

Introduction

Nucleation is highly sensitive to small changes in temperature, which may lead to differences in nucleation rates of several orders of magnitude. Yet, in canonical NVT simulations, it is no trivial task to keep the temperature constant.

One way is to manipulate the vapor directly, e.g. by an iso-kinetic or a Nosé-Hoover thermostat. However, this may lead to an undesirable manipulation of the temperature of a condensing cluster, because the thermostat cannot distinguish between a one-phase and a two-phase system.

In another approach, we can mimic the experiment by introducing a thermostated carrier gas into the system. Here, the condensable species is cooled only by collisions with the carrier gas.

General Method

We investigate the influence of a the thermostat on nucleation of Lennard-Jones argon by extensive MD simulations.

We simulated a system at two different supersaturations without and with three different concentrations of carrier gas. In the simulations without carrier gas, either an iso-kinetic velocity scaling or a Nosé-Hoover thermostat was applied. Each simulation was repeated up to 1000 times yielding a previously unmatched accuracy of the statistics.

First, we will show the effect of the different thermostats on the nucleation rate.

Second, we will explain the observed behavior by analyzing the mean temperature of the biggest cluster in the system.

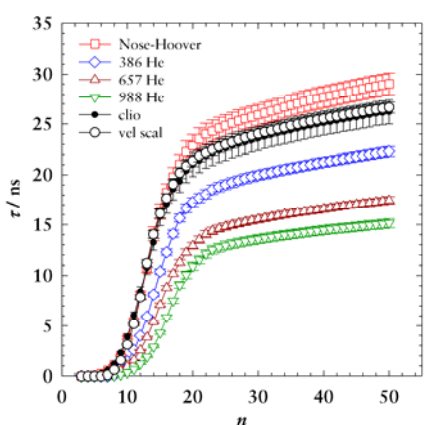


Fig 1: Mean-first-passage-times, low barrier.

Influence on Nucleation Rate

Fig. 1 and 2 show the mean-first-passage-times (MFPT)¹⁾ as a function of the cluster size n in a system with a low (Fig. 1, left) and a high (Fig. 2, right) nucleation barrier. The MFPT at the plateau corresponds to the inverse of the nucleation rate.

The nucleation rates of systems with carrier gas are the highest and increase with the amount of carrier gas. Accordingly, the direct methods yield lower rates. At a higher nucleation barrier this deviation is less pronounced. Here, the condensation rate is lower and consequently the system has more time to equilibrate the temperature of a growing cluster.¹⁾

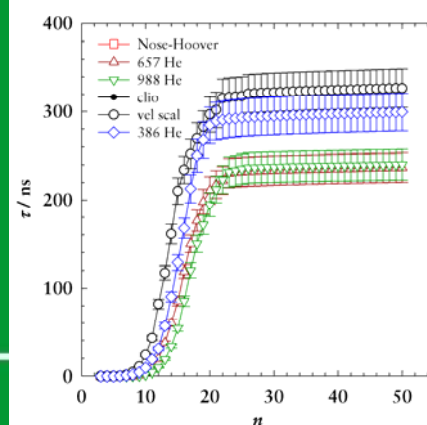


Fig 2: Mean-first-passage-times, high barrier.

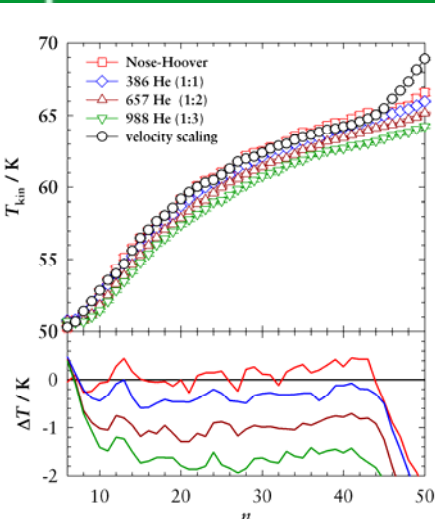


Fig 4: Mean cluster temperature (low barrier, top) and deviation of the mean temperature with respect to velocity scaling (bottom),

Mean Cluster Temperatures

How can we explain the different nucleation rates for different thermostats?

We determined the mean kinetic temperature of the largest cluster in these system by averaging the cluster temperature as a function of n in each run and finally by averaging over all simulation runs. Fig. 3 and 4 show that clusters thermostated by a carrier gas are consistently colder than those cooled by direct methods. A colder cluster however has a smaller evaporation rate, while the condensation rate only depends on the supersaturation.¹⁾ Thus, the nucleation rate will be higher for colder cluster, just as we find in the MD simulations.

Yet, a deviation of less than a factor of two in the rate is small in nucleation where deviations of several orders of magnitude are common.

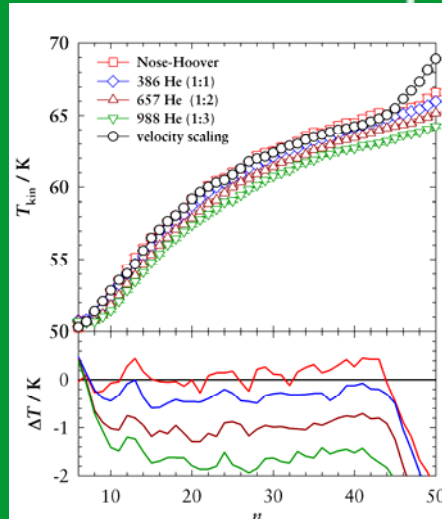


Fig 4: Mean cluster temperature (high barrier, top) and deviation of the mean temperature with respect to velocity scaling (bottom),

Conclusion

As could be expected, the most effective thermostat is a carrier gas. However, this method also is the least efficient one in terms of calculation time.

It turns out that the choice of the thermostat does not have a significant influence on the nucleation rate of Lennard-Jones argon. Therefore, velocity scaling, the simplest and least-cost thermostat in terms of calculation time, may be used for nucleation.

Yet, these results cannot be generalized to other situations, for instance the formation of iron nanoclusters where the interactions of molecules are much stronger.³⁾ In addition, care should be taken when simulating larger, growing clusters where artifacts of direct thermostat become more and more pronounced.

References:

- 1.) Abraham, Homogeneous Nucleation Theory. (Academic Press, New York, 1974).
- 2.) Reguera and Wedekind, at the The 80th ACS Colloid and Surface Science Symposium, Boulder, Colorado, USA, 2006 (unpublished).
- 3) Erhart and K. Albe, Applied Surface Science 226 (1-3), 12 (2004).

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