Grand canonical steady-state simulation of nucleation

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Grand canonical molecular dynamics (GCMD) is applied to the nucleation process in a metastable phase near the spinodal, where nucleation occurs almost instantaneously and is limited to a very short time interval. With a variant of Maxwell's demon, proposed by McDonald [Am. J. Phys. 31 (1962): 31], all nuclei exceeding a specified size are removed. In such a steady-state simulation, the nucleation process is sampled over an arbitrary timespan and all properties of the metastable state, including the nucleation rate, can be obtained with an increased precision. As an example, a series of GCMD simulations with McDonald's demon is carried out for homogeneous vapor to liquid nucleation of the truncated-shifted Lennard-Jones (tsLJ) fluid, covering the entire relevant temperature range. The results are in agreement with direct non-equilibrium MD simulation in the canonical ensemble. It is confirmed for supersaturated vapors of the tsLJ fluid that the classical nucleation theory underpredicts the nucleation rate by two orders of magnitude.

I. INTRODUCTION

The key properties of nucleation processes are the nucleation rate $\mathcal{J}$ that indicates how many embryos of the emerging phase appear in a given volume per time and the height $\Delta\Omega^\star$ of the free energy barrier that must be overcome to form stable nuclei. The most widespread approach for calculating these quantities is the classical nucleation theory (CNT)[1], which has significant shortcomings, e.g., it overestimates $\Delta\Omega^\star$ for homogeneous vapor to liquid nucleation[2]. A more accurate theory of homogeneous nucleation, which is sought after, would also increase the reliability for more complex applications such as heterogeneous and ion-induced nucleation in the earth's atmosphere.

An important problem of CNT is that the underlying basic assumptions do not apply to nanoscopic nuclei[3]. Properties of such nuclei are hard to investigate experimentally, but are well accessible by molecular simulation. For instance, equilibria[4,5] and vaporization processes[6,7] of single liquid droplets can be simulated to obtain the surface tension as well as heat and mass transfer properties of strongly curved interfaces. Similarly, very fast nucleation processes that occur in the immediate vicinity of the spinodal are experimentally inaccessible, whereas they can be studied by Monte Carlo (MC)[8] and molecular dynamics (MD)[9,10] simulation of systems with a large number of particles. Hence, molecular simulation is crucial for the further development of nucleation theory.

According to the current state of the art, direct non-equilibrium MD simulation of nucleation is conducted in the canonical ensemble. As proposed by Yasuoka and Matsumoto (YM)[9], the nucleation rate is obtained from the number of nuclei formed over time, using a linear fit, where only nuclei that exceed a sufficiently large threshold size are counted. Nucleation occurs after the metastable state is equilibrated and before nucleus growth becomes dominant. However, the timespan corresponding to nucleation is very short for the high nucleation rates that are accessible to direct MD simulation, which restricts the statistical basis and the precision of the results. Near the spinodal, the regimes of equilibration, nucleation, and growth even start to overlap and the YM method becomes unreliable. Wedekind *et al.*[11] recently developed a more rigorous method which is based on mean first passage times (MFPT) obtained by averaging over hundreds of simulation runs. But as Chkonia *et al.*[12] point out, 'the computational costs of making the necessary repetitions to evaluate the MFPT can be very high,' whereas 'YM requires many clusters forming and it therefore becomes more sensible to deviations coming from vapor depletion or coalescence of clusters.'

In the present work, a direct equilibrium MD simulation method is introduced to simulate nucleation in the grand canonical ensemble as a stationary process, sampling exclusively nucleation as opposed to nucleus growth and coalescence. While the precision of the results is increased by maintaining the steady state over an arbitrarily long time interval, the advantages of the YM non-equilibrium method are retained as well. In particular, only one MD simulation run is required and the nucleation rate is obtained from the number of large nuclei formed over time. This is achieved by combining grand canonical molecular dynamics (GCMD), introduced by Cielinski[13], and an 'intelligent being' that continuously removes all large nuclei: McDonald's demon[14].

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II. SIMULATION METHOD

In a closed system, nucleation is an instationary process because the metastable phase is depleted by the emerging nuclei. The idea behind the present approach is to simulate the production of nuclei up to a given size for a specified metastable state. Nuclei above the given size are extracted, and particles are inserted as monomers into the system to replenish the metastable phase.

GCMD regulates the chemical potential and samples the grand canonical ensemble: alternating with standard MD steps, particles are deleted from and inserted into the system probabilistically with the usual grand canonical acceptance criteria[13,15]. For a test deletion, a random particle is removed, and for a test insertion, random coordinates are chosen for an additional particle. The potential energy difference $\delta\mathcal{V}$ is determined for each of the test operations and compared with the residual chemical potential. Applying the Metropolis method, the acceptance probability is

$$\mathcal{P} = \min\left(\rho\Lambda^3 \exp\left[\frac{-\mu - \delta\mathcal{V}}{k_\mathrm{B}T}\right], 1\right), \tag{1}$$

for deletions, and similar for insertions[16]. In this expression, ρ is the density, Λ is the thermal wavelength, and μ is the chemical potential. The number of test deletions and insertions per simulation time step was chosen in this work between 10^{-6} and 10^{-3} times the number of particles.

Whenever a nucleus exceeds the specified threshold size Θ, an intervention of McDonald's demon[14], called Szilárd's demon by Schmelzer *et al.*[17], removes it from the system and replaces it by a representative configuration of the metastable phase. If a dense phase is simulated, this can be achieved by, e.g., inserting an equilibrated homogeneous configuration in the center of the free volume, followed by preferential test insertions and deletions in the affected region. In a supersaturated vapor, however, the density is usually so low that it is sufficient to leave a vacuum behind as suggested by McDonald[14]. The intervention rate $\mathcal{J}_\Theta$ is related to the nucleation rate $\mathcal{J}$ by[18]

$$\mathcal{J}_\Theta \int_0^\Theta \exp\left(\frac{2\Omega_\nu}{k_\mathrm{B}T}\right) d\nu = \mathcal{J} \int_0^\infty \exp\left(\frac{2\Omega_\nu}{k_\mathrm{B}T}\right) d\nu, \tag{2}$$

where Ω_ν is the free energy of the system with a single nucleus that contains ν particles and in particular, $\mathcal{J} \approx \mathcal{J}_\Theta$ for a threshold size sufficiently above $\nu^\star$.

The truncated-shifted Lennard-Jones (tsLJ) fluid accurately describes the fluid phase coexistence of noble gases and methane[4], avoiding long-range corrections which are tedious for inhomogeneous systems. Homogeneous vapor to liquid nucleation of the tsLJ fluid was studied here by GCMD simulation with McDonald's demon at temperatures of 0.65 to 0.95, in units of ε/k_B (where ε is the energy parameter of the Lennard-Jones potential). Note that the triple point temperature of the tsLJ fluid is $T_3 = 0.65$[19] while the critical temperature is $T_\mathrm{c} = 1.078$[4], so that the entire relevant temperature range is covered.

Molecular simulation has to rely on cluster criteria to distinguish the emerging liquid from the surrounding supersaturated vapor[20]. In the present work, the Stillinger criterion[21] was used to define the liquid phase, and nuclei were determined as biconnected components.

III. SIMULATION RESULTS

Figure 1 shows the aggregated number of demon interventions in one of the present GCMD simulations and, for comparison, the number of nuclei in a MD simulation of the canonical ensemble under similar conditions. The constant supersaturation $S = \exp\left[(\mu - \mu_\sigma(T))/(k_\mathrm{B}T)\right]$ of the GCMD simulation agreed approximately with the time-dependent S in the NVT simulation about $t = 400$ after simulation onset in reduced time units, i.e., $\sigma(m/\varepsilon)^{1/2}$ wherein σ is the size parameter of the Lennard-Jones potential and m is the mass of a particle.

During the NVT run, however, S decreased from about 3 to 1.5. The observed rate of formation was significantly lower for larger nuclei, which is partly due to the the depletion of the vapor over simulation time. Depletion causes less monomers to interact with a nucleus surface when large nuclei are formed because by that time, a substantial amount of particles already belong to the liquid. Moreover, a small nucleus will eventually decay with a certain probability, given by 1 - $\mathcal{J}/\mathcal{J}_\nu$, instead of growing to arbitrarily large sizes, cf. Eq. (2). Therefore, large nuclei are necessarily formed at a lower rate.

In Fig. 2, it can be seen how the decreasing supersaturation in the canonical ensemble MD simulation affects the nucleus size distribution. Around $t = 400$, the distribution of small nuclei present per volume was similar in both simulation approaches. Near and above the critical size, i.e., 27 particles according to CNT, deviations arise because of the different boundary conditions. A comparison with the theoretical prediction confirms that CNT overestimates the free energy of nucleus formation and therefore underpredicts the number of nuclei present in the metastable state[2].

CNT is also known to underestimate the nucleation rate of unpolar fluids[10]. The determined demon intervention rates confirm this conclusion and as shown in Fig. 3, the Hale[22] scaling law (HSL) is significantly more accurate than CNT for low temperatures. For $T = 0.85$, HSL and CNT lead to similar predictions, deviating from simulation results by two orders of magnitude. At $T = 0.95$ (not shown graphically), a nucleation rate of $\ln \mathcal{J}$ = -16.1 ± 0.3 was obtained for $S = 1.146$ (using $\Theta = 564$), where HSL predicts $\ln \mathcal{J}_{\mathrm{HSL}}$ = -24.3 as opposed to $\ln \mathcal{J}_{\mathrm{CNT}}$ = -20.0. Thus, HSL breaks down at high temperatures for the tsLJ fluid. Present results generally agree with nucleation rates obtained by NVT simulation at temperatures between 0.65 and 0.95, as can be seen by comparison with the surface property corrected (SPC) modification of CNT that was correlated to these data[10].

With a threshold far below the critical size, the intervention rate of McDonald's demon is many orders of magnitude higher than the steady-state nucleation rate. In agreement with Eq. (2), $\mathcal{J}_\Theta$ reaches a plateau for $\Theta > \nu^\star$, cf. Fig. 4. In particular, the approximation $\mathcal{J} \approx \mathcal{J}_\Theta$ is valid for all values shown in Fig. 3.

Figure 5 shows how the choice of Θ affects the nucleus temperature. For $\nu \ll \Theta$, the influence of Θ is insignificant, whereas the largest nuclei allowed to remain in the system have a highly elevated temperature. The amount of nucleus overheating observed in the steady state can be explained by considering the boundary condition that McDonald's demon imposes on size fluctuations. Only nuclei that do not fluctuate to sizes above Θ remain in the system for a significant time. Almost all nuclei with $\nu \approx \Theta$ approach the point where overheating due to the enthalpy of vaporization released during condensation countervails the supercooling of the vapor.

The nucleation processes from Fig. 5 occur at a supersaturated pressure of $p \approx 0.134$ which corresponds to a supercooling of $\Delta T = -0.0965$, given that $p_\sigma(T_\sigma) = 0.134$ for $T_\sigma = 0.7965$[4]. It can be seen that the overheating of nuclei with $\nu \approx \Theta$ is of the same order of magnitude as the supercooling of the vapor. Note that this effect is much stronger than the overheating of the critical nucleus $\Delta T^\star$ due to nucleation kinetics. From a discussion of heat transfer during homogeneous nucleation by Feder *et al.*[1], the expression

$$\Delta h^{\mathrm{v}} \Delta T^\star = 2 f_{\mathrm{Z}} k_{\mathrm{B}} T^2, \tag{3}$$

can be deduced, where f_{Z} is the Zeldovič factor and Δh^{v} is the enthalpy of vaporization. In the present case, that evaluates to $\Delta T^\star = 0.00608$.

IV. CONCLUSION

GCMD with McDonald's demon was established as a method for steady-state simulation of nucleation processes. For vapor to liquid nucleation of the tsLJ fluid, a series of simulations was conducted over a wide range of temperatures.

The maximal overheating of nuclei was found to be similar in magnitude to the supercooling of the vapor. For the nucleation rate, good agreement was reached with canonical ensemble MD simulation results. It was confirmed that CNT overstates the free energy of nucleus formation and underpredicts the nucleation rate. HSL accurately describes vapor to liquid nucleation of the tsLJ fluid near the triple point temperature. However, significant deviations arise at high temperatures.

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Figure 1 Top: number per unit volume ρ_n of nuclei containing $\nu > 25$ ($\cdot\,\cdot$ –), 50 (—), and 150 (– –) particles in a NVT simulation at $T = 0.7$ and $\rho = 0.004044$ (in units of σ^{-3}), number per unit volume ρ_n of nuclei with $\nu \geq 25$ (□) in a GCMD simulation with $T = 0.7$, $S = 2.8658$ as well as $\Theta = 50$, and the aggregated number of McDonald's demon interventions per unit volume in the GCMD simulation, over simulation time; bottom: pressure over simulation time for the NVT simulation (– –) and the GCMD simulation with McDonald's demon (—).

Figure 2 Nucleus number per unit volume ρ_n over nucleus size ν from NVT simulation at $T = 0.7$ and $\rho = 0.004044$, with sampling intervals of $320 \leq t \leq 480$ (○) and $970 \leq t \leq 1130$ (◇) after simulation onset, and from GCMD simulation with $\Theta = 50$ (●) at $T = 0.7$ and $S = 2.8658$ in comparison with a prediction for the same conditions based on CNT (—).

Figure 3 Nucleation rate logarithm $\ln \mathcal{J}$ over supersaturation S at $T = 0.65$, 0.7, and 0.85 according to CNT (—), the SPC modification (– –) as well as HSL ($\cdot\,\cdot\,\cdot$) in comparison with present GCMD simulation results with McDonald's demon (○).

Figure 4 Intervention rate logarithm $\ln \mathcal{J}_\Theta$ over intervention threshold size Θ of McDonald's demon during GCMD simulation at $T = 0.7$ and $S = 2.4958$ (□) in comparison with predictions based on CNT (—) and the SPC modification (– –); dotted line: CNT prediction shifted to the actual value of the nucleation rate; vertical line: critical size according to the SPC modification.

Figure 5 Nucleus temperature over nucleus size from GCMD simulation with McDonald's demon at $T = 0.7$ and $S = 2.4958$ for an intervention threshold size of $\Theta = 15$ (▲), 30 (○), 48 (●), 65 (▽), and 74 particles (■); dotted line: saturation temperature of the vapor; dashed lines: guide to the eye.

Figure 1:

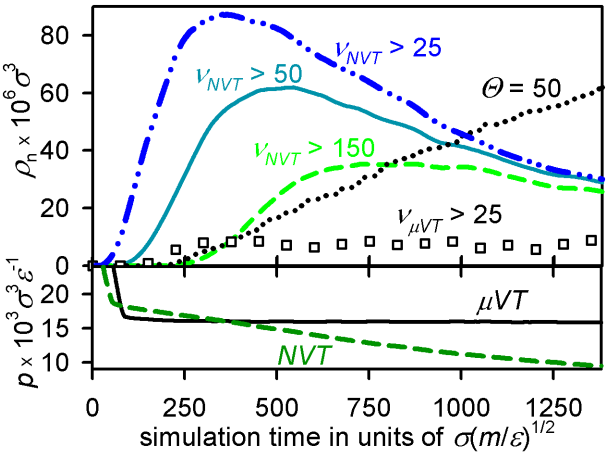
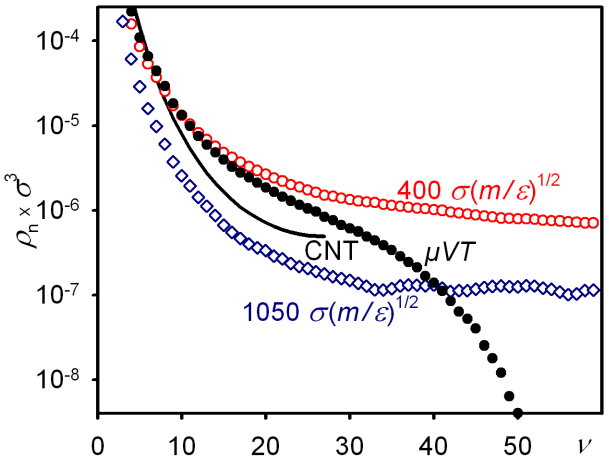


Figure 2:



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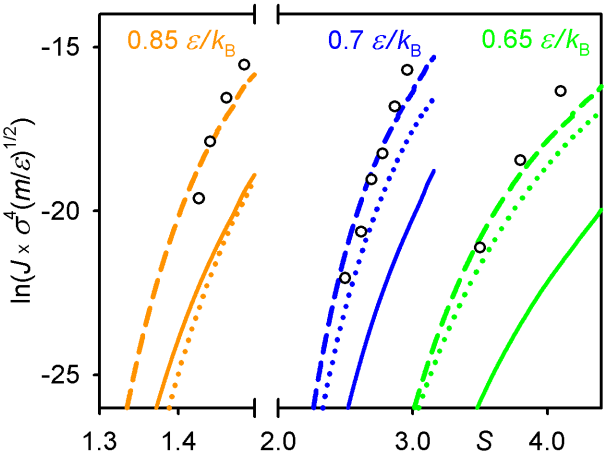

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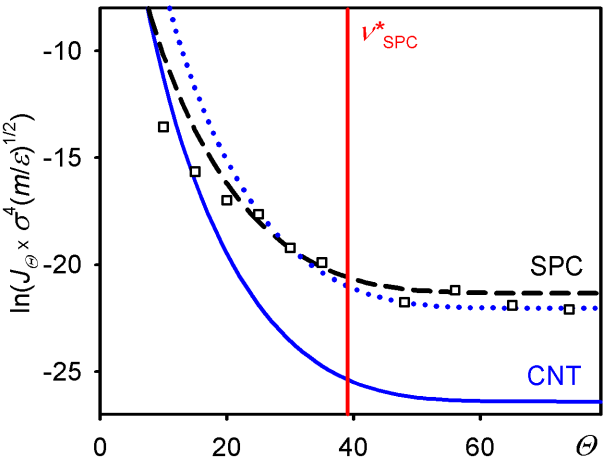

Figure 5: