

The role of dimers in evaporation of small argon clusters

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Evaporation of small Lennard-Jones argon clusters has been studied using molecular dynamic simulations. An extensive library of clusters with 4, 5, 6, 11, and 21 atoms has been obtained from an earlier study. Analysis of the evaporation properties of the clusters indicate, that the fraction of dimer evaporations of all evaporation events increases with the total energy of the cluster. The fraction of evaporated dimers from clusters with a constant lifetime is independent of the cluster size for short-lived clusters and increases with cluster size for long-lived clusters. Only a few percent of the clusters which are long lived enough to participate in vapor–liquid nucleation decay by emitting dimers. The mean cluster lifetime as a function of total energy shows the same exponentially decreasing trend for monomer and dimer evaporation channels. The fraction of trimer evaporations is found to be vanishingly small. © 2004 American Institute of Physics.
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I. INTRODUCTION

A specific example of nucleation phenomenon is the formation of small molecular aggregates in a vapor phase. This process has been studied for decades because of its importance in atmospheric sciences.¹ However, both the theoretical description and the practical applications of nucleation are far from perfect. A well known fact is that the classical thermodynamic model leads to problems in the binary nucleation of surface active systems.^{2,3} Some of the reasons for this are known³ but not easily remedied. The rush to find better theories and amendments to binary nucleation theory has evidenced the fact that there still are discrepancies between theory and experiment in unary nucleation. Most of these problems are connected to the complex nature of the molecules or the use of bulk properties when small systems are concerned.

The widely accepted scenario describes gas–liquid nucleation as a stepwise process where single molecules (monomers) are added into a cluster or removed from it



The forward and backward reactions in Eq. (1) are governed by the condensation coefficient β and evaporation coefficient α . These coefficients can be approximated by thermodynamic and geometric means or obtained directly, for example, from simulations. By inserting the coefficients to a kinetic master equation the nucleation rate can be calculated.¹ However, this simplistic picture assumes that growth and decay of clusters is mediated by monomers alone, an assumption which cannot be taken *a priori* for granted. A more general depiction would involve collisions and evaporations of fragments of all sizes m



The problem becomes much more complicated because the condensation and evaporation coefficients depend both on the cluster and the fragment. Therefore, knowledge of decay routes other than monomer evaporation is needed for a comprehensive picture of gas–liquid nucleation.

The purpose of this paper is to estimate the importance of the dimer evaporation channel of small Lennard-Jones (LJ) argon clusters by molecular dynamics simulation. Our research is motivated by experimental and simulation work on water, sodium, and metal clusters,^{4–9} where the evaporation of dimers (or higher n -mers) was found significant or even predominant fragmentation channel.

Evaporation of LJ clusters has been studied extensively before.^{10–16} However, these works have concentrated on monomer processes according to Eq. (1) and in some of them^{13,16} the clusters were thermally equilibrated. We are principally interested in the first stages of nucleation where the clusters are out of equilibrium and thermalization of clusters would invalidate the physical situation. The apparent lack of reports on dimer (or n -mer) evaporation in argon systems suggests that monomer evaporation is by far the most important decay mechanism, but quantitative tests to that effect are still missing. A further motivation to our study is given by the frequent use of LJ fluid as a testbed for various theoretical ideas on nucleation. It is therefore crucial to know if some properties of clusters can be ignored and how simple LJ clusters differ from those composed of more complex molecules.

Quite recently, we performed a simulation study of condensation properties of LJ clusters.¹⁷ This work resulted in a database which can be analyzed to obtain information on the relative importance of different fragmentation channels. We will show that evaporation of dimers is a comparatively rare phenomenon; however, in high-energy clusters the dimer de-

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TABLE I. Total number of observed evaporation events N_{evap} , and the number of evaporated monomers N_{mon} , dimers N_{dim} , and trimers N_{trim} in each size class.

Size	N_{evap}	N_{mon}	N_{dim}	N_{trim}
4	36 248	35 958	290	—
5	37 044	36 425	619	—
6	43 143	42 714	416	13
11	57 104	56 966	138	0
21	67 824	67 721	102	1

cay may become important. In Sec. II we give a short description of our simulation methods and the analysis of the data. Results are presented and discussed in Sec. III, specifically in connection with gas–liquid nucleation. In Sec. IV we conclude with implications of our findings.

II. SIMULATION DETAILS

This work is based on the data we accumulated in our previous study on atom–cluster collision processes.¹⁷ In that work we considered formation of new clusters as a result of collisions between target clusters of 2–20 atoms and monomers, and related the results to the total energy and size of the target cluster. To assess the probability of dimer and trimer evaporation we have analyzed the database which contains information on the lifetime of the new clusters, velocity of the colliding monomer, and the size of the evaporating entity.

The simulated systems consist of argon (Ar) clusters with 4, 5, 6, 11, and 21 atoms. The interaction between the atoms is described by the LJ potential with energy parameter $\epsilon/k_B = 120.77$ K and length parameter $\sigma = 3.4$ Å. The mass of an Ar atom is 40 amu. The particle trajectories are calculated in the NVE system using the standard velocity Verlet algorithm.¹⁸

During the course of the simulation we follow the trajectories to determine the instant of evaporation. In our cluster analysis we use the Stillinger cluster definition¹⁹ with the nearest neighbor distance of 2σ . It has been shown that the Stillinger definition underestimates lifetime of the cluster, because the evaporating n -mer may easily be recaptured by the cluster.¹⁴ To obtain a more accurate estimate of the lifetime we follow the escaping fragment up to 10 ps after the evaporation and continue the simulation if the fragment rejoins the cluster. In case of actual breakup we record the size of the fragment at 10 ps after the evaporation to avoid confusing a dimer with two monomer evaporations occurring at short time intervals. Hence, the evaporating dimer or trimer in our simulations must have a minimum lifetime of 10 ps.

III. RESULTS AND DISCUSSION

Table I shows the number of evaporation events and the number of evaporated n -mers (monomer, dimer, trimer) in each size class. It can be seen that the total number of evaporation events increases with cluster size. The amount of monomer–cluster collisions, from which the clusters of this study were obtained, was the same for all cluster sizes (see Ref. 17 for details). However, in many cases the monomer

did not attach to the cluster; for example, at high impact parameters the monomer often passed the target cluster and the new cluster was never formed. Also, the probability of a successful collision is higher if the target cluster is big because, in addition to larger physical size, a big cluster presents a deeper attractive potential well. This, together with the fact that a big cluster is more able to absorb the kinetic energy of the colliding monomer without breaking down, explains why the total number of evaporation events (and the number of clusters) increases with the cluster size. Because the overwhelming majority of evaporations occur via monomers, the number of monomer evaporation events also increases with size.

Apparently, however, the absolute number of dimer evaporations decreases with increasing cluster size if the cluster has more than five molecules. This trend does hold for clusters of four atoms; the breakup in this case means splitting the cluster into two equal halves. Evaporation of trimers is a very rare event, and only a handful were observed in our simulations. On the basis of clusters of 6, 11, and 21 atoms we can nonetheless assume that the number of trimer evaporations also decreases with cluster size. It must be noted, however, that we cannot make any definitive conclusions on the number of evaporated dimers (or trimers) as a function of cluster size alone, because any overrepresentation of low (or high) total energies in the sample may cause unwanted bias in the results. The deductions must then be made by relating the evaporation properties of dimers to corresponding properties of monomers. To this end we have divided the cluster energies into energy bins, in which case the relative amount of evaporated monomers and dimers as a function of the cluster energy yields to quantitative analysis. Despite the large number of simulated clusters only 0.65% of them emitted a dimer. This results in inevitable scatter of data points in any plot depicting properties of dimer evaporation. To reduce the scatter we have tried to choose an optimized number of energy bins for each cluster size. In practice, the energy scale is divided into 10–20 bins.

We point out that in Table I the lower limit for the lifetime of the cluster was set to 20 ps. This somewhat arbitrary limit excludes transitory monomer–cluster encounters in the cluster formation process, where a fast-moving monomer resides a couple of picoseconds in the vicinity of target cluster (according to the cluster definition) and then leaves it or disrupts the cluster before a new cluster is properly formed. We present our results assuming the limit of 20 ps, but we discuss the choice of the limiting lifetime at the end of this section.

For a given energy there is a distribution of cluster lifetimes. Figure 1 represents the mean values of cluster lifetime distributions as a function of total energy for monomer and dimer evaporation channels. In all cases the lifetime increases with decreasing energy. The relation between the energy and logarithmic lifetime is not linear although nearly so for the largest cluster size. Regardless of the cluster size the mean cluster lifetime does not seem to depend on whether the decay channel is by monomer or dimer emission. Note, however, that in each energy bin the monomer decays are far more abundant than dimer decays.

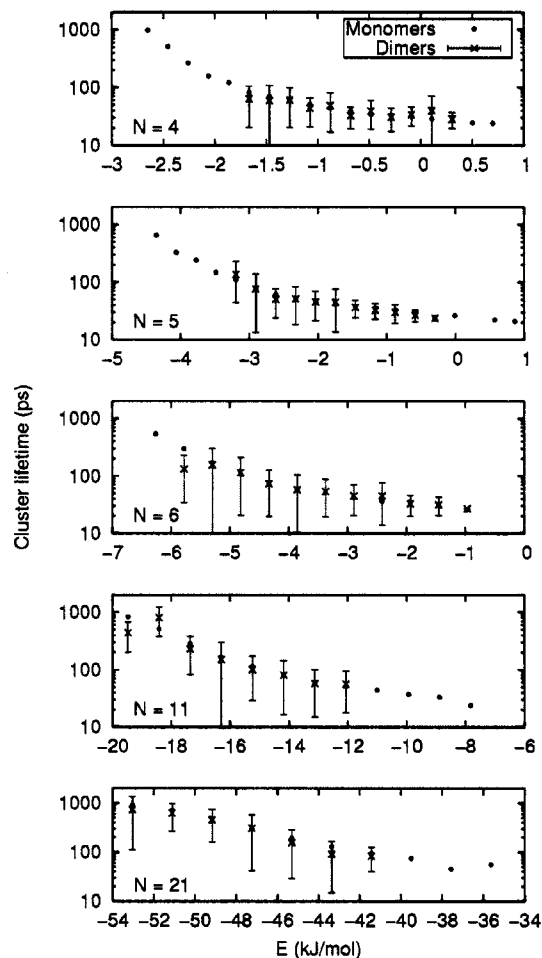


FIG. 1. Mean values of cluster lifetime distributions as a function of the total energy of the cluster. Dots indicate monomer evaporation and crosses dimer evaporation channels. The size of the cluster is shown in the legend. The vertical bars show standard deviation of the lifetime distribution in the case of dimer events.

The energy dependence of the fraction of evaporated dimers is shown in Fig. 2. The evaporation fraction of dimers is defined as the number of evaporated dimers divided by the number of total evaporation events. The fraction increases with energy and can easily exceed 10% when the cluster is small and energetic. This behavior can be explained by the

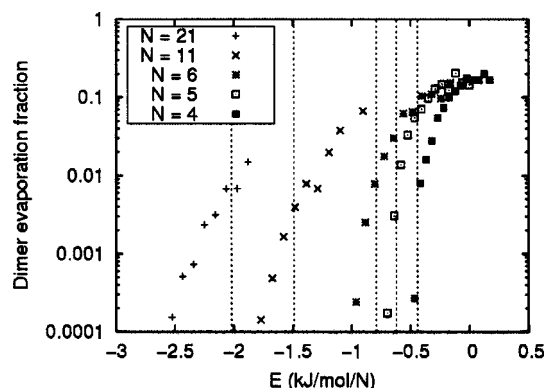


FIG. 2. The fraction of evaporated dimers of all evaporations as a function of the total energy per particle. The vertical lines correspond to clusters with average lifetime of 100 ps for each cluster size.

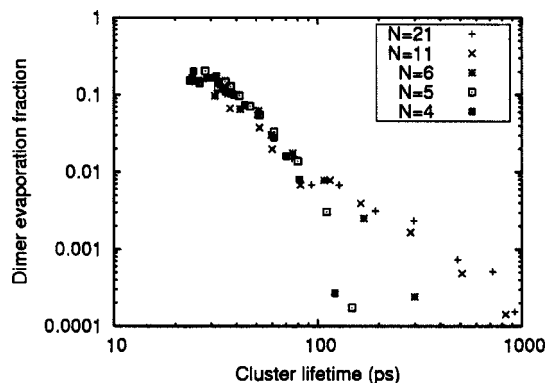


FIG. 3. The dependence of the dimer evaporation fraction on the average cluster lifetime.

“looseness” of clusters with high kinetic energy. The cluster is then more prone to form temporary dimers which belong to the cluster and can be emitted from it intact. For example, the cluster may consist of two dimers orbiting each other. In these cases the cluster has a very short average lifetime. As pointed out in earlier studies,^{17,20} the cluster should be sufficiently long lived to be able to experience further collisions with vapor molecules, thus making the growth of the cluster possible. A simple calculation shows¹⁷ that e.g., a 100 ps interval between monomer–cluster collisions corresponds to a vapor saturation ratio of 3–8 for the cluster sizes in this study. The energy at which the average lifetime is 100 ps is shown in Fig. 2 as a vertical dotted line. If the cluster energy is higher than indicated by this line, the average cluster lifetime is shorter than 100 ps.

By comparing Figs. 1 and 2 one might be led into thinking that the long-lived clusters of 4, 5, and 6 atoms decay by the monomer route almost exclusively and larger clusters do not evaporate dimers even if they have short lifetimes. This, however, is an artifact caused by the disparate effect of colliding monomers on target clusters with different sizes in the cluster formation process. The colliding monomers, which are sampled randomly from a thermal ensemble at the same temperature, add more to the relative energy of the cluster (with respect to the energy of the target cluster) when the cluster is small. The collision process then forms more small high-energy clusters than big ones.

In view of the fact that we are principally interested in the cluster formation and evaporation process as a part of the gas–liquid nucleation, the most revealing information is gained from the lifetime rather than energy dependence of the dimer evaporation fraction. Figure 2 shows that the dimer evaporation fraction is about 0.01 for clusters with a lifetime of 100 ps. In fact, when we plot the dimer evaporation fraction as a function of the average cluster lifetime, as shown in Fig. 3, we see that the lifetime dependence is identical for all cluster sizes if the lifetime is less than approximately 100 ps. On the other hand, the tendency to evaporate dimers increases with cluster size if the cluster is long lived. Obviously, small long-lived clusters are likely to assume a more ordered state than bigger clusters and thus do not exhibit the above-mentioned “loose” configurations.

Figure 2 indicates that the dimer evaporation fraction of

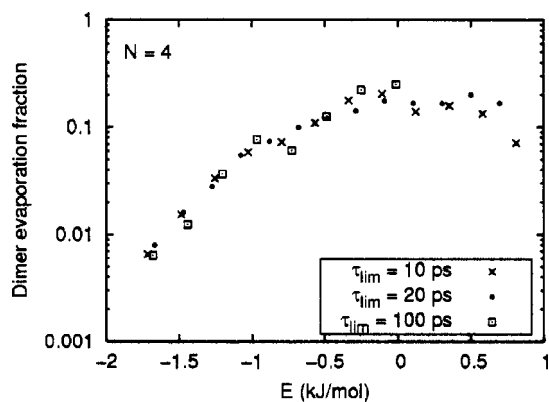


FIG. 4. The fraction of evaporated dimers as a function of the total energy of the cluster. Included are only those clusters which have longer lifetime than indicated in the legend. The cluster size is four atoms.

small clusters reaches a maximum of about 0.2 at high cluster energies; the samples of 10- and 20-atom clusters do not include enough high-energy configurations to see if this limiting behavior also applies to larger clusters. Since the energetic clusters have short average lifetimes, it is justified to ask how the choice of the lower limit for the lifetime affects the results. Figure 4 depicts the dimer evaporation fraction of four atom clusters assuming three different values for the minimum lifetime τ_{lim} . If τ_{lim} is increased from 10 to 100 ps, the most energetic clusters are cut off from the plot, but the relationship between the energy and the dimer evaporation fraction remains the same. The energy dependence disappears at positive energies if $\tau_{\text{lim}}=20$. For $\tau_{\text{lim}}=10$ ps the dimer evaporation fraction seems to decrease at the highest energies, but this may be an artificial effect, because the shortest observable lifetime in our simulations was 10 ps. The disappearance of the energy dependence can also be seen for clusters of five and six atoms, although less clearly (see Fig. 2). It is quite likely that the clusters with lifetimes of less than a couple of tens of picoseconds have not reached an internal quasiequilibrium and therefore the energy plays no role in determining the dimer evaporation fraction. The almost constant lifetime of small clusters at high energies in Fig. 1 lends support to this notion. We further note that from the perspective of gas-liquid nucleation these clusters are of little consequence.

IV. CONCLUSIONS

We have investigated evaporation of small LJ argon clusters using molecular dynamics. We have considered the evaporation of dimers as a function of total energy of the cluster and found that the fraction of dimer evaporations increases approximately exponentially with the cluster energy at low total energies but reaches a maximum value at high energies. All the clusters decay mainly by the monomer route, and the clusters copiously emitting dimers are very short lived. The fraction of evaporated dimers is not dependent on the cluster size for clusters with equal lifetimes if the lifetime is shorter than 100 ps; for long-lived clusters the

tendency to evaporate dimers increases with cluster size. In the course of the simulations we observed several trimer evaporations as well, but these are too rare to have an effect on any nucleation scheme.

For nucleation to proceed the cluster should not break down before a new collision with a vapor molecule occurs. We have considered placing a lower limit for average cluster lifetime at 100 ps. This limit is quite low and a significantly shorter time between molecular collisions would probably require vapor which is close to the spinodal or even in the unstable region. On average, clusters with lifetimes close to 100 ps are rather energetic, which could imply viable decay channels other than ejection of monomers, but our simulations indicate that dimer evaporation fraction is less than 1%. Then, at least for LJ argon atoms the simple formation route presented in Eq. (1) is quite accurate. If a more elaborate description is required, our simulations could in principle be used to obtain the evaporation coefficient of dimers if the corresponding coefficient for monomers is known.

One should be careful not to make any general conclusions on molecular systems on the basis of this study. As observed in other systems, dimer evaporation can be an important phenomenon, for example in metal clusters.^{4,9} Experimental and theoretical work also indicates^{5,7} that water could be included in this category with the obvious consequence that in all atmospheric nucleation processes the evaporation of dimers may be a viable decay route of small clusters. Due to the absence of internal structure of LJ atoms the dynamical behavior of LJ argon cannot be used as a strict guideline in the assessment of the dynamics of complex molecules, and that should be taken into account when using LJ fluid as a modeling tool.

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