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On the similarity of equilibrium and critical clusters in atomic vapors

Ismo Napari and Hanna Vehkamäki
Department of Physics, University of Helsinki, P.O. Box 64, Helsinki 00014, Finland

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In a previous paper [I. Napari, J. Julin, and H. Vehkamäki, J. Chem. Phys. **131**, 244511 (2009)] we compared sizes of critical and equilibrium clusters in Lennard-Jones vapors using various geometrical clusters definitions. In particular, we found that the critical and equilibrium clusters were of the same size if each constituent atom in the cluster was required to have at least five neighboring atoms (ten Wolde-Frenkel cluster) but the critical clusters were much larger if only one neighboring atom was sufficient to fulfill the cluster definition (Stillinger cluster). The conclusion was that the critical clusters at high vapor densities have more ramified structure than the corresponding equilibrium clusters. In this study we have performed new molecular dynamics simulations to enlighten this matter. It is found that the surprising conclusion of the earlier work can be traced to the mean first passage time method which was used to obtain critical cluster sizes from simulations. When a certain sized Stillinger cluster first appears in the simulation, the cluster tends to have a more ramified structure than Stillinger clusters of that size observed later in the simulation. However, for the latter clusters the ratio of Stillinger and ten Wolde-Frenkel sizes in the vapor is the same as in the equilibrium simulations, implying similar structure of critical and equilibrium clusters. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794997]

I. INTRODUCTION

The most readily obtained physical quantity in gas-liquid nucleation is nucleation rate, that is the rate of appearance of critical clusters in a unit volume and time. Experimentally more elusive but equally important quantity is the size of the critical cluster. In nucleation thermodynamics the critical cluster is found at the maximum of the free energy barrier for nucleation and in an analysis of experimental results a thermodynamic relation called the first nucleation theorem[1] can be used to obtain the size the critical cluster if nucleation rate as a function of vapor density (or pressure) is known. The same approach is valid in molecular dynamics (MD) simulations but, as the molecular-level details are available in simulations, various cluster definitions can be applied as well.

In our previous study[2] we investigated cluster sizes in Lennard-Jones (LJ) vapors using geometrical cluster definitions: each atomic member of the cluster was required to have a certain number of neighboring atoms within a given connectivity distance. The number of neighbors was varied from one (Stillinger cluster[3]) to five (ten Wolde-Frenkel (TWF) cluster[4]). The connectivity distance was fixed to 1.5σ, where σ is the LJ length parameter.

Using these cluster definitions we then compared equilibrium and critical clusters. Equilibrium cluster sizes were gained from simulations where a cluster with a surrounding vapor was placed in a simulation box.[2] With a properly chosen box size the cluster does not vanish into vapor; instead, its size fluctuates in time around a mean value giving a time-averaged equilibrium size for the cluster. On the other hand, the critical cluster sizes were obtained from simulations of metastable vapor until a nucleation event happens[2] (direct nucleation simulation). Averaging over a set of simulation runs, the mean first passage time (MFPT) formalism was used to extract the nucleation rates and critical cluster sizes for different vapor conditions.

MFPT method[5,6] applied to gas-liquid nucleation[7] consists of recording the first instance when a cluster of given size appears in the vapor. By combining many simulation runs a sigmoidal curve showing the average time $\tau(N)$ it takes to observe a cluster of size N can be constructed. The data is then fitted to

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

where $\mathrm{erf}(x)$ is the error function. The fit gives the critical cluster size N^*, the Zeldovich factor $Z = b/\sqrt{\pi}$, and nucleation rate $J = 1/(V\tau_J)$, where V is the size of the simulation box. An example of a MFPT plot which uses the data of our previous study[2] and pertains to the simulation conditions of the present study is shown in Fig. 1. (The simulations end when the TWF size exceeds 250, but because large jumps in cluster size can occur and because the data includes the first TWF cluster larger than 250 from each simulation run, large scatter in the TWF curve ensues near the limiting value.)

The main result of our earlier work[2] was that the TWF cluster sizes were equal in the direct and equilibrium simulations, but the Stillinger clusters were considerably larger in the direct simulations. This comparison suggested a crude picture of the relative structural differences between the critical and equilibrium clusters, indicating a more diffuse appearance of the critical clusters. The result was surprising, because there was no prior indication of such a difference.

In this work we show that the proposed discrepancy practically vanishes if one distinguishes between typical clusters in metastable vapors and the clusters recorded in the MFPT analysis. For that purpose a new set of direct nucleation simulations were performed, as described in Sec. II. The results

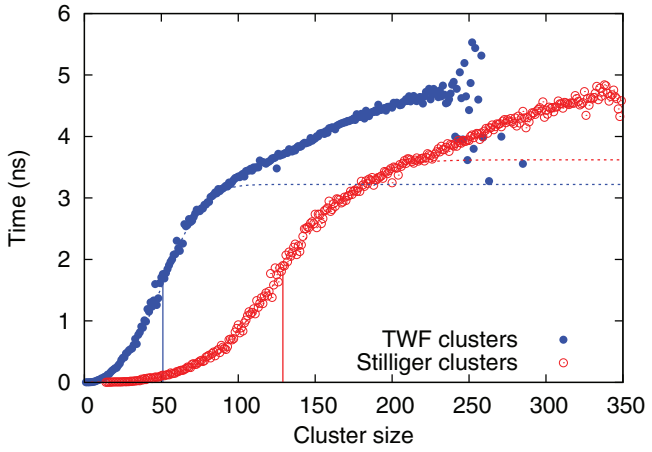

FIG. 1. MFPT plots for the Stillinger and TWF clusters. The vertical lines show the critical cluster sizes obtained from the fit to the MFPT data.

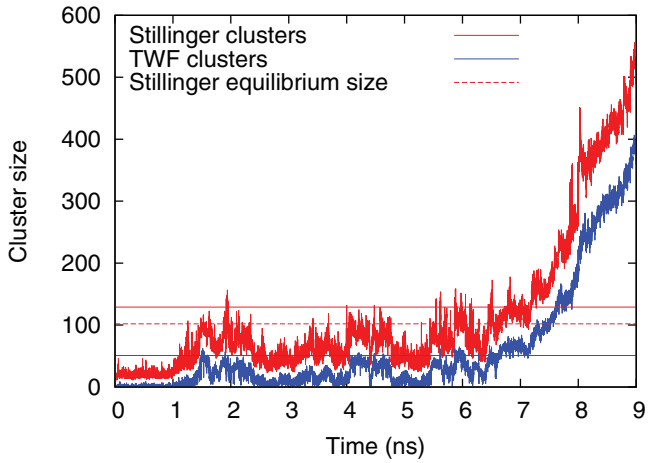

FIG. 2. Time evolution of the Stillinger and TWF cluster sizes in a single simulation run. The vertical lines show the critical cluster sizes obtained from the MFPT analysis. The dashed line shows the Stillinger size from the cluster-vapor equilibrium simulations. For the TWF clusters the critical size is the same as the equilibrium size.

presented in Sec. III indicate that the ratio of the Stillinger and TWF cluster sizes in a metastable vapor is identical to the ratio in a cluster-vapor equilibrium when the TWF size is the same as the critical size from the MFPT method. However, the clusters counted in the MFPT analysis have larger Stillinger/TWF size ratio than clusters in the vapor state on average. The reason for the difference is proposed at the end of Sec. III and implications are presented in Sec. IV.

II. SIMULATIONS

The studied system was the same as in our earlier study: a LJ-vapor with the interaction potential cut and shifted at 2.5σ. In that work we considered two temperatures, $k_BT/\epsilon = 0.65$ and $k_BT/\epsilon = 0.8$ (ϵ is the LJ energy parameter), and four vapor conditions with closely spaced density values at each temperature. The greatest discrepancy between the equilibrium and critical clusters was observed at $k_BT/\epsilon = 0.8$. In the current study we therefore focused on this higher temperature and did new simulations at vapor number density $\rho = 0.049\sigma^3$. At these conditions we previously[2] obtained for the critical cluster a Stillinger size $N_{\mathrm{Still}} = 129$ and TWF size $N_{\mathrm{TWF}} = 51$, while the corresponding values from equilibrium simulations were 102 and 51.

The new simulations consist of a set of ten runs each with 4000 atoms arranged initially on a cubic grid at $k_BT/\epsilon = 1.076$. Initial velocities to each atom were randomly assigned from Maxwellian velocity distribution. The system was quenched to the target temperature $k_BT/\epsilon = 0.8$ at 1 ns and the data collection for the cluster analysis started immediately after the quench.

The previous direct nucleation simulations gave us the size of the largest cluster as a function of simulation time. However, the Stillinger and TWF clusters were treated quite separately and without checking whether the largest Stillinger cluster contained any of the atoms of the largest TWF cluster. In other words, to get the results we reported, we could have performed two separate sets of simulations, first recording the Stillinger sizes and then TWF sizes. In this original analysis scheme it may happen that a Stillinger cluster entering the MFPT analysis has a small TWF core while at the same time a larger TWF cluster is found elsewhere in the simulation box. The obtained ratio of cluster sizes (Stillinger vs. TWF) would then be incorrect. To rule out this possibility we have modified the cluster analysis to record the size of the largest Stillinger cluster and the size of the TWF cluster contained in that Stillinger cluster.

Figure 2 shows the size of the largest cluster in one simulation run at each time step with the horizontal lines depicting the critical and equilibrium sizes. Figure 2 illustrates the fact that in the direct simulations the size of the largest cluster varies widely; however, with the fixed vapor density $\rho = 0.049\sigma^3$ only one cluster size corresponds to the equilibrium size in that vapor. Figure 2 also suggests that the simulation run can be divided roughly into two periods: a metastable stage where rather small clusters are abundant and a growth stage where the cluster grows at a fairly constant rate. In this study we focus on the metastable stage, since our primary interest is to investigate the relationship between the Stillinger and TWF cluster sizes in the vicinity of the previously obtained critical size and to find out how the relationship compares with that of the equilibrium clusters and the critical cluster.

The relationship between the Stillinger and TWF cluster sizes or, more precisely, the ratio of the two is calculated as follows. Cluster analysis is performed every 0.5 ps and the Stillinger and TWF cluster sizes are recorded. After data from all ten simulation runs are accumulated, the average value of Stillinger size corresponding to each TWF size is calculated.

III. RESULTS AND DISCUSSION

Figure 3 shows the average Stillinger size from the direct simulation runs as function of the TWF size. The Stillinger size coincides with the Stillinger size from the equilibrium simulations when the TWF size is between 20 and 60 atoms and notably this range includes the previously obtained critical TWF size of 51 atoms. The critical Stillinger size from the

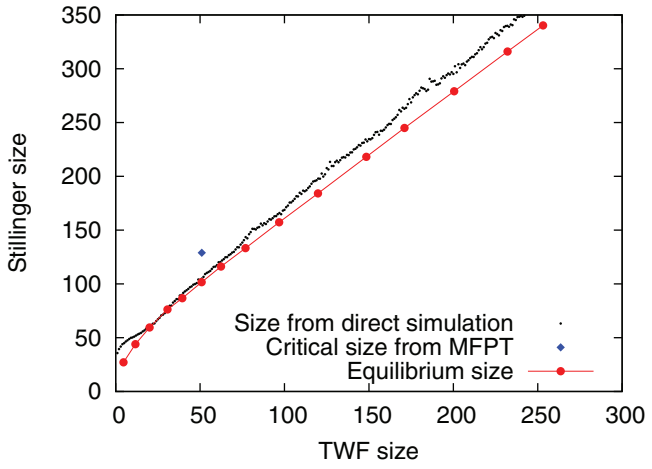

FIG. 3. The Stillinger cluster size as a function the TWF cluster size. The small dots indicate the sizes gained from the metastable and growth stages (see text for details). Also shown are the sizes from the cluster-vapor equilibrium simulations and the critical cluster size from MFPT analysis according to the Stillinger definition.

MFPT analysis, denoted by a diamond in Fig. 3 is well above the data points of the current simulations.

For larger clusters there seems to be a clear difference between the direct and equilibrium simulations. This happens because the larger clusters in the direct simulations belong to the growth stage where they are in a denser vapor environment than in the equilibrium vapor corresponding to that size and hence surrounded by extra vapor molecules and smaller clusters. Some of these vapor molecules and clusters are then included in the Stillinger definition, resulting in a larger Stillinger size. For example, our equilibrium simulations[2] show that a Stillinger cluster containing 200 atoms is at equilibrium with a vapor having density $\rho = 0.036\sigma^3$. This is a considerably lower value than in the current simulations ($\rho = 0.049\sigma^3$), although the vapor is already slightly depleted at this stage. If the simulation is continued long enough (over 10 ns), a stable equilibrium between the cluster and the vapor is reached. When this happens the Stillinger and TWF sizes are about 2200 and 2000, respectively.

A considerable difference between the equilibrium and direct simulations is also seen at the smallest cluster sizes, but there the equilibrium simulations probably do not give a truthful description of the vapor phase due to the small system size.[2]

Figure 3 suggests that clusters close to the critical size in the cluster-vapor equilibrium and in the metastable vapor are structurally similar, that is both simulations methods yield similar Stillinger sizes for a given TWF size. What is then the reason for the large Stillinger critical cluster size obtained from the MFPT analysis? As explained above, the vapor surrounding the large non-equilibrium clusters increases the Stillinger size in the growth stage, but this reason is hardly valid for smaller clusters embedded in a vapor with (nearly) equilibrium density. The correct explanation is related to the structure of the Stillinger clusters used in the MFPT analysis.

Let us first consider the cluster size ratios $N_{\mathrm{Still}}/N_{\mathrm{TWF}}$ at the metastable and growth stages. During the growth stage a

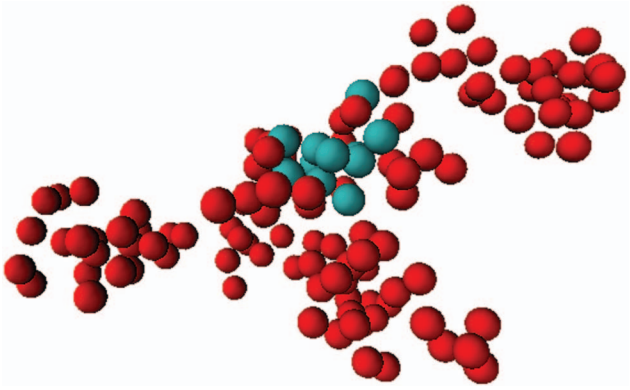

FIG. 4. A snapshot showing a large Stillinger cluster with a small TWF core (blue atoms). The Stillinger size is 128 and the TWF size 12.

Stillinger cluster always has a sizable TWF core, which invariably also is the largest TWF cluster in the system. Typically, a Stillinger cluster in the metastable stage also has a TWF core; however, a close scrutiny of Fig. 2 reveals that there are moments when a TWF core is missing or the core is very small compared to the Stillinger size. An example of the latter is shown in Fig. 4, where the Stillinger cluster consists of three or four relatively compact regions that are loosely connected. In the case of Fig. 4 the ratio $N_{\mathrm{Still}}/N_{\mathrm{TWF}}$ is 10.7. A general idea of the probability of finding a TWF core of certain size in a Stillinger cluster is illustrated in the histogram of Fig. 5, where the size ratio data gained from the simulations is presented. The Stillinger size in Fig. 5 varies between $N_{\mathrm{Still}} = 124 - 134$, that is around the critical size 129 according to MFPT. The average ratio is about 2, which is in accordance with Fig. 3. The ratio can occasionally exceed 10 (as in Fig. 4), but these cases are rare and they contribute little to the average value.

The previous paragraph applies to clusters in general independent of when they appear in the two stages of the simulation run (metastable or growth). But now remember that the MFPT analysis stores the times of first appearances of clusters of given size irrespective of the state of clusters of the same size later in the simulation. It turns out that this

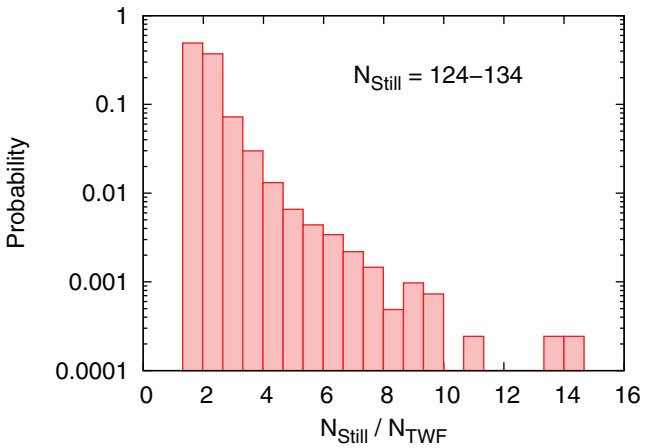

FIG. 5. Histograms for the size ratio of the Stillinger and TWF clusters when the Stillinger size is between 124 and 134.

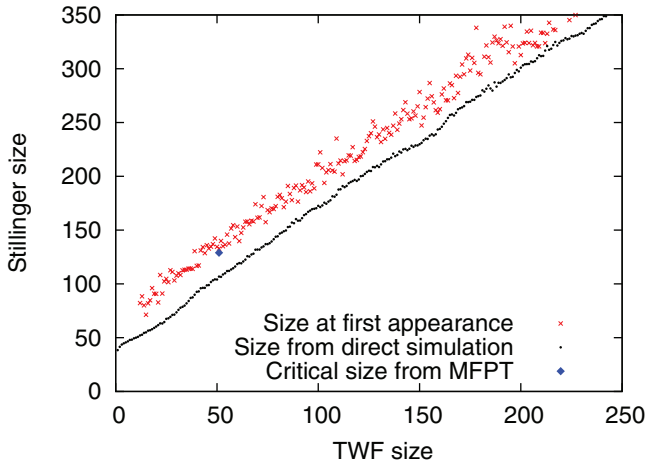

FIG. 6. The Stillinger size at its the first appearance in the simulation as a function of the TWF size. Also shown are the sizes from Fig. 3 as black dots.

sampling leads to different results than one would obtain on the basis of the data recorded throughout the metastable state. Figure 6 shows in red the relationship between the Stillinger and TWF sizes at the first appearance of the Stillinger clusters. For all cluster sizes the ratio $N_{\mathrm{Still}}/N_{\mathrm{TWF}}$ is much higher than the values of Fig. 3, shown also as black dots in Fig. 6. This is especially true for the critical-sized clusters for which $N_{\mathrm{Still}}/N_{\mathrm{TWF}} \approx 3.4$.

The immediate conclusion from Fig. 6 is that the first-appearing Stillinger clusters have smaller TWF core than clusters of the same Stillinger size found later in the simulation. This further suggests that the Stillinger clusters counted in the MFPT plot bear closer resemblance to the ramified cluster of Fig. 4 than a compact spherical cluster. In dense vapors it is likely that such a cluster results when two Stillinger clusters come near enough each other to form a large Stillinger cluster. After that the cluster can evolve in two ways: the large cluster exists only momentarily before the loosely connected regions drift apart or the regions coalesce to form a more compact Stillinger cluster with a substantial TWF core. Both the cases are taken into account when the average cluster sizes are calculated (as in Fig. 3); however, the MFPT analysis only captures the very beginning of the formation process and loses information on what happens afterwards.

IV. CONCLUSIONS

Our new analysis suggests that the ratio of the Stillinger and TWF sizes is the same for the clusters in a stable cluster-vapor equilibrium and for the clusters in a metastable vapor. This means that the evidence presented in Ref. 2 for dissimilar structure of the equilibrium and critical clusters does not exist. Our contradictory claim in Ref. 2 is shown to originate from the fact that a cluster of given TWF size at its first appearance in the vapor has higher $N_{\mathrm{Still}}/N_{\mathrm{TWF}}$ ratio than a cluster of same size in that vapor on average. Such clusters are less dense and probably more ramified than more compact forms appearing later. However, it is just these clusters that are recorded for the MFPT analysis and further used to obtain the size of the critical cluster.

The ramified Stillinger clusters are likely to originate from a chance encounter of two (or more) smaller Stillinger clusters. At low temperatures and in low-density vapors cluster-cluster encounters are rare and Stillinger clusters are likely to be compact. It is then expected that the problems with the MFPT method will vanish. We note that in our earlier study at $k_BT/\epsilon = 0.65$ we found a moderate agreement between the MFPT method and the cluster-vapor equilibrium simulations.[2]

One should note that main purpose of the MFPT analysis, the evaluation of nucleation rate, is not compromised by the current findings. The large, ramified Stillinger clusters only shift the MFPT plot (Fig. 1) in horizontal direction. In terms of Eq. (1) this means that the parameter τ_J, which determines the nucleation rate, is affected little or not at all. From the data of our previous investigation[2] we found that the nucleation rate at the simulation conditions of the present study is 6.5×10^{-9} (in LJ units) when the Stillinger sizes are used in the MFPT analysis and 7.3×10^{-9} when the TWF sizes are used. This means that cluster size serves as a reliable reaction coordinate for the MFPT analysis even in high-density vapors.

The present results are at least pertinent to LJ vapors. The observed problems with MFPT analysis may not arise, for example, with molecular species having strong hydrogen bonding, such as water. On the other hand, it is possible that an investigation involving only simple atomic particles can miss some essential features which may lead to differences between equilibrium and critical clusters. We also point out that in the present work we have not studied in detail the very beginning of the growth stage, where the properties of the cluster just starting to grow may differ markedly from the other clusters of the same size. Such an investigation is left for future work.

ACKNOWLEDGMENTS

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