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Finite-size effects in simulations of nucleation

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We investigate the importance of finite-size effects in simulations of nucleation processes. Most molecular dynamics simulations of first order phase transitions, such as vapor-liquid nucleation, are performed in the canonical *NVT* ensemble where, owing to the fixed total number of molecules *N*, the growth of the new phase causes the depletion of the metastable phase. This effect may lead to significant errors in the simulation and even to the impossibility of observing nucleation in a small finite system. We present a theory to estimate the system size beyond which these finite-size effects are expected to be negligible. This optimization saves valuable calculation time and can extend the range of supersaturations and rates attainable by simulations by several orders of magnitude. Our results are applicable to diverse situations, such as crystallization, capillary condensation, or the melting of nanoclusters. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402167]

I. INTRODUCTION

First order phase transitions play a significant role in science and nature as well as in technical applications. Examples range from condensation and melting to protein crystallization and galaxy formation, thus embracing a wide variety of scientific fields. These apparently very different phenomena share in common that their appearance requires the formation of a small embryo or nucleus of the new phase, which involves the overcoming of an energetic barrier. This initiating process is called nucleation and it is inherent in most first order phase transitions.[1,2] A proper understanding of the molecular mechanisms underlying this phenomenon is therefore of outmost interest.

In recent years, computer simulations have become an invaluable resource to investigate nucleation at a molecular scale. In particular, molecular dynamics (MD) simulations open up the possibility of tracking the actual dynamics of the birth of the new phase in time.[3,4] The real process of nucleation can be reproduced on the computer by starting from a homogeneous supersaturated vapor and letting the system evolve until a nucleus or a subsequently stable drop forms. However, the formation of a nucleus is a rare event and difficult to observe in such a "brute-force" simulation. Much higher supersaturations and consequently lower nucleation barriers than in experiment are needed to observe at least one nucleation event in the limited time accessible in a simulation. Typically, the accessible range in terms of nucleation rates is around $10^{22}-10^{24}$ cm^{-3} s^{-1}, whereas the experimentally measured rates in diffusion and expansion chambers are commonly smaller than 10^{10} cm^{-3} s^{-1}. Therefore, the limitations in time scales and number of molecules imposed by computer capabilities restrict the conditions at which nucleation can be simulated to be very far from those in experiments, unless a very small system or more complicated and indirect simulation techniques are used.[5–7]

MD simulations are usually performed in the canonical *NVT* ensemble in contrast to constant pressure or constant chemical potential conditions typical in experiments, although in fact these conditions are rather assumed than achieved by any experimental constraint. Naturally, the vapor molecules condense to liquid droplets but the reduction of the pressure of the vapor due to this effect is completely negligible for the comparatively low nucleation rates (the number of nuclei formed per unit time and space) encountered in experiments. It is therefore reasonable to assume that for the nucleation stage, the system is an "open" system with a constant pressure or constant chemical potential.

However, there are very important differences between the process occurring in a closed (i.e., *NVT*) or in an open (i.e., μVT or *NpT*) system that become dramatically manifested in small systems. In particular, in a closed system the formation of the new phase causes a rapid consumption of the metastable phase, leading to significant finite-size effects. These are aggravated by the relatively small number of molecules that can be handled and the very high nucleation rates required for observing a nucleation event in the short time scale of a simulation. Just as an example, consider a cluster forming in a system containing 100 molecules. Here, each condensing molecule already reduces the supersaturation of the vapor by 1%. This depletion thus may give rise to severe discrepancies between the results obtained from simulations and those of experiments or theoretical models, because the nucleation rate is extremely sensitive to the actual supersaturation of the system at hand. In addition, the fact that one has to work with a small number of molecules and high super-

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[a)] Electronic mail: jan.wedekind@uni-koeln.de saturations leads to very small system volumes in the simulation, which may also have a significant influence on the results.

Another complication is that nucleation in itself is a highly stochastic process, and a single simulation of a nucleation event usually does not provide much information. If we repeat a real experiment under the same conditions many times, the resulting nucleation rate will show considerable scattering. Even worse in a simulation, the onset of nucleation will occur after a nonpredictable time gap or not even occur at all in the simulated time span depending on the starting configuration. Thus, a large number of simulation runs, with different starting configurations of the condensing gas phase, have to be performed to accumulate a sufficient statistics from many nucleation events. At first glance, one might argue that it could be possible to improve the statistics by simulating a system big enough so that it shows more than one nucleation event, e.g., 10 or 100 clusters. However, such a situation is not desirable for many reasons: first, a much larger system is needed leading to much longer calculation times. Second, the supersaturation must be even higher, potentially leading to even stronger depletion effects of the kind we are about to discuss in more detail in this paper. Third, clusters would not form at the same time but consecutively under different conditions. The accurate description of the rate and the work of formation for each cluster would then be an even more complicated task.

In order to minimize these finite-size effects, there is typically no objective criterion to select the number of molecules N in a simulation besides "the bigger, the better." However, calculation time scales as $O(N^2)$ or, in the best case, as $O(N \log N)$, so that we quickly reach the limitations of computer capabilities. The question that naturally arises is: how small can I safely choose my system without significant size effects? In this paper, we address this question by investigating the importance of finite-size effects in (MD) simulations of nucleation. The modified liquid drop (MLD) model introduced by Weakliem and Reiss[8] and further developed by Reguera *et al.*[9] provides us the ideal framework to answer this question. We will show that the depletion of the mother phase that accompanies the formation of the new phase in a canonical simulation may lead to significant finite-size errors in small systems, and even to situations in which nucleation cannot be observed at all in a simulation. We will describe a theory that estimates these finite-size effects and show how to use these predictions to optimize the system size for a simulation. Using this optimization, it is possible to extend the range of supersaturations and rates attainable by direct simulations by several orders of magnitude. We will focus on the effects related directly to the finite number of molecules and its depletion without entering the discussion of other kinds of finite-size effects already discussed elsewhere.[4,10–14] For the sake of simplicity, we will study one of the simplest examples of a nucleation process, namely, the condensation of a vapor, although the methods and results can be applied to many other situations.

The structure of this paper is as follows: first, in Sec. II, we shall review the basic features (and weaknesses) of classical nucleation theory (CNT) and introduce the MLD to describe nucleation in a finite closed system. In the third section, we shall quantify the importance of finite-size effects for a typical situation and use this information to optimize nucleation simulations in terms of system size. In addition, we will discuss the potential relevance of these deviations to some MD results found in literature. Section IV presents results from MD simulations illustrating the validity of our findings. Finally, the main conclusions are summarized in Sec. V.

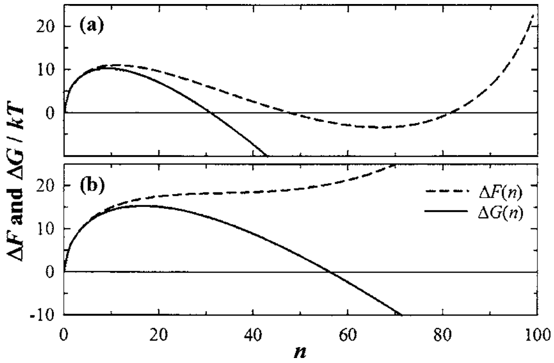

FIG. 1. (a) Free energy barriers according to CNT (solid) and MLD (dashed) as a function of cluster size n for a system containing 100 Lennard-Jones atoms at 85 K in a volume of $4000\sigma_{\mathrm{LJ}}^3$. (b) Same for a volume of $6000\sigma_{\mathrm{LJ}}^3$.

II. CNT IN A FINITE SYSTEM: THE MODIFIED LIQUID DROP MODEL

In the classical picture, the condensation of a vapor is initiated by the formation of small aggregates or clusters of molecules. At a constant pressure or chemical potential, the work of formation $\Delta G(n)$ of a cluster of size n is given by the simple classical nucleation theory (CNT) expression,[1,15–18]

$$\Delta G(n) = -n\Delta\mu + \gamma A, \tag{1}$$

which consists of a volume term related to the difference in chemical potential $\Delta\mu$ between the vapor and the liquid phase, and a surface work needed to build the liquid interface of area A and the surface tension γ. In CNT, the vapor is considered as ideal, and the liquid cluster is assumed as an incompressible spherical drop with a sharp interface and the density and planar surface tension γ of the bulk liquid. With these assumptions, the difference in chemical potentials becomes $\Delta\mu = kT \ln S_0 + p_{\mathrm{eq}} v_l (S_0 - 1)$, and $\Delta G(n)$ finally reads as

$$\Delta G(n) = -nkT \ln S_0 + \gamma s_1 n^{2/3} + p_{\mathrm{eq}} n v_l (S_0 - 1), \tag{2}$$

where $S_0 = p_0 / p_{\mathrm{eq}}$ is the supersaturation, $p_0 = NkT/V$ is the pressure of the (ideal) vapor, k is the Boltzmann constant, $s_1 = (36\pi v_l^2)^{1/3}$ is the surface area per monomer, v_l is the volume per molecule in the bulk liquid, and p_{eq} is the equilibrium vapor pressure of the bulk liquid at temperature T. The last term is the pressure-volume work required to grow a cluster within the vapor, which is usually very small and commonly neglected, but we will keep it in our analysis for the sake of accuracy.

Figure 1(a) plots $\Delta G(n)$ versus the size n of the cluster

TABLE I. Parameters and physicochemical quantities used in this work.

Argon properties

Mass: $M=0.04$ kg/mol
Critical temperature[a]: $T_c=150.86$ K
Critical pressure[a]: $p_c=4.86$ MPa
Triple point[a]: $T_{\text{triple}}=83.8$ K

Phase change data (gas-liquid, bulk properties, $\varepsilon=1-T/T_c$):
Vapor pressure[b]: $p=p_c \exp\left[\frac{T_c}{T}(-5.904\varepsilon+11.25\varepsilon^{1.5}-0.763\varepsilon^3-1.697\varepsilon^6)\right]$

Liquid density[c]: $\rho=565.13(1+0.241\,66\varepsilon+1.941\,54\varepsilon^{0.41469})$
Surface tension[d]: $\sigma=0.037\,78\varepsilon^{1.277}$

Lennard-Jones parameters: $\varepsilon_{\text{LJ}}=120$ K, $\sigma_{\text{LJ}}=0.3405$ nm

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[a] Reference 39.
[b] Reference 40.
[c] Reference 41.
[d] Reference 42.

for a typical system of 100 Lennard-Jones (LJ) argon atoms in a volume of $4000(\sigma_{\text{LJ}})^3$ at $T=85$ K (parameters used for all calculations are compiled in Table I). The competition between the volume and surface terms gives rise to a maximum of $\Delta G(n)$, known as the nucleation barrier that occurs at the critical nucleus size,

$$n^* = \left(\frac{2s_1}{3}\frac{\gamma}{\Delta\mu}\right)^3, \tag{3}$$

and has a value $\Delta G^*=\Delta G(n^*)=(n^*\Delta\mu/2)$. Once again we would like to point out that we deal with an open ensemble in the framework of CNT: we assume the vapor pressure and thus the supersaturation to be constant for the nucleation stage of the phase transition.

In contrast, most simulations are performed in the canonical ensemble, where *NVT* are fixed. In this case, the formation of a drop of n molecules implies the subtraction of n molecules from the vapor, and thus changes the supersaturation in the system. Consequently, the work of formation of a drop is generally different. Using the same approximations involved in CNT, the MLD model (Ref. 9) yields the work of formation $\Delta F(n)$ of a cluster of n molecules in a closed *NVT* system to be

$$\Delta F(n) = -nkT\ln\frac{p_1}{p_{\text{eq}}} + \gamma A + n(kT - p_{\text{eq}}) + NkT\ln\frac{p_1}{p_0}, \tag{4}$$

where $p_1=(N-n)kT/(V-nv_l)$ is the actual vapor pressure exerted by the remaining $(N-n)$ vapor molecules when a cluster of size n is present in the system. In Eq. (4), the first three terms are similar to CNT except for the fact that the pressure p_1 is not fixed but depends on n. The fourth term arises from the depletion of vapor molecules when a droplet is formed. In the thermodynamic limit, Eq. (2) is recovered. Again, the size of the critical cluster n^*_{NVT} and the height of the nucleation barrier in the closed system are given by $(\partial\Delta F/\partial n)_{n^*_{NVT}}=0$ and $\Delta F^*\equiv\Delta F(n^*_{NVT})$.

The differences between the work of formation in a closed or in an open system are evident in Fig. 1. The dashed curve in Fig. 1(a) plots $\Delta F(n)$ for the same system discussed above. Contrary to the case of an open system and the CNT expression, $\Delta F(n)$ shows a second extremum, a minimum corresponding to a *stable* droplet in equilibrium with the remaining vapor in the system. Additionally, the shape of $\Delta F(n)$ and the height and location of the barrier ΔF^* depend critically on the system size. Figure 1(b) now shows $\Delta F(n)$ and $\Delta G(n)$ in a larger volume of $6000(\sigma_{\text{LJ}})^3$ at the same temperature. In the closed system, we no longer have a maximum in the free energy of formation: a simulation under those conditions will not show a nucleation event, even though the system is supersaturated. The special nature of a closed system prevents nucleation at conditions in which they would occur experimentally in an open system. In other words, it is not possible to observe nucleation at an arbitrary supersaturation in very small systems.

The quantity of prime interest besides the size and work of formation of a critical cluster is the nucleation rate. The nucleation rate J generally is calculated in the framework of the Zeldovich-Frenkel theory[18,19] as

$$J = K\exp\left(-\frac{\Delta W^*}{kT}\right), \tag{5}$$

where K is the so called kinetic prefactor, which can be obtained from kinetic theory and it is generally found to be comparatively invariant towards smaller changes in the parameters of the system.[20] In Eq. (5) we denoted the work of formation by W to indicate that depending on the constraints of the system at hand we might need to use the Helmholtz or Gibbs free energy to evaluate the nucleation rate.

Both CNT and MLD share the same approximations and shortcomings, namely, the assumptions of considering an ideal vapor, an incompressible liquid with bulk density, and the planar surface tension used in the description of the system. Additionally, one might argue that it is questionable to apply thermodynamics to a system that only consists of a handful of particles. Still, it has been found that this approach, despite its simplicity, describes the general behavior of the system surprisingly well. For example, the critical cluster size is predicted pretty accurately in most cases.[21–26] Unfortunately, the predictions of CNT for the actual nucleation barrier are not that precise. However, since we are only interested in the *deviations* that may arise from finite-size effects, knowledge of the actual quantitatively correct value of W^* is not strictly necessary. Moreover, it has been observed empirically and represented by the McGraw-Laaksonen scaling relations that the difference between CNT and the correct work of formation can be accounted for by just one temperature dependent constant.[27] Thus, the deviations from finite size will, as a first approximation, simply add to the potential error of the CNT result. Accordingly, even though quantitatively both CNT and MLD might be inaccurate, the correction arising from finite-size effects is expected to be roughly the same. If we know the difference between ΔF^* and ΔG^* we thus may predict the deviation in the nucleation rate due to finite-size effects by

$$\Delta J \equiv \frac{J_{\text{MLD}}}{J_{\text{CNT}}} = \exp\left(\frac{\Delta G^* - \Delta F^*}{kT}\right). \tag{6}$$

This deviation between the open and the closed systems depends on the system size and provides an estimate of the discrepancy one may expect between the simulation results and the actual nucleation rates. In the next section, we will analyze the importance of these deviations for the condensation of LJ argon in typical situations.

III. RESULTS AND DISCUSSION

A. A case study

We will study the differences between nucleation in a closed versus an open system under different sizes and conditions in order to show the influence of finite-size effects in more depth. As an example, let us analyze a system of LJ argon atoms whose properties are summarized in Table I.

Figure 2 is a contour plot of the difference in nucleation barriers $\Delta F^{*}-\Delta G^{*}$, in critical cluster sizes $\Delta n=(n_{NVT}^{*}-n^{*})$, and in nucleation rates ΔJ for a system of LJ argon atoms at 85 K as a function of N and V. The straight 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, ΔG^{*}, n^{*}, and J_{CNT} are constant along these lines. The deviations in the barrier and the critical size are in the range of a few kT or atoms, respectively, which translates in ΔJ of 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 light gray 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 approximately 30 molecules or obtain nucleation rates below $10^{20}\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ in a simulation with less than 200 molecules. We can also see how big and how far we are from the range accessible to experimental nucleation rates, which for instance in the case of expansion chambers is typically of $10^{5}-10^{10}\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$.[22,25,26]

One aspect might appear puzzling or counterintuitive at first sight: if we look at a constant number of molecules, say $N=100$, and then increase the volume we finally reach the region where the vapor is still supersaturated but no nucleation is possible. The reason is that the initial supersaturation gets smaller as we increase the volume. Accordingly, the size of the critical cluster gets bigger which increases the depletion effects to the extent that a developing cluster has consumed so many vapor molecules on his way to the critical size that the system is not supersaturated anymore—the cluster cannot keep on growing and dissolves again.

Figure 3 plots the deviations in the nucleation barrier for systems of up to 1000 molecules at the same temperature. We can observe that the range of volumes for which the error in the nucleation barrier is within a reasonable limit of $0.5kT$ expands as the number of particles is increased. Similarly, the range of cluster sizes and nucleation rates accessible in a simulation increases for bigger systems.

Just to get a better idea and to simplify the comparison let us analyze the influence of the size at a fixed value of the density N/V, or equivalently, the supersaturation. Figure 4 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., the density. Essentially, we look at cuts through Fig. 2 along the straight dashed lines of constant 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 supersaturation S_0 or, equivalently, the higher the nucleation barrier

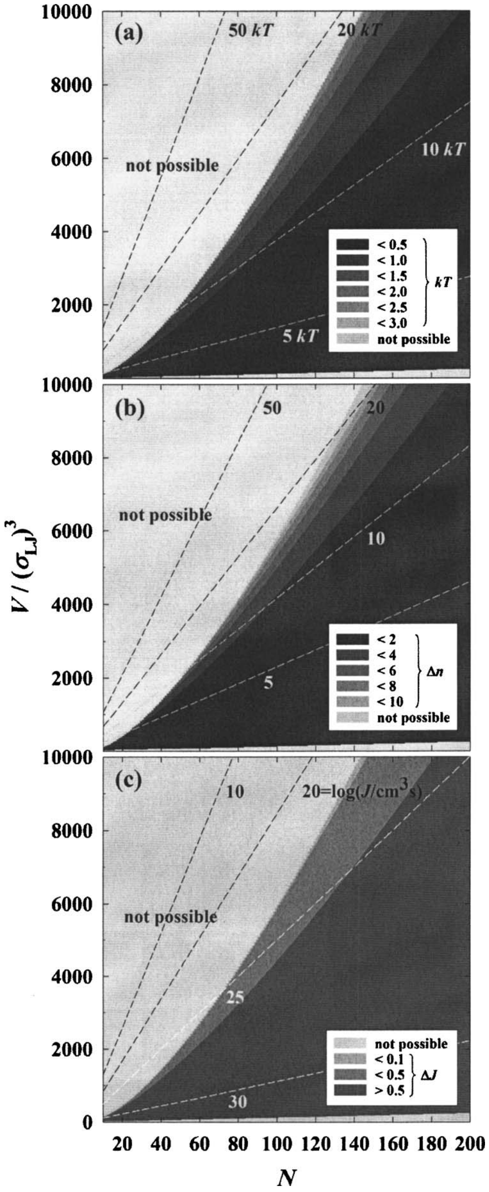

FIG. 2. (a) Contour plot of the differences in the nucleation barrier between the open and the closed systems, in units of kT for a system of Lennard-Jones argon atoms at 85 K, as a function of the total number of molecules N and the volume V. The light gray areas indicate regions where nucleation is not possible in the finite system. The dashed lines indicate different constant values of $\Delta G^{*}=5$, 10, 20, and $50kT$. (b) Contour plot of the differences in the size of the critical nucleus between the open and the closed systems for the same conditions. The dashed lines indicate different constant values of the size of the critical nucleus $n^{*}=5$, 10, 20, and 50 predicted by CNT. (c) Ratio of nucleation rates in the closed vs the open system for the same conditions. The dashed lines in this case indicate different values of the logarithm of the classical rate, i.e., $\log(J_{\mathrm{CNT}}/\mathrm{cm}^{3}\ \mathrm{s})=10$, 20, 25, and 30.

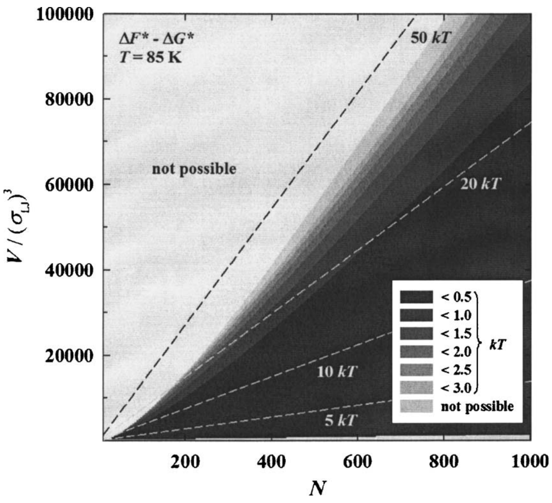

FIG. 3. Same as Fig. 2(a) for a larger range of sizes and volumes.

ΔG^* and n^*. It is also evident that depending on the value of the supersaturation we are interested in, there is a minimum system size required for nucleation in a finite system to be feasible and accurate. For example, notice the deviations in the rate in Fig. 4(c). Let us assume that a deviation smaller than 50% in the rate is acceptable, as indicated by the horizontal line. We then face a dilemma: higher barriers that are closer to experimental conditions result in much longer simulation times because the rate exponentially decreases with ΔG^*. We will naturally be tempted to reduce the system size N in order to reach longer time scales on the computer.

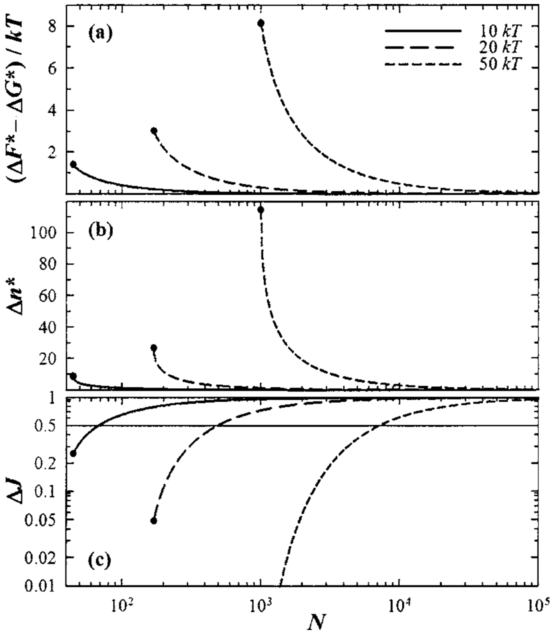

FIG. 4. (a) Plot of the differences in the nucleation barrier between the open and the closed systems, in units of kT for a system of Lennard-Jones molecules at 85 K, as a function of the total number of molecules N for three different values of the density. The densities correspond to $\Delta G^* = 10kT$ (solid line), $20kT$ (long-dashed line), and $50kT$ (short-dashed line). (b) Differences in the size of the critical nucleus between the open and the closed systems for fixed densities corresponding to $n^* = 10$ (solid line), 20 (long-dashed line), and 50 (short-dashed). (c) Ratio of nucleation rates in the closed vs the open system for fixed densities corresponding to $\log(J_{\mathrm{CNT}}/\mathrm{cm}^3\,\mathrm{s}) = 10$ (solid line), 20 (long-dashed line), and 25 (short-dashed line).

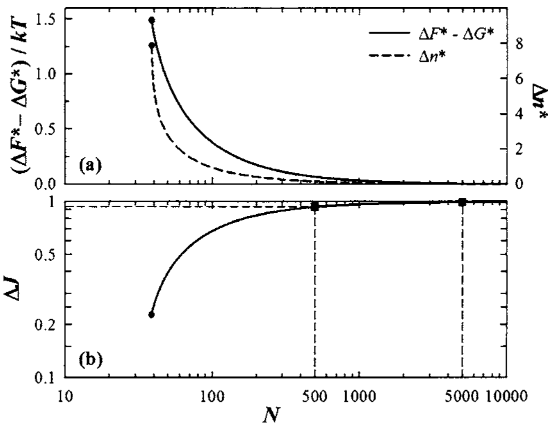

FIG. 5. (a) Difference of nucleation barriers (solid) and critical cluster sizes (dashed) in CNT and MLD for a Lennard-Jones argon system at the density chosen by Yasuoka and Matsumoto (Ref. 28) as a function of the total number of particles N. (b) Deviation of the nucleation rate for the same system. The two squares indicate the original system simulated with $N = 5000$ in comparison with a system at $N = 500$.

However, we encounter significantly higher finite-size effects for higher barriers and we are forced to use even larger N to compensate. As a result, we might end up running in circles when trying to reach experimental conditions in a MD simulation.

B. Optimization of the system size

Let us get back to the most practical question: which is the optimal system size we can choose for a given problem? We can use our previous analysis to optimize the size and estimate a bound of the size effect deviation in choosing a particular system size. 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. 22. Yasuoka and Matsumoto[28] simulated a system containing 5000 LJ-argon atoms at $T = 80.4$ K in a cubic box of $V = (60\sigma_{\mathrm{LJ}})^3$. The chosen volume and number of particles as well as the temperature are typical for a number of MD simulations of nucleation.[24,29–32] Figure 5 shows the predicted 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: first, at a system size of, e.g., 500 atoms, the deviation is still less than $0.1kT$ in the barrier or less than 10% in the rate, but we can save a factor of up to 100 in the calculation time. In other words, almost 100 times more simulations or two orders of magnitude of nucleation rates closer to experiment can be simulated in the same disposable time. 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.[20] Second, Fig. 5 impressively shows that a further increase of N is meaningless at this density because the error does not become significantly smaller for larger N. Simulating a system of, say, 50 000 atoms can be considered therefore as a waste of simulation time because no further information is gained and the error inherited by finite size is not changed at all, being practically zero. We also repeated the simulations in Ref. 22 at $N=500$, and we were able to reproduce the reported rate with an error of less than 10% in the rate.

Many simulations of nucleation have been performed on Lennard-Jones argon.[24,28–30,32,33] In the absence of any clear criterion to select the size, the number of molecules typically used in these simulations tends to be the largest possible in terms of computer capacity, on the range of $10^3 - 10^5$ molecules. Our analysis indicates that most of these simulations are practically unaffected by inaccuracies due to finite-size effects of the kind discussed in this paper—at the expense of a system that was mostly much larger than actually needed.

IV. MD SIMULATIONS OF SMALL SYSTEMS

In order to verify the validity of the predictions of the finite-size effects study, a number of MD simulations of LJ argon were performed at different system sizes from $N=32$ to 512 atoms. The simulations were performed at $T=50$ K for a high supersaturation ($S_0=869$) and a low supersaturation ($S_0=610$) with the corresponding system densities (N/V) of $343/(16\text{ nm})^3$ and $343/(18\text{ nm})^3$. The CNT predictions for the barriers are $\Delta G^*=22.5kT$ and $\Delta G^*=25kT$, respectively. The size of $N=343$ was predicted to be sufficiently large in the way described in the previous section. A carrier gas was used to thermostat the system in order to rule out any serious artifacts possibly arising from direct thermostating methods. The simulation method and parameters of argon are similar to the ones in Ref. 22 except that we used a simple velocity-scaling thermostat instead of a Nosé-Hoover thermostat on the carrier gas. The vapor-carrier-gas ratio was always 1:1 and each condition was simulated at least 100 times, each run starting from a different configuration of the vapor. Typically, each system showed one nucleation event. The rates were obtained by a newly developed method based on the concept of mean first-passage time (MFPT). The method will be discussed in more detail elsewhere,[34] but the idea is very simple: for each simulation, the size of the largest cluster in the system is noted at regular intervals (1000 time steps in our case), and the time at which each size n appears for the first time, $t_i(n)$, is stored. The *mean* first-passage time $\tau(n)$ for each size n is simply obtained by averaging $t_i(n)$ over several repetitions of the simulations with different initial configurations. The MFPT $\tau(n)$ is then fitted to the simple expression,

$$\tau(n) = \frac{\tau_J}{2}[1 + \mathrm{erf}(b(n^* - n))], \tag{7}$$

where τ_J, n^*, and b are the three fitting parameters, and $\mathrm{erf}(x)$ is the error function. The nucleation rate J is then given in terms of τ_J as

$$J = \frac{1}{\tau_J V}. \tag{8}$$

Figure 6(a) shows the predicted deviation of the nucleation rate as a function of the total number of atoms N, similar to Fig. 5(b). In Fig. 6(b) the nucleation rates of the MD simulations are given. The simulations clearly follow the same trend as predicted by the finite-size effects analysis: for smaller systems, the nucleation rate drops considerably. More notably, most simulation runs for the smallest system size did not succeed to nucleate a cluster. For $S_0=869$ (open symbols) at $N=32$, a cluster of size 30 was found only in 34 out of 100 simulations and none of the systems showed a fully condensed cluster of 32 atoms, indicating that the cluster may have reached a stable minimum such as the example in Fig. 1(a). In the case of the higher barrier ($S_0=610$, filled symbols) at $N=32$, no system has succeeded in forming a cluster larger than $n=15$, confirming that the finite-size effects are more pronounced in the high barrier case. For the cases in which the formation of a nucleus occurred so rarely, the reported "rates" for these systems in Fig. 6(b) are estimated as the fraction of systems that succeeded to nucleate a cluster in 100 simulations in the total simulation time (500 ns in this study). For the system with $N=32$ and $S_0=610$ mentioned above, the reported rate is just very roughly estimated as one nucleus per 100 simulations to at least indicate how sharply the nucleation rate drops at small system sizes.

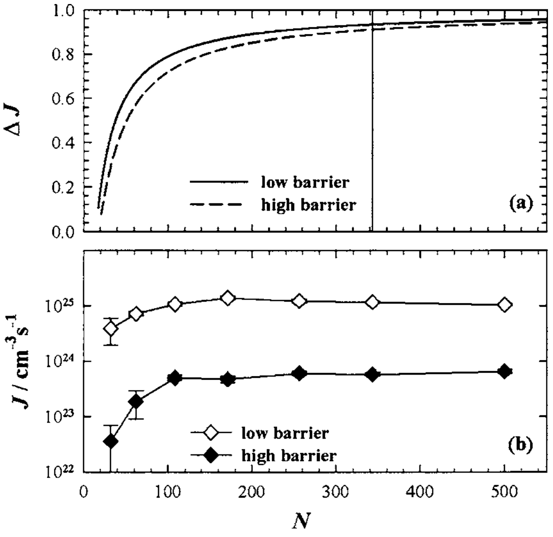

FIG. 6. (a) Predicted deviation of the nucleation rate ΔJ as a function of N at 50 K for a system of LJ argon atoms with a low (solid) and high (dashed) nucleation barriers. The vertical line marks the starting system size of $N=343$ atoms. (b) Nucleation rates obtained from MD simulations at 50 K and constant density as a function of N. The open symbols correspond to a high density, low barrier system ($S_0=869$ and $\Delta G^*=22.5kT$), while the filled symbols represent a system with a higher nucleation barrier ($S_0=610$ and $\Delta G^*=25kT$). The nucleation rate drops for small systems as predicted.

The nucleation rate shows no significant change beyond a size of $N=200$, which is in good agreement with the prediction shown in Fig. 6(a). Note that the latter case shows the difference in rate compared to an open system, while Fig. 6(b) only shows the actual rate itself. Although the nucleation rates seem to drop again slightly for higher N in the low barrier case, these small deviations most likely arise from other competing factors such as the thermostating effects. The larger the system, the higher the chance that the system will show more than one nucleus or at least a higher number of larger fluctuations, which will inevitably increase the latent heat released to the system. Since the cooling of the system is performed by the same relative amount of carrier gas, the rate will go slightly down. This would also explain the slightly different trend in the high barrier case because this "thermostat effect" is less pronounced at a higher barrier, i.e., a lower nucleation rate. A thorough discussion of the influence of different thermostats on simulations of nucleation is currently in preparation.[35]

V. CONCLUSION

The process of nucleation and, in particular, the formation of a liquid drop proceeds differently in closed and open systems. In the closed system, finite-size effects can become very important, for example, in molecular dynamics simulation of nucleation, where we typically deal with a fixed number of molecules and a fixed volume of the system. The relevance of these effects can be quantified using a rigorous thermodynamic description in terms of the modified liquid drop (MLD) model. This model properly accounts for the effects of the finite volume and the depletion of molecules involved in the formation of one liquid drop in a finite system. Our analysis can be extended to the potential presence of two or more clusters in the system and the usage of a real instead of an ideal gas without changing the implications of our results.

In the cases studied, the magnitude of the deviations can reach several kT in the nucleation barrier or tens of molecules in the size of the critical cluster, which translate in deviations of the nucleation rate of up to two or three orders of magnitude for very small systems. A more crucial effect of the confinement is the alteration of the onsets of nucleation. For small systems, it is impossible to observe nucleation in a wide range of supersaturation at which it would easily occur in a big system or experiment. These effects become increasingly less important as the number of molecules in the system grows. In fact, the results of most MD simulations of nucleation found in literature show only little and commonly negligible size effects. However, it turns out that these simulations could have been performed safely at much smaller systems without encountering significant size effects on the results.

The method described in this paper provides a simple starting point to estimate a minimum system size beyond which finite-size effects become insignificant. It can save valuable simulation time on single simulations in favor of more simulations at the same conditions of nucleation, leading to better statistics of the observed state. Alternatively, simulations with a smaller number of atoms can run longer, making lower supersaturations more accessible. We could also verify the validity of the predictions by MD simulations of LJ argon vapor.

Although most Monte-Carlo (MC) simulations of nucleation are performed in the NPT or μVT ensemble, these conclusions will also affect MC simulations in the canonical ensemble. Finally, our analysis and results are also applicable to other situations, such as crystallization,[36] capillary condensation,[37] or the melting of nanoclusters.[38]

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[1] D. W. Oxtoby, J. Phys.: Condens. Matter **4**, 7627 (1992).
[2] D. Kashchiev, *Nucleation: Basic Theory With Applications* (Butterworth-Heinemann, Oxford, 2000).
[3] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).
[4] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed. (Academic, San Diego, 2002).
[5] S. Auer and D. Frenkel, Nature (London) **413**, 711 (2001).
[6] P. R. ten Wolde and D. Frenkel, J. Chem. Phys. **109**, 9901 (1998).
[7] B. Chen, J. I. Siepmann, K. J. Oh, and M. L. Klein, J. Chem. Phys. **115**, 10903 (2001).
[8] C. L. Weakliem and H. Reiss, J. Chem. Phys. **99**, 5374 (1993).
[9] D. Reguera, R. K. Bowles, Y. Djikaev, and H. Reiss, J. Chem. Phys. **118**, 340 (2003).
[10] K. K. Mon and K. Binder, J. Chem. Phys. **96**, 6989 (1992).
[11] M. S. S. Challa, D. P. Landau, and K. Binder, Phys. Rev. B **34**, 1841 (1986).
[12] L. G. MacDowell, V. K. Shen, and J. R. Errington, J. Chem. Phys. **125**, 034705 (2006).
[13] F. H. Streitz, J. N. Glosli, and M. V. Patel, Phys. Rev. Lett. **96**, 225701 (2006).
[14] R. S. Aga, J. R. Morris, J. J. Hoyt, and M. Mendelev, Phys. Rev. Lett. **96**, 245701 (2006).
[15] F. F. Abraham, *Homogeneous Nucleation Theory: The Pretransition Theory of Vapor Condensation* (Academic, New York, 1974).
[16] M. Volmer and A. Weber, Z. Phys. Chem **119**, 227 (1926).
[17] R. Becker and W. Döring, Ann. Phys. **24**, 719 (1935).
[18] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946).
[19] Y. B. Zeldovich, Acta Physicochim. URSS **18**, 1 (1943).
[20] A. Laaksonen, V. Talanquer, and D. W. Oxtoby, Annu. Rev. Phys. Chem. **46**, 489 (1995).
[21] R. Strey, P. E. Wagner, and T. Schmeling, J. Chem. Phys. **84**, 2325 (1986).
[22] R. Strey, P. E. Wagner, and Y. Viisanen, J. Phys. Chem. **98**, 7748 (1994).
[23] J. Hrubý, Y. Viisanen, and R. Strey, J. Chem. Phys. **104**, 5181 (1996).
[24] K. Laasonen, S. Wonczak, R. Strey, and A. Laaksonen, J. Chem. Phys. **113**, 9741 (2000).
[25] J. Wölk and R. Strey, J. Phys. Chem. B **105**, 11683 (2001).
[26] K. Iland, J. Wedekind, J. Wölk, P. E. Wagner, and R. Strey, J. Chem. Phys. **121**, 12259 (2004).
[27] R. McGraw and A. Laaksonen, Phys. Rev. Lett. **76**, 2754 (1996).
[28] K. Yasuoka and M. Matsumoto, J. Chem. Phys. **109**, 8451 (1998).
[29] S. Toxvaerd, J. Chem. Phys. **115**, 8913 (2001).
[30] S. Toxvaerd, J. Chem. Phys. **119**, 10764 (2003).
[31] S. Toxvaerd, Mol. Simul. **30**, 179 (2004).
[32] K. K. Tanaka, K. Kawamura, H. Tanaka, and K. Nakazawa, J. Chem. Phys. **122**, 184514 (2005).
[33] S. Wonczak, Ph.D. thesis, Universität zu Köln, 2001.
[34] J. Wedekind, R. Strey, and D. Reguera, J. Chem. Phys. (submitted).
[35] J. Wedekind, R. Strey, and D. Reguera, J. Chem. Phys. (in preparation).
[36] Y. Chushak and L. S. Bartell, J. Phys. Chem. A **104**, 9328 (2000).
[37] P. I. Ravikovitch, A. Vishnyakov, and A. V. Neimark, Phys. Rev. E **64** 011602 (2001).
[38] F. Baletto and R. Ferrando, Rev. Mod. Phys. **77**, 371 (2005).
[39] A. L. Gosman and R. D. McCarty, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.), (U.S. GPO, Washington, D.C., 1969), Vol. 27.
[40] R. B. Stewart and R. T. Jacobsen, J. Phys. Chem. Ref. Data **18**, 639 (1989).
[41] C. A. Crommelin, Commun. Phys. Lab. Univ. Leiden **118a**, 1 (1911).
[42] F. B. Sprow and J. M. Prausnitz, Trans. Faraday Soc. **62**, 1097 (1966).