

Cluster sizes in direct and indirect molecular dynamics simulations of nucleation

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We performed molecular dynamics simulations of a Lennard-Jones fluid, and compared the sizes of critical clusters in direct simulations of a nucleation event in vapor phase with the sizes of clusters in stable equilibrium with the surrounding vapor. By applying different cluster criteria it is shown that both the critical clusters and the equilibrium clusters have dense cores of similar size but the critical clusters have more outlying cluster atoms surrounding this core. The cluster definition introduced by ten Wolde and Frenkel [J. Chem. Phys. **109**, 9901 (1998)], where each cluster atom must have at least five neighboring atoms within the distance of 1.5 times the Lennard-Jones length parameter, agrees well with the cluster size obtained from classical nucleation theory, and we find this agreement to be independent of temperature. The cluster size obtained from the observed nucleation rates by the first nucleation theorem is larger than the classical estimate and much smaller than the size given by the density profile of the equilibrium cluster. © 2009 American Institute of Physics. [doi:10.1063/1.3279127]

I. INTRODUCTION

One of the major advantages of the molecular dynamics (MD) method in the simulation of gas-liquid transformation by nucleation is the possibility of tracking the formation of the clusters out of the homogeneous vapor phase. The application of the MD method is very much akin to a real nucleation experiment: molecules at gas-phase density are placed in a simulation box and the simulation is run until the critical cluster appears and starts growing. Contrary to a real experiment MD simulations offer first-hand information on the size and evolution of the clusters. In recent literature this kind of MD method has been termed “direct nucleation simulation.”^{1,2} Unfortunately, the rate of appearance of critical clusters (nucleation rate) must be exceedingly high for the simulation to be completed in a reasonable time. The nucleation rate in a MD simulation is much higher and the size of the critical cluster much smaller than those observed in typical experimental conditions.

Alternatively, one can perform MD simulations which start from a liquidlike cluster surrounded by a vapor phase. In this case the system is in a compact volume to enforce a cluster-vapor equilibrium state. This method is known as “indirect nucleation simulation.”¹⁻³ Large clusters can be simulated in this way and, assuming that the stable equilibrium cluster corresponds to the unstable critical cluster in a direct simulation, important information on the size and the structure of the critical cluster can be gained. The indirect method does not give the nucleation rate or the formation free energy of the cluster (the actual formation of the critical cluster is not simulated), but the first nucleation theorem^{4,5} can be used to assess these quantities, possibly with the aid of the direct simulation method for small critical clusters.¹

Direct nucleation simulation method has been used extensively in recent years and some studies applying the indirect method have been published. Most studies concentrated on the computationally efficient Lennard-Jones (LJ) fluid^{2,6-8} but other substances have been studied as well.⁹ In a recent work,¹ we simulated the nucleation of LJ fluid by direct and indirect means and used thermodynamic integration to obtain formation energies. We saw that the relation between the equilibrium cluster size and the chemical potential of the vapor appears linear as in classical nucleation theory (CNT), but the slope is different from CNT. The result is not in agreement with Monte Carlo (MC) simulations¹⁰ and a scaling theory.¹¹ On the other hand, we found that the MD results were bolstered up by density functional calculations.¹

In our previous work¹ the MD simulations were done only at one temperature close to the triple point. We were not able to compare cluster sizes from direct and indirect simulations at the same vapor conditions; instead the correspondence of clusters in those methods was based on the fact that the clusters seemed to lie on the same line. Furthermore, of the many possibilities to define a cluster and to calculate its particle content, only the Stillinger definition¹² and the excess number of particles obtained from density profile were considered. In the present study, we compare direct and indirect MD simulations of a LJ system at two widely separated temperatures and using different cluster definitions. The results are also compared with recently reported data.^{1,2,13}

In Sec. II we present our simulated systems and the simulation methodologies. Results are shown and discussed in Sec. III, and the conclusions presented in Sec. IV. We show that the cluster definition originally presented by ten Wolde and Frenkel¹⁴ is in good agreement with CNT and fairly close to the particle content given by the nucleation

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theorem. The simulations however suggest that there are important differences in cluster structure between equilibrium clusters and critical clusters.

II. METHODS

A. Cluster definitions

The most commonly used cluster definition is the Stillinger criterion,¹² which requires each particle to have a neighbor within a certain radius r_c in order to belong to the same cluster. More recently, ten Wolde and Frenkel argued¹⁴ that a cluster particle should reside in a liquidlike environment with the local density much higher than the vapor density and proposed a definition where a cluster atom should have at least five neighboring atoms. The more stringent requirement eliminates outlying particles, which, although belonging to the Stillinger cluster, are rather part of the vapor. Other variants of the original ten Wolde–Frenkel (TWF) can also be considered, for example, one could include particles with five neighbors and their neighbors, independent of how many neighbors the latter particles have.¹⁵ We studied the TWF clusters according to the original definition but varying the minimum number of neighbors from one to five. In the following, we denote clusters where each atom has at least n neighbors by TWF(n). Thus, TWF(1) is the Stillinger cluster. In all cases we used the conventional value $r_c=1.5\sigma$ for the connectivity distance.

A quite different cluster definition gives the particle content of a cluster as an excess number of particles over the vapor:

$$\Delta N^* = 4\pi \int_0^\infty dr r^2 (\rho(r) - \rho_v), \quad (1)$$

where $\rho(r)$ is the radial density profile and ρ_v is the density of the homogeneous vapor. Compared to the cluster definitions above, the definition according to Eq. (1) corresponds more closely to the thermodynamic idea of cluster being a density fluctuation.

Comparison of the observed cluster sizes with CNT values requires knowledge of bulk equilibrium properties. In CNT the number of particles in the critical cluster is given by

$$\Delta N^* = \frac{32\pi\gamma_\infty^3}{3\rho_l^2(\Delta\mu)^3}, \quad (2)$$

where the needed input data are surface tension of planar interface γ_∞ , density of bulk liquid ρ_l , and chemical potential difference $\Delta\mu$ between the supersaturated and saturated vapor. The first two quantities are obtained from recent fits to MD data by Vrabec *et al.*¹⁶ To calculate chemical potential we simulated pressure-density correlation in bulk vapor systems using the method of Linhart *et al.*¹⁷ and fitted the data to a polynomial function. We then used the Gibbs–Duhem equation to obtain the chemical potential. A more detailed description of the steps taken in this procedure can be found in Ref. 1. The value of the chemical potential of saturated vapor was found by using the equilibrium vapor density from Ref. 16.

B. Indirect simulations

The simulated systems consist of LJ particles with the potential truncated and shifted at 2.5σ , where σ is the LJ length parameter. We chose a rather short cutoff to be able to simulate cluster-vapor equilibrium in very small simulation boxes. A long cutoff makes it necessary to use a large simulation box, and if the box volume exceeds evaporation boundary,¹⁸ stable cluster-vapor equilibrium cannot be simulated. Also, there are accurate bulk equilibrium data available for LJ fluid with cutoff at 2.5σ .¹⁶

The indirect simulations were started by placing an intact cluster in a cubic simulation box with periodic boundaries. The minimum energy configurations provided in the Cambridge Cluster Database¹⁹ were used for the startup. During an initialization period of 500 ps vapor phase formed from the atoms evaporated from the cluster. After the initialization, data on cluster size according to various definitions were collected for 10 ns. An average of ten simulation runs was calculated to obtain better statistics, totaling to 100 ns simulation time for each system size. We also calculated the number of particles in 0.1σ -thick spherical layers centered to the center of mass of the cluster to obtain radial density profiles. For temperature regulation the system was coupled to a Berendsen thermostat, and to ensure constant temperature at every part of the system the cluster and the vapor were thermostatted separately. The size of the simulation box was determined by the method of trial and error. In a too large box the cluster size fluctuated wildly and sometimes the cluster vanished altogether. In a too compact box the density profile did not reach a constant vapor density near to the box edge.

The simulations were performed at temperatures $T=0.65$ and $T=0.8$. Here the unit of temperature is ϵ/k_B , where ϵ is the LJ energy parameter. The critical temperature of the LJ fluid with the potential cut and shifted at 2.5σ is $T_c=1.0779$,¹⁶ so that $T=0.8$ is a relatively high temperature. The triple point temperature is $T_{tr}=0.618$,²⁰ which places both the investigated temperatures above the triple point. The total number of particles in the indirect simulations varied from 30 to 350 at $T=0.65$ and from 50 to 500 at $T=0.8$.

C. Direct simulations

We also performed direct simulations with the same potential cutoff and temperatures as in the indirect simulations. The temperature was regulated with the Berendsen thermostat. Random starting configurations were obtained by running the simulations first at a higher temperature, after which the temperature was quenched to the desired value. The simulations were run until the largest TWF(5) cluster reached the size of 250 atoms.

The system sizes were chosen so that the finite-size effects on the nucleation rate were less than about 10%. This was done with the method presented in Ref. 21, with the modification that instead of assuming the vapor surrounding the cluster to be ideal, we used our simulated pressure-density correlations. The system sizes used are listed in Table I.

TABLE I. Results of the direct nucleation simulations. Given are temperature T (in units of ϵ/k_B), saturation ratio S , number of particles in the system N_{sys} , nucleation rate J (in units of $\sqrt{\epsilon n^{-1}}/\sigma^4$), and the critical size N^* . The indices TWF(1) and TWF(5) indicate that TWF cluster definition with 1 and 5 neighbors, respectively, were used.

T	S	N_{sys}	$J_{\text{TWF}(1)}$	$J_{\text{TWF}(5)}$	$N_{\text{TWF}(1)}^*$	$N_{\text{TWF}(5)}^*$
0.65	3.415	2800	1.1×10^{-10}	1.1×10^{-10}	51	27
0.65	3.530	2300	3.4×10^{-10}	3.4×10^{-10}	50	27
0.65	3.638	2000	1.1×10^{-9}	1.1×10^{-9}	46	23
0.65	3.836	1400	4.9×10^{-9}	5.1×10^{-9}	47	22
0.65	4.011	1100	1.7×10^{-8}	1.9×10^{-8}	41	17
0.80	1.671	5600	2.5×10^{-9}	2.9×10^{-9}	131	53
0.80	1.684	4000	4.3×10^{-9}	4.6×10^{-9}	128	52
0.80	1.696	4500	6.5×10^{-9}	7.3×10^{-9}	129	51
0.80	1.708	3400	9.4×10^{-9}	1.2×10^{-8}	129	47

The nucleation rate and critical size were obtained using the mean first passage time (MFPT) method.⁶ The MFPT data were gathered for all the different TWF(n) neighbor conditions. The obtained nucleation rates are relatively insensitive to the cluster definition used (as can be seen in Table I and in Ref. 13), but the MFPT critical sizes from different cluster definitions are quite different from each other.¹³

The critical size can also be obtained from the nucleation rate using the nucleation theorem, written in the form

$$\frac{\partial \ln J}{\partial \ln S} \approx \Delta N^* + 1, \quad (3)$$

where the saturation ratio is $S = \exp(\Delta\mu/(k_B T))$. The critical size is found by making a linear fit to a $\ln J / (\ln S)^{-2}$ plot, which corresponds to the CNT scaling. With cluster definition-independent MFPT nucleation rates, the critical size from Eq. (3) can also be considered independent of the cluster definitions.¹³

There are some obstacles that limit the range of supersaturations available for direct nucleation simulations in general and the MFPT method in particular. The limiting factor at lower supersaturations is the excessive computational time required as nucleation onset will on average occur later than in more dense vapors, and at the same time the system size required to avoid the finite-size effects becomes larger. At high supersaturations on the other hand it becomes increasingly difficult to distinguish nucleation from the subsequent growth of the cluster from a MFPT plot, making it eventually impossible to reliably use the MFPT method.⁶

III. RESULTS AND DISCUSSION

A. Indirect simulations

Our results for cluster-vapor equilibrium are shown in Fig. 1. The cluster sizes obtained from the Stillinger definition and from the density profile [Eq. (1)] agree qualitatively with our previous work;¹ both definitions yield larger sizes than CNT and they scale linearly as a function of $(\Delta\mu)^{-3}$ (beyond a size larger than a certain threshold size). There are nevertheless some noticeable differences compared to our previous results. The Stillinger and excess number sizes do not extrapolate to zero as $(\Delta\mu)^{-3} \rightarrow 0$; this is more obvious at

$T=0.8$. Also, the sizes from the Stillinger definition are larger than from the profile, which is again more clearly seen at $T=0.8$, whereas in our previous work¹ we found that these sizes were practically equivalent. In those simulations, however, the temperature was lower (relative to the critical temperature). In the present simulations the profile size coincides with the TWF(3) size at $T=0.8$ and with the TWF(2) size at $T=0.65$. If the temperature was still lower, a good agreement with the Stillinger size, TWF(1), would probably be found.

Increasing the required number of neighboring cluster particles from one to five makes the cluster sizes approach CNT size. The best case is $n=5$, which is the original TWF definition.¹⁴ The results for TWF(5) clusters shown in Fig. 1

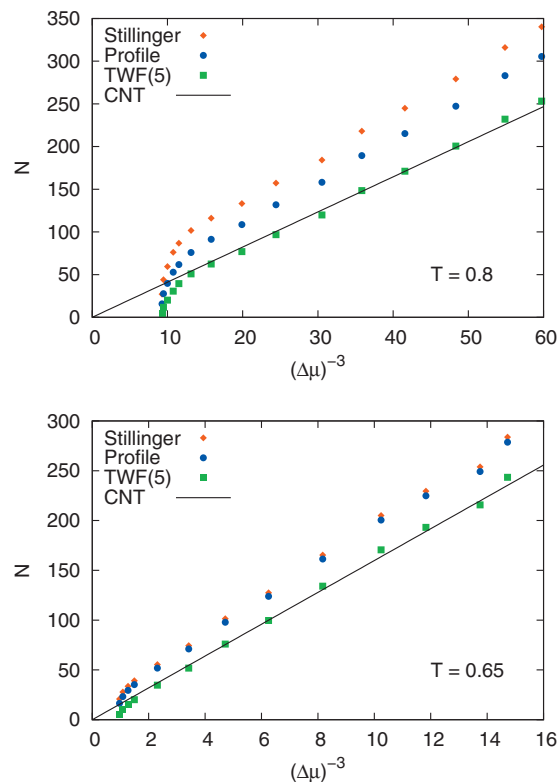


FIG. 1. The number of particles in the equilibrium clusters as a function of $(\Delta\mu)^{-3}$ at $T=0.8$ (upper figure) and $T=0.65$ (lower figure). Temperature is given in units of ϵ/k_B and chemical potential μ in units of ϵ . CNT is compared with Stillinger cluster definition, TWF cluster with five neighbors, and excess number of particles obtained from the density profile.

indicate very good agreement with CNT data. It is noteworthy that the size of the TWF(5) clusters and CNT clusters agree equally well at both temperatures.

The cluster sizes in Fig. 1 seem to converge to zero at a common value on the $\Delta\mu^{-3}$ scale. While this point is approximately where the spinodal is located according to our simulations of bulk vapor, we do not claim that the simulations actually imply decreasing and finally vanishing cluster size when spinodal is approached, because there is significant problems involved in simulations of very small systems. For the simulation to yield meaningful results, the vapor surrounding the cluster should be a fair approximation of the bulk vapor at the density given by the tail part of the density profile. This is not an issue at low temperatures where the vapor is almost solely monomers, but at high temperatures quite large clusters appear in the vapor. In a small simulation box there is not enough space for such clusters to form, and the pressure of the vapor is not the same as the pressure of the bulk vapor in a large volume. In other words, the bulk equation of state is not valid. We believe that this is what happens for the cases where the cluster size deviates from the linear scaling in Fig. 1. The linear part of the data begins where the equilibrium cluster size is approximately twice the average size of the largest cluster observed in those simulations of large vapor systems that we used to obtain the pressure-density correlation. Undoubtedly, a cluster-vapor equilibrium is also simulated in our very small systems, but the vapor around the cluster does not have the properties of the bulk vapor.

The particle content of clusters derived from various cluster definitions are compared in Fig. 2 relative to the CNT prediction. Also here we see that the results for TWF(5) clusters are closest to CNT, although CNT tends slightly to overestimate the size of small clusters and underestimate the size of larger ones. The different cluster definitions converge and approach CNT value as the cluster size grows. We stress again that the results for the smallest clusters, where $N/N_{\text{CNT}} < 0.9$, do not describe an equilibrium with a realistic bulk vapor.

The number of particles in the cluster according to CNT should properly be compared with the excess number of particles obtained from the profile, because they are both thermal quantities referring to the equimolar surface of the cluster. Therefore, the difference of the two definitions quantifies the deviation of CNT from the true particle content. It is intriguing to note from Figs. 1 and 2 that the profile size is always larger than the CNT size, although nothing definitive cannot be said about the smallest clusters.

In this work we only studied small clusters, which are the most relevant to nucleation. In a recent paper Horsch *et al.*² simulated large clusters for the same LJ system at temperatures $T=0.65$ – 1.0 . In Fig. 3 we show their data together with ours at $T=0.65$ and $T=0.8$. The clusters in Fig. 3 are TWF(4) clusters. It can be seen that the data sets follow the same linear scaling. Data for large TWF(5) clusters are not available, but Figs. 1 and 3 together suggest that also large TWF(5) clusters conform to CNT.

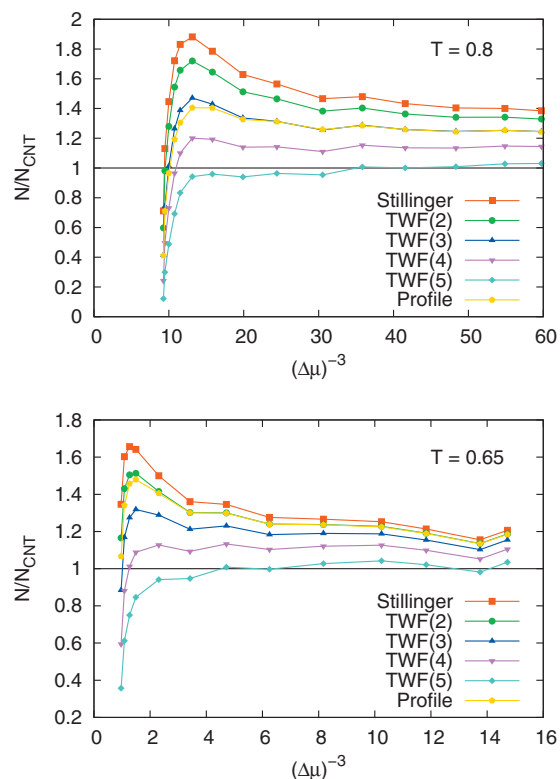


FIG. 2. The particle number content of equilibrium clusters with respect to CNT prediction at $T=0.8$ (upper figure) and $T=0.65$ (lower figure). Stillinger clusters, TWF(n) clusters with $n=2$ – 5 neighbors, and excess number of particles (profile) are compared.

B. Direct simulations

The MFPT analysis results of the direct simulations are shown in Table I. Our simulations confirm that the nucleation rates obtained from MFPT with different cluster definitions are quite close to each other, as was found by Wedekind and Reguera.¹³ The lower the density the closer the nucleation rates from different cluster definitions are to each other. The logarithmic nucleation rate values $\ln J((\ln S)^{-2})$ can be fitted well to a line, and the slope of this line gives the number of particles in the cluster by Eq. (3).

The cluster sizes from direct simulations along with part of the data from indirect simulations are shown in Fig. 4. The cluster sizes TWF(1)–TWF(5) from indirect simulations are shown by the red lines with the topmost line representing

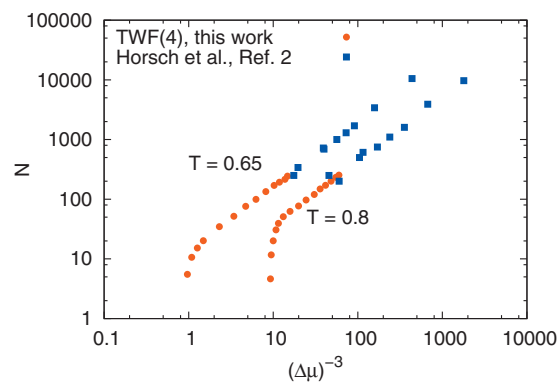


FIG. 3. Comparison of cluster sizes from present simulations and from Ref. 2. TWF cluster definition with four neighbors is used.

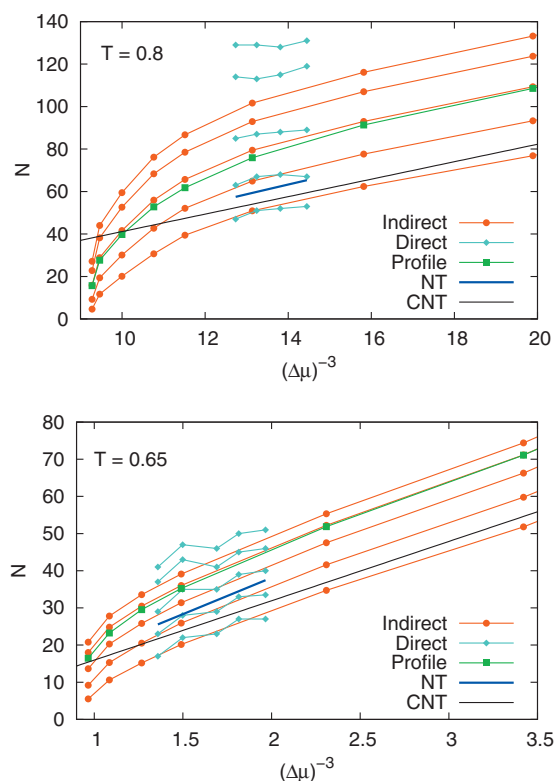


FIG. 4. Comparison of direct and indirect simulations. The two sets of curves (direct and indirect) correspond to TWF(n) clusters from $n=1$ (top-most curves) to $n=5$. Also shown is particle number content of the cluster obtained from the density profile, nucleation theorem and CNT.

TWF(1) (Stillinger) clusters. The sizes from the density profile are also shown (green line). The shorter lines are the TWF(n) sizes from the direct simulations via MFPT analysis, again the topmost line being the TWF(1) clusters. Finally, critical sizes obtained using the nucleation theorem are shown by thick blue lines.

The TWF(4) and TWF(5) sizes from direct and indirect simulations agree quite well, but for TWF(1) and TWF(2) clusters there is a marked discrepancy between the two methods, especially at $T=0.8$. These observations indicate that the dense core of the equilibrium cluster has the same size as the core of the critical cluster in the same vapor, but the critical cluster has more outlying members around the core. The latter particles are only counted belonging to the cluster in a definition where the cluster atom is not required to have many neighbors.

The cluster size obtained using the nucleation theorem is somewhat larger than the size given by CNT. Wedekind and Reguera¹³ reported that the nucleation theorem size is in close agreement with the TWF(5) size in direct MD simulations of a LJ system when Stillinger radius 1.5σ is used, but our simulations do not support that observation. The nucleation theorem size does not coincide with any of the TWF(n) clusters at the studied temperatures. At $T=0.65$ the nucleation theorem sizes are found to be between the TWF(3) and TWF(4) sizes, and for $T=0.8$ between the TWF(4) and TWF(5) sizes. Obviously temperature is a cause for the differences, while the difference in the potential cutoff between the present work and Ref. 13 is another possible factor.

It is reasonable to assume that nucleation theorem should give the correct size of the density fluctuation (cluster), which in turn should be equal to the size obtained from the density profile. Figure 4 indicates, however, that the profile size is considerably larger than the nucleation theorem size at both the temperatures. This could be seen as a further indication of the structural dissimilarity between the critical cluster and the equilibrium cluster. On the other hand, the TWF(n) sizes show that there are more molecules in the vicinity of the core of the critical cluster than in the vicinity of the equilibrium cluster, which suggests that the excess density of the critical cluster profile should encompass larger amount of atoms than the equilibrium profile. The discrepancy between the profile size and the nucleation theorem size would then be even worse. No definitive conclusion, however, can be made without knowing the critical cluster profile, the calculation of which would require a significantly larger number of simulation runs, and was thus beyond the scope of this study.

IV. CONCLUSIONS

We used MD method to simulate nucleation events in LJ vapors and LJ clusters in equilibrium with a vapor. Both the equilibrium clusters and the critical clusters were observed in similar vapor conditions. By applying different variants of TWF cluster definition we were able to obtain a rough picture of cluster structure. We found that even though the dense cores (i.e., clusters with more stringent neighbor requirement) are of comparable size, the critical clusters have more particles surrounding this cluster core. The cluster size given by the original TWF definition, where each cluster member is required to have at least five neighbors, is in a good agreement with the CNT estimate for both the critical and equilibrium clusters. The cluster size from nucleation theorem is somewhat larger than the CNT size and its relation to the TWF cluster sizes seems to be dependent on at least temperature, and possibly also on potential cutoff. The observation that the critical clusters and equilibrium clusters are not commensurate (at least in MD simulations) casts doubt on whether equilibrium simulations can be used to obtain properties of real critical clusters.^{1,2,22} However, more simulation studies involving diverse molecular species are needed to fully assess the importance of the difference.

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