



Molecular Dynamics Simulations of Argon Nucleation

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Phase Transitions and Nucleation

First order phase transitions such as condensation or melting play an important role in science, nature and technical applications. The **initiating process of most first-order phase transitions is called nucleation**: the new phase first manifests itself in small nuclei which are formed from fluctuations inside the old phase. The nucleation of a pure substance is called *homogeneous*.¹⁾

One of the most accessible phase transition is the condensation from a supersaturated gas phase. Lately, new experimental techniques have made it possible to investigate the **condensation of argon vapor**.^{2,3)} Astonishingly, these experiments yielded **deviations** from the Classical Nucleation Theory¹⁾ by up to **26 orders of magnitude**, which comes as a huge surprise: most researchers assumed a smaller discrepancy for an almost ideally behaved substance such as argon. Thus, deviations found in experiments on substances such as water cannot be accounted for by non-idealities of the investigated substance at hand, but are inherent in the theoretical approach. These experimental results and the fact that argon can easily be modeled using a Lennard-Jones (LJ) potential motivated a new set of simulations in the same temperature region as the experiments at $45 < T/K < 70$.

Simulation Details

We use **standard Molecular Dynamics (MD)** to simulate the condensation of an argon droplet in an *NVT* system. The program package CLUSTER⁴⁾ employs the velocity-Verlet algorithm on a system of **LJ-argon particles** in a cubic box with periodic boundary conditions. The chosen timestep is 2 fs, and the simulation time is up to 2000 ns. Clusters are identified by the Stillinger-definition: each atom whose centers of mass are within a certain radius constitute a cluster. Even though this method appears crude and void of a more meaningful physical definition of a "liquid"-like cluster, results are shown not to depend critically on the exact value of this Stillinger radius.⁵⁾ Fig. 1 shows two snapshots of a typical simulation run of 343 argon atoms at 50 K.

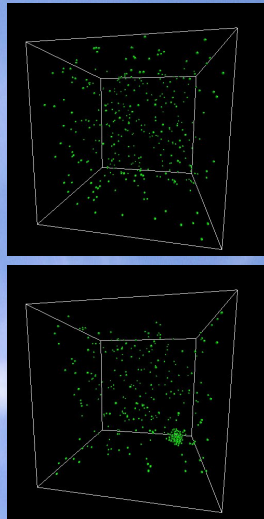


Figure 1: Example snapshots of a MD-simulation run. The upper picture shows the initial vapor; the lower picture a condensing argon droplet.

The Right Thermostat

The **temperature** is kept **constant by a simple isokinetic scheme**. Intensive tests with different amounts of carrier-gas showed, that the **error obtained** from applying this naive velocity-scaling is **negligible** when comparing with experiment or theory, while at the same time it is saving valuable calculation time. Fig. 2 shows the average kinetic temperature of cluster of size *n* for systems using velocity-scaling or different amounts of LJ-helium carrier-gas as a thermostat: the cluster warm up from the heat of condensation, as expected, but the differences between the different systems and methods are small.⁶⁾

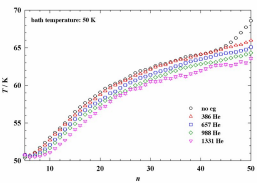
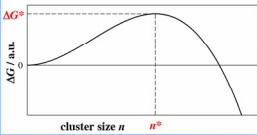


Figure 2: Average kinetic temperature of clusters of size *n* using velocity scaling and different amounts of carrier gas. The bath temperature is set to $T = 50$ K.

Figure 3: Work of formation $\Delta G(n)$ of a cluster of size *n* according to CNT. ΔG^* and n^* denote the nucleation barrier and the critical cluster size, respectively.



Optimizing the System Size

One simulation of a single nucleation event usually **does not yield a lot of information**: nucleation in itself is a highly stochastic process. Many simulation runs have to be performed to accumulate a sufficient statistics. Simulating a system big enough to show more than one nucleation event, e.g. 10 or 100 clusters, is not advisable because:

- we need a larger system leading to a much longer calculation time,
- the supersaturation must be very high, which is even further from experiments and may lead to strong depletion effects, and
- clusters would not form at the same time but consecutively under different conditions,

which makes an accurate description of the work of formation of each individual cluster even more complicated than necessary. We developed a **new method to estimate the minimum system size** beyond which **finite size effects** arising from the depletion of vapor during the condensation **become negligible**.⁷⁾ This minimization saves valuable calculation time on single simulations in favor of many runs for better statistics.

Classical Nucleation Theory (CNT)

In CNT,¹⁾ and all subsequent phenomenological models, the **nucleation rate** is evaluated by a Boltzmann-approach:

$$J = K \exp(-\Delta G^* / kT)$$

The **work of formation ΔG^*** of the critical cluster is evaluated assuming an ideal vapor and a spherical, incompressible droplet with bulk liquid properties (capillarity approximation). Despite these obvious shortcomings, CNT is still widely used, since the parameters needed for calculation are readily available for most substances. Fig. 3 shows a sketch of the work of formation, where the maximum denotes ΔG^* , also called the **nucleation barrier**, which is located at the **critical cluster size n^*** . The kinetic pre-factor *K* is diffusion based and much less sensitive to system changes than ΔG^* .

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A New Approach To Analyze Rates: Mean-First-Passage-Times

Typically, the way to evaluate the rate of formation *J* is to count the number of clusters *N* passing through a threshold size during some time interval *t*, or, similarly, by taking the time one cluster needs to pass through that size and average over many simulation runs:⁸⁾

$$J = N / t_j V$$

However, this threshold size is arbitrary and not connected to the critical cluster size n^* . Also, Fig. 4 shows five typical growth curves from the simulations: If we took $n = 15$ as the threshold size, some clusters reach that size but decay again, so that the time noted is **not** the onset of condensation but just a fluctuation.

Instead of one threshold, we take the first passage-times of one cluster passing through **any** cluster size *n* (see Fig. 4) and average these times over all simulation runs. Fig. 5 shows the resulting **mean-first-passage-times $\tau(n)$** as a function of cluster size *n*. From the fit we can obtain the nucleation time t_j , the critical cluster size n_{PT}^* – directly and **solely from the kinetics and independently of thermodynamics**.

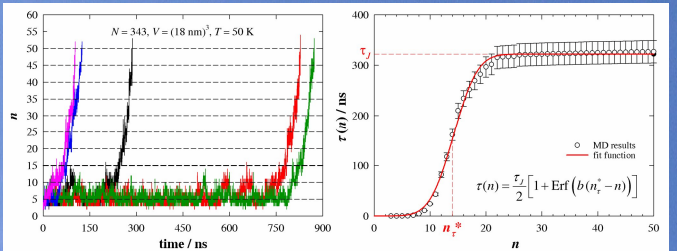


Figure 4: Five typical growth curves of simulated clusters taken from the simulations. Dashed lines mark different constant *n*.

Figure 5: Mean-first-passage-times curve resulting from Fig. 4, but averaged over 200 simulation runs. Red line: fit with the given function.

Results: Nucleation Rate Isotherms

So far we have performed MD simulations at different supersaturations at six temperatures in the range of $45 < T/K < 70$. Fig. 6 shows preliminary results as **nucleation rate isotherms**, with **at least 100 simulation runs per point**. Just like in nucleation experiments, we are now able to obtain the **critical cluster size n_{PT}^*** by help of the nucleation theorem^{10,11)} from the slope of the rate isotherm – independently from the kinetic values from the mean-first-passage-times analysis or CNT. Fig. 6 also gives the critical cluster sizes obtained from CNT, the nucleation theorem and from mean-first-passage-times analysis in comparison.

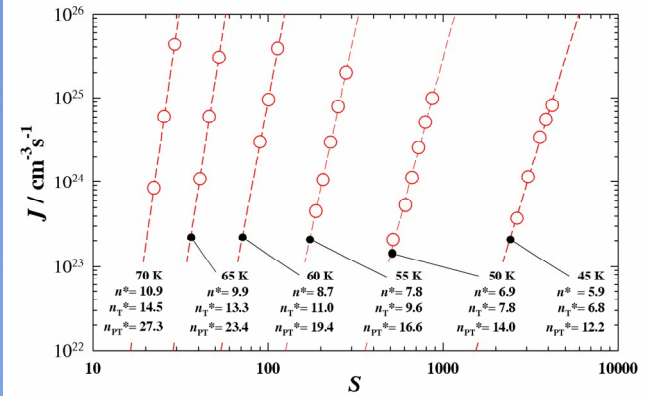


Figure 6: Nucleation rates *J* as function of supersaturation *S*.

The critical cluster size from kinetics is always the largest value, while the values from the nucleation theorem and CNT are smaller and closer to each other. The meaning of these discrepancies is currently subject to closer investigation. We plan at least 200 simulation runs for at least five supersaturations at each temperature to further increase the accuracy of our results.

Comparison with Experiment and Theory

Fig. 7 shows the nucleation rates from the simulations and the experiment scaled on CNT as a function of the inverse temperature. The deviations of MD are smaller, but still range from 2 to 6 orders of magnitude – which is still small compared to the 16 to 26 orders of magnitude found in experiment. The deviations of MD simulations from CNT found in this work is consistent with previous works and once again stresses the need for a new phenomenological model that predicts correct nucleation rates for noble gases. The high deviations of experimental results still remain a puzzle to be solved.

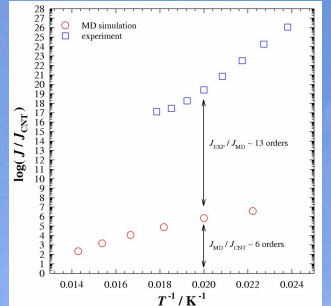


Figure 7: MD and experiment in comparison, scaled on CNT as a function of the inverse temperature.

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