturated bulk liquid. A more accurate theory of homogeneous nucleation, which is sought after, would increase the reliability for applications such as the analysis of heterogeneous and ion-induced nucleation processes in the atmosphere [1].

The basic assumptions of CNT are not valid for nanoscopic droplets. Their properties are hard to investigate experimentally, but are well accessible by molecular simulation. Similarly, the spinodal line can be detected with, e.g., Monte Carlo (MC) simulation methods [2], whereas in experiments, nucleation processes with a low free energy barrier can hardly be discriminated from spontaneous spinodal decomposition. Nanoscopic droplets in equilibrium with a supersaturated vapor can be simulated to obtain droplet properties [3]. Moreover, molecular dynamics (MD) [4] as well as MC [5] simulation of supersaturated systems with a large number of particles are useful for the study of very fast nucleation processes directly. Hence, molecular simulation methods are crucial for the development of nucleation theory.

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Extending previous studies [3, 4], the present work regards the vapor to liquid nucleation on the basis of the truncated and shifted Lennard-Jones (tsLJ) fluid. Nucleation kinetics and steady-state properties of the near-spinodal supersaturated vapor were investigated by combining grand canonical molecular dynamics (GCMD) [6, 7], and an "intelligent being" that continuously removes droplets above a given threshold size: McDonald's demon [8, 9].

SIMULATION METHOD

The condensation process originates from a supersaturated vapor state and is initially manifested by the spontaneous formation of clusters which grow over time by addition of monomers or coalescence with other clusters. Scientifically, the most interesting step of condensation is the droplet formation up to the critical size. In a closed system, this is an instationary process, as the vapor is depleted by the emerging liquid proto-phase.

Equilibrium simulations are useful to investigate single droplets surrounded by supersaturated vapor. However, they are unable to reproduce kinetic and non-equilibrium properties of nucleation processes, such as the overheating of droplets. On the other hand, direct MD simulations of nucleation in the canonical ensemble [10] sample nucleation properties – e.g., the nucleation rate – in an instationary way. The idea behind the present approach is to simulate the production of droplets up to a given size for a specified state at constant supersaturation. Particles are inserted into the system to replenish the vapor phase and droplets above a threshold size are extracted from the system. In this way, nucleation is studied by a quasi-steady-state simulation.

For the present simulations, the Stillinger criterion [11] was used to define the liquid phase, and droplets were determined as biconnected components [4]. Alternating with canonical ensemble MD steps, monomers were inserted into and deleted from the system probabilistically, with the usual grand canonical acceptance criterion. The acceptance probability for an insertion at random coordinates is given by

$$P = \min\left[1, \exp\left(\frac{\mu_\mathrm{r} - \Delta U_\mathrm{pot}}{kT}\right)\right], \tag{1}$$

where ΔU_pot is the potential energy difference due to the insertion and

$$\mu_\mathrm{r} = \mu - \mu_\mathrm{id}(T) - kT \ln\left(\sigma^3 \rho\right), \tag{2}$$

is the residual chemical potential, while $\mu_\mathrm{id}(T)$ is the solely temperature dependent ideal contribution to the chemical potential and σ is the size parameter of the Lennard-Jones potential. The acceptance probability for the deletion of a random particle is analogous, with $-\mu_\mathrm{r}$ instead of μ_r.

The behavior of McDonald's demon is determined by the intervention threshold size θ. For very small values of θ, the intervention rate J_θ of the demon is much higher than the nucleation rate J at the given supersaturation. If θ equals the critical droplet size ν^*, we have $J_\theta = 2J$, because a critical droplet has equal probabilities of complete vaporization and growth to macroscopic size (but eventually, one of these options occurs for each droplet). Therefore, J and J_θ are of the same order of magnitude for $\theta \gtrsim \nu^*$.

THEORETICAL APPROACHES

The free energy of droplet formation is the same for the grand canonical and the isothermal-isobaric ensemble [12]. It has a maximum $\Delta\Omega^*$ for the size v^* of the critical droplet. The difference between the saturated chemical potential $\mu_\sigma(T)$ at the temperature T and the chemical potential μ of a vapor can be expressed in terms of the supersaturation $S = \exp((\mu - \mu_\sigma) / (kT))$.

In CNT, it is assumed that the density ρ^I and the chemical potential μ_σ of the saturated bulk liquid apply to droplets as well. The droplet surface tension $\gamma_v = (\partial G/\partial A)_{p,T}$ is approximated by the tension γ of the planar vapor-liquid interface, and all droplets are treated as spheres. Including the Zeldovich factor f_Z and the thermal non-accomodation factor $f_{\Delta T}$ [13], the nucleation rate is

$$J = f_{\Delta T} f_\mathrm{Z} \frac{N_1}{V} \exp\left(\frac{-\Delta\Omega^*}{kT}\right) \frac{6\pi v^* p \lambda}{\rho^\mathrm{I} h}, \tag{3}$$

where N_1 is the number of vapor molecules in the system, λ is the thermal wavelength, and h is the Planck constant. It turns out that CNT significantly overestimates the free energy of droplet formation [14]. While for bubbles, the approximation $\gamma_v = \gamma$ was found to be fairly accurate by some authors [15], it is unsuitable for small droplets [16]. Values of γ_v as low as 0.4γ were found in equilibrium MD simulations [3], leading to a surface property corrected (SPC) modification [4] of CNT. The SPC modification assumes a non-spherical surface and determines the droplet surface tension from a fit of the Tolman equation [16] to equilibrium MD simulation results.

A different approach is given by the scaling model of Hale [17]. It predicts

$$J \sim \rho^{-2/3} \left(\frac{\gamma}{T}\right)^{1/2} p^2 \exp\left[\frac{4\gamma^3}{27(\ln S)^2}\right], \tag{4}$$

where the proportionality constant only depends on properties of the critical point.

SIMULATION RESULTS

The supersaturation is shown in Fig. 1 (left) as a function of the supersaturated vapor density, determined from GCMD simulations with McDonald's demon, at constant temperatures of 0.7 and 0.85 ε/k, where ε is the energy parameter of the Lennard-Jones potential. These values agree well with the metastable vapor pressure isotherm of the tsLJ fluid, obtained from MD simulation in the canonical ensemble, where the supersaturation is calculated by integrating the Gibbs-Duhem equation.

With a temporal delay between 100 ps and 1 ns, the intervention rate reaches a constant value. The results agree very well with nucleation rates obtained from canonical ensemble MD simulations [4]. Thus, the applicability of the new method is established by comparison with results from *NVT* simulations.

CNT is known to overestimate the nucleation rate of the tsLJ fluid [4]. The intervention rate confirms this result, cf. Fig. 1 (right). The SPC modification and the Hale scaling model are significantly more accurate in the present case.

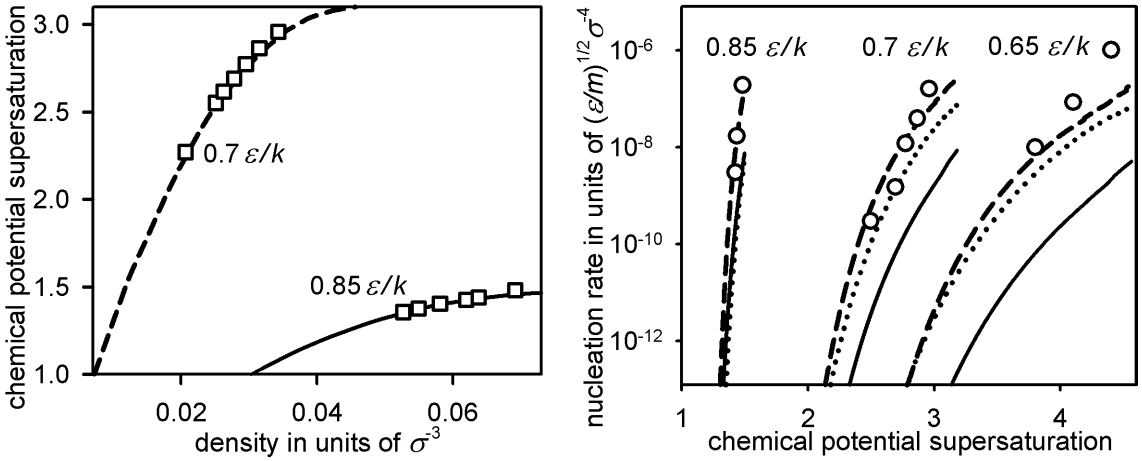

Figure 1. Left: density dependence of the supersaturation for tsLJ vapor, obtained from GCMD simulation with McDonald's demon (squares) and by integration of the Gibbs-Duhem equation using data from canonical ensemble MD simulation with $T = 0.7\ \varepsilon/k$ (dashed line) and $0.85\ \varepsilon/k$ (solid line). Right: nucleation rate over supersaturation for the tsLJ fluid at temperatures of 0.65, 0.7, and 0.85 ε/k, according to CNT (solid lines), the SPC modification (dashed lines), and the Hale model (dotted lines), in comparison with results from GCMD simulation with McDonald's demon (circles).

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