



# Finite-Size Effects in Simulations of Nucleation

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## Abstract

Most molecular dynamics (MD) simulations of vapor-liquid nucleation are performed in a closed, canonical NVT system. Under these conditions the vapor pressure and thus the supersaturation change during the condensation and growth of a droplet due to the fixed total number of molecules  $N$ . Moreover, the possibility of observing a nucleation event significantly depends on the system size. We investigate the importance of finite size-effects in NVT simulations of nucleation and their implications on the results reported in literature. Furthermore, we show how to estimate the system size in terms of  $N$  or similarly  $V$ , beyond which finite-size effect errors are negligible.

## The General Approach

In **classical nucleation theory (CNT)**<sup>1</sup> the formation of the new phase involves the overcoming of an **free energy barrier  $\Delta G(n)$** , the work of formation of a cluster:

$$\Delta G(n) = -n k_B T \ln \frac{p_0}{p_{eq}} + \sigma s_1 n^{2/3} + p_{eq} n v (S-1),$$

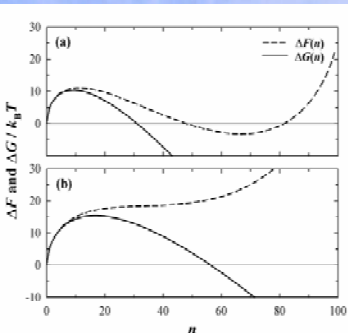
where  $s_1 = (36\pi v^2)^{1/3}$ .

Fig. 1(a) plots  $\Delta G(n)$  vs. the size  $n$  of the cluster for a system of 100 Lennard-Jones atoms in  $V = 4000(\sigma_0)^3$  at 85 K, yielding the well-known form of the nucleation barrier.

In a **NVT simulation, the work of formation generally is different**. The formation of a drop of  $n$  molecules implies the subtraction of  $n$  molecules from the vapor. A rigorous expression for the work of formation  $\Delta F(n)$  of a cluster of  $n$  molecules in a closed NVT-system was derived in the framework of the modified liquid drop model:

$$\Delta F(n) = -n k_B T \ln \frac{p_1}{p_0} + \sigma A + n(k_B T - v p_{eq}) + N k_B T \ln \frac{p_1}{p_0}.$$

The first two terms are similar to the CNT expression, except that the supersaturation is not fixed but depends on  $n$ . The dashed curve in Fig. 1 (a) plots  $\Delta F(n)$  for the same system discussed above.



Contrary to an open system and CNT, the  $\Delta F(n)$  shows a minimum corresponding to a **stable droplet** in equilibrium with the remaining vapor. Fig. 1 (b) plots the same system, but now in  $V = 6000(\sigma_0)^3$ . Whereas in the open system there still is a barrier, the NVT-system no longer has a maximum in the free energy of formation. If we perform a NVT simulation at these conditions, **no nucleation will occur**, even though the system is supersaturated and CNT predicts nucleation!

FIG. 1:  $\Delta G(n)$  and  $\Delta F(n)$  for 100 argon atoms at 85K in  $V = 4000(\sigma_0)^3$  (a) and  $6000(\sigma_0)^3$  (b).

## Optimization of the System Size

Which is the **optimal system size** I can choose for my problem? For a given system, we can simply look at the error as a function of  $N$  at the density (or supersaturation) of interest. For the sake of discussing a real case, let us focus on Ref. 2: Yasuoka and Matsumoto simulated a system containing 5000 LJ-argon atoms at  $T = 80.4$  K in a cubic box of  $V=(60\sigma)^3$ .

Fig. 4 shows the **finite-size error** as a function of  $N$ , **keeping the original density constant**. The system size chosen by the authors clearly does not show any significant size effects. Still, two things need to be stressed:

- At  $N = 500$  atoms, the **deviation is still less than 0.1 kT** in  $\Delta G^*$  or less than 10% in the rate.
- A **further increase of  $N$  is meaningless**, because the error does not become significantly smaller for larger  $N$ .

Thus, at  $N = 500$  we could **save a factor of up to 100** in the calculation time without danger.

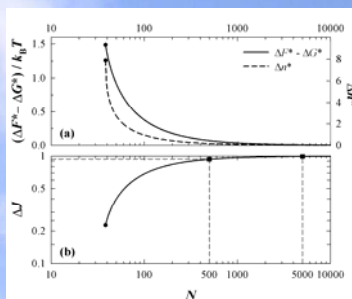


FIG. 4: Difference of nucleation barriers (solid) and critical cluster sizes (dashed) in CNT and MLD (a) Deviation of the rate for the same system (b).

An error of less than 10% is negligible for nucleation rates, where several orders of magnitude of deviation are common when comparing theory and experiment or different experiments.<sup>3</sup>

We repeated the simulations in Ref. 2 at  $N=500$  and we were able to reproduce the reported rates with an error <5%.

## References:

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## General Results and Discussion: A Case Study

We will study the differences between nucleation in a closed vs. an open system under different sizes and conditions. As an example, we will analyze the importance of these effects in a system of Lennard-Jones argon atoms.

Fig. 2 is a contour plot of the difference in nucleation barriers  $\Delta F^*$  and  $\Delta G^*$ , in critical cluster size, and in  $\Delta J$  for a system at 85 K as a function of  $N$  and  $V$ . The dashed lines mark constant densities and, since the vapor is assumed to be ideal, constant supersaturations  $S_0$ . At a fixed temperature, the predictions of CNT only depend on  $S_0$  and therefore,  $\Delta G^*$ ,  $n^*$  and  $J_{CNT}$  are constants along these lines.

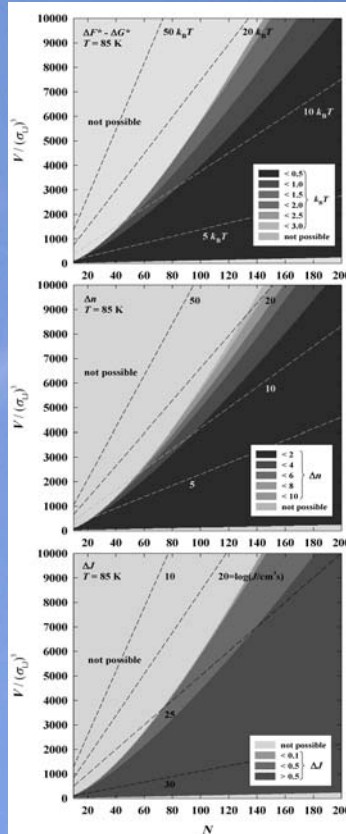


FIG. 2: Contour plots of the differences in the nucleation barrier between the open and the closed system (a), the differences in the size of the critical nucleus (b), and ratio of nucleation rates (c). (d): same as (a) for a larger  $N$  and  $V$ .

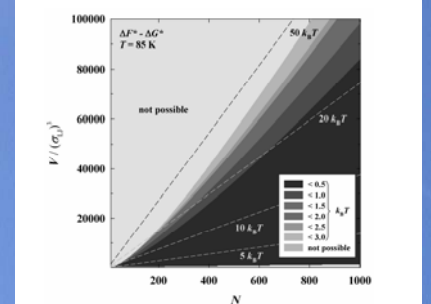
The **deviations** in the barrier and the critical size are in the range of a **several kT or atoms**, respectively. The difference in the rate is given by

$$\Delta J \equiv J_{NVT}/J_{CNT} = \exp((\Delta G^* - \Delta F^*)/kT)$$

and may reach up to **several orders of magnitude**. A more dramatic effect of the confinement is the existence of an important region of parameters, denoted by the white areas in the plot, where **nucleation in the small finite system is not possible at all**. This also imposes a severe limitation on the order of magnitude of the nucleation rates that can be obtained. In this case, it would not be possible to have a critical cluster bigger than approx. 30 molecules or obtain nucleation rates below  $10^{20} \text{ cm}^{-3}\text{s}^{-1}$  in a simulation with less than 200 molecules.

As  $N$  increases, the range of  $V$  for which the error in the nucleation barrier is within a reasonable limit of  $0.5kT$  expands. Similarly, the range of cluster sizes and nucleation rates accessible in a simulation increases.

To simplify the comparison, Fig. 3 plots the differences in the barrier, the critical cluster size and the rate as a function of  $N$  for three different values of the supersaturation  $S_0$ , i.e. fixed density.



The deviations arising from **finite-size effects** can obviously be **very significant for systems of a few hundred atoms**, but become **increasingly less important for larger  $N$** . In addition, the discrepancies get bigger the smaller the value of  $S_0$  or, equivalently, the higher  $\Delta G^*$  and  $n_{CNT}^*$ .

This poses another dilemma: higher barriers, i.e. closer to experimental conditions, mean longer simulation times, because the rate exponentially decreases with  $\Delta G^*$ . Yet on top of that, we encounter significantly higher finite-size effects and are forced to go to larger  $N$  to compensate this error.

As a result, we might end up **running in circles when trying to reach experimental conditions** in a simulation.

FIG. 3: Differences in the nucleation barrier between the open and the closed system (a) Differences in the size of the critical nucleus (b).

## Conclusion

Size effects can be very large in small systems, but become increasingly less important for larger  $N$ . Many simulations of nucleation have been performed on LJ argon<sup>2,4-8</sup>. In the absence of any clear criterion to select the size except "the bigger, the better", the number of molecules typically used in these simulations tends to be the largest possible in the range of  $10^3 - 10^5$  molecules. However most of these simulations are practically unaffected by inaccuracies due to finite-size effects – at the expense of a system that mostly was much larger than actually needed.

The method described here can serve as a starting point to optimize the system size. This optimization saves valuable calculation time and can extend the range of supersaturations and rates attainable in simulations by several orders of magnitude. Our results are also applicable to other situations, such as crystallization, capillary condensation or the melting of nanoclusters.

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