

## Postcollision relaxation of small atomic clusters

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Molecular-dynamics simulations are performed to investigate the effects caused by the lack of internal equilibration on the dynamics and properties of atomic clusters. The studied systems consist of Lennard-Jones clusters of five to ten atoms and a colliding vapor monomer. Cluster radius and potential energy are shown to reach a time-independent value within 30 ps after a collision with a vapor monomer. The relaxation in terms of rotational energy takes at least 200 ps. During the first couple of picoseconds after the collision time-dependent cluster decay rates are observed. The unrelaxed cluster states are expected to have minimal effect on gas-liquid nucleation rates.

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### I. INTRODUCTION

Nucleation is the initiating process in first-order phase transformations. Nucleation means localized appearance of a new phase into the old phase, driven by the tendency of the system to reach the lowest possible free-energy state and, at the same time, hindered by the energy needed to form a boundary between the new and old phases. Nucleation can be observed in systems as diverse as the formation of hadron matter in the early universe<sup>1</sup> or magnetic transformations in solids,<sup>2</sup> not to mention more familiar examples of condensation and evaporation phenomena in fluids.<sup>3</sup> The most studied nucleation phenomenon is the condensation of supersaturated gases, whereby tiny molecular clusters appear in the vapor phase. The importance of this process lies among other things in the fact that atmospheric particles are mostly produced by gas-liquid nucleation,<sup>4,5</sup> and the rate of appearance of the particles have an influence on meteorological phenomena and climate change.<sup>6,7</sup>

Dynamics of cluster populations in gas-liquid nucleation can be described in terms of rate equations<sup>8</sup>

$$\frac{dn_i}{dt} = \beta_{i-1}n_{i-1} - \gamma_i n_i - \beta_i n_i + \gamma_{i+1}n_{i+1}, \quad (1)$$

where the forward (condensation) coefficient  $\beta_i$  is the mean rate of cluster growth from size  $i$  to  $i+1$  and  $\gamma_i$  is the mean backward (evaporation) rate from size  $i$  to  $i+1$ . In this simple scheme condensation and evaporation of dimers or larger fragments are neglected. The rate of appearance of clusters of size  $i$  is obtained from

$$J = \beta_i n_i - \gamma_{i+1} n_{i+1}. \quad (2)$$

Equations (1) and (2) constitute a kinetic approach to nucleation. In steady-state conditions the cluster populations are independent of time and the fluxes  $J$  are equal for all the cluster sizes  $i$ . In particular, they are identical to nucleation rate, which is the rate of appearance of critical clusters or clusters having equal probabilities of growing to macroscopic size and decaying back to vapor. While in practical

situations the kinetic coefficients are usually determined by resorting to bulk thermodynamics, more sophisticated and general methods, for example, numerical simulations, can be used for this purpose.<sup>9</sup>

Irrespective of the method applied to obtain the condensation and evaporation rate coefficients, an essential feature of the coefficients is that they are assumed independent on time; if this were not the case, they would depend on the history of the cluster. In other words the transition from a smaller size to a larger size, or vice versa, would not be a Markovian process. Then, one has to assume that the clusters are in an internal equilibrium, or quasiequilibrium, state in the sense that the rate constants measured for a large number of clusters of the same size at time  $t_1$  after the formation of the cluster are equal to those measured at another time  $t_2$ . Such measurements are impossible in real situations but feasible when numerical simulation methods are used.

The aim of this work is to find out how fast argon (Ar) clusters relax to an internal equilibrium state after a collision with a monomer. In other words we study clusters resulting from reactions



For this purpose we simulate dynamically collisions of simple Lennard-Jones (LJ) argon clusters with LJ atoms and study the time evolution of newly formed clusters. As indicators of equilibration we follow the radius and energetic properties of the clusters. Finally, we assess the effect of the unrelaxed state of the clusters on the evaporation and lifetime of the clusters. Our results indicate that the different properties have very different relaxation times, but there is little effect on the condensation and evaporation rates.

### II. SIMULATED SYSTEMS AND METHODS

The simulated systems consist of atomic clusters and an incoming vapor monomer interacting via the LJ pair potential  $\phi_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , with the potential parameters of argon ( $\epsilon/k_B = 120.77$  K,  $\sigma = 3.4$  Å, and mass of 40 amu). Since each individual simulation involves only a few molecules, full LJ potential without cutoff was used. The sys-

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tems were simulated using standard molecular-dynamics (MD) methods (more details can be found in Ref. 10). We have not used thermostats to regulate the temperature. In this work we are interested in the effect of the incoming monomer on the cluster; thermostats, however, control the temperature by changing the velocity of molecules in the cluster core as well as on its surface and thus cause additional disturbances to the cluster.

Average values of a quite large number of simulations were needed to obtain good statistics. Therefore we only studied some representative cases: two target cluster sizes (five and ten molecules) and five different velocities for the vapor molecule (100, 150, 200, 250, and 300 m/s). In all cases we considered configurations where the monomer was aimed at the center of mass (CM) of the cluster (impact parameter  $b=0$  Å) or to the cluster edge ( $b=5$  Å and  $b=6$  Å for the five-atom and ten-atom target clusters, respectively). We note that the nonzero impact parameters are small enough to result in a successful collision in every case.<sup>10</sup> In other words the cluster is always formed according to the cluster definition. In this work we have used Stillinger cluster definition<sup>11</sup> with the nearest-neighbor distance of  $2\sigma$ .

The monomer velocities cover typical values found in a LJ argon vapor (200 m/s is the most probable velocity at 75 K). The five-atom target cluster has a total energy of  $-5.5$  kJ/mol and the ten-atom cluster has  $-17.0$  kJ/mol. The target clusters were chosen such that they are well equilibrated and stable long enough (over 3 ns in both cases) for the vapor atom to reach the cluster. On the other hand, the resulting clusters (with 6 or 11 atoms) should be relatively long lived on the average (at least tens of picoseconds<sup>10,12</sup>) to be able to participate to subsequent cluster growth, but with lifetimes that do not lengthen the simulations unnecessarily. Despite the long lifetime and the low energy, both target clusters are liquidlike. The average kinetic temperatures of the six-atom clusters are between 32 and 42 K, depending on the impact parameter and with the monomer velocities varying between 100 and 300 m/s. The temperatures of the 11-atom clusters are between 38 and 44 K.

For each choice of parameter values (target cluster size, monomer velocity, and impact parameter), the data was averaged over  $10^5$  simulations. In each individual run the initial distance between the monomer and the target cluster was varied, so that the configuration of the target cluster was different each time the monomer collided with it.

During the simulation we collected data on cluster radius and energy. The radius was measured from the cluster CM. We considered three different radii: the distance of the farthest atom  $R_{\max}$ , the distance of the colliding monomer  $R_{\text{coll}}$ , and the distance of a randomly chosen target cluster atom  $R_{\text{target}}$ . The maximum radius  $R_{\max}$  reveals how “bloated” the cluster is after collision, whereas  $R_{\text{coll}}$  and  $R_{\text{target}}$  convey information on the mixing of the incoming monomer to the cluster. Of the energetic contributions, potential energy and rotational kinetic energy were recorded.

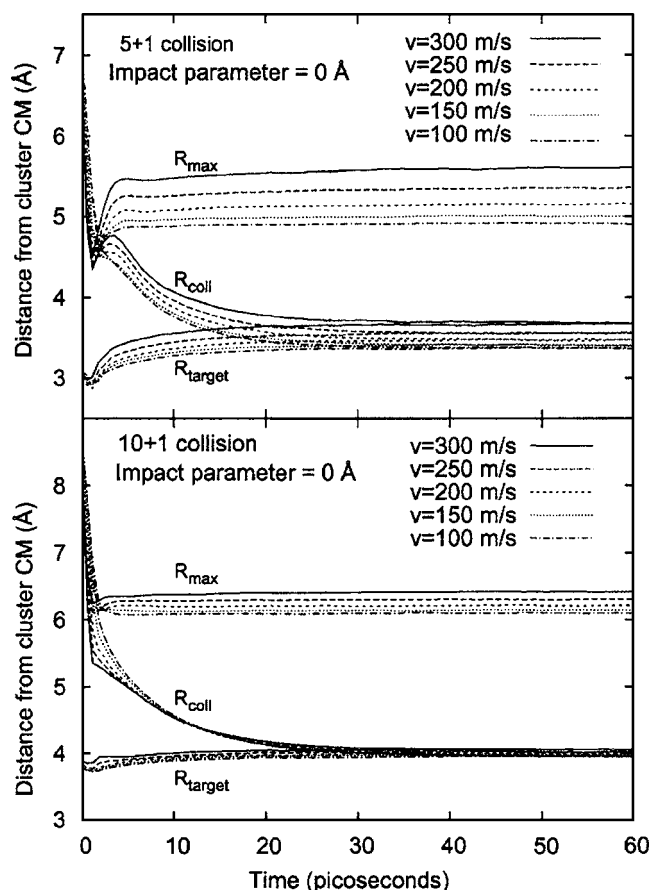


FIG. 1. Cluster radius as a function of simulation time. The clusters were formed as a result of a collision between a monomer and a target cluster. Upper panel: five-atom target cluster (5+1 collision). Lower panel: ten-atom target cluster (10+1 collision). The velocity of the incoming monomer is given in the legend. See text for explanation of the different radii.

### III. RESULTS

#### A. Cluster radius

The upper panel of Fig. 1 shows the radii  $R_{\max}$ ,  $R_{\text{coll}}$ , and  $R_{\text{target}}$  for clusters formed as a result of monomer collisions with the five-atom target cluster (5+1 collision). The impact parameter is  $b=0$  Å. The zero of the horizontal axis is the time when the cluster was born according to Stillinger cluster definition. During the first couple of picoseconds the new cluster is compressed, as indicated by a dip in the curve of  $R_{\max}$ . After that the cluster experiences a recoil with, at least in the case of the fastest monomer, a low maximum in the  $R_{\max}$  curve at 4 ps. A constant value of  $R_{\max}$  is reached approximately at 30 ps. The distance of the colliding monomer  $R_{\text{coll}}$  follows the line of  $R_{\max}$  until the cluster starts to recoil, indicating that the colliding atom is the outermost one up to this point. The radii  $R_{\text{coll}}$  and  $R_{\text{target}}$  reach constant (and equal) values at similar time scales as  $R_{\max}$ , after which the colliding atom can be considered to have lost its identity. However, for example, at 10 ps, the two radii differ considerably. This shows that the mixing of the colliding monomer to the cluster takes surprisingly long even in a cluster of only six molecules.

A similar plot of the cluster radii for 10+1 collisions is depicted in the lower panel of Fig. 1.  $R_{\max}$  seems to attain the

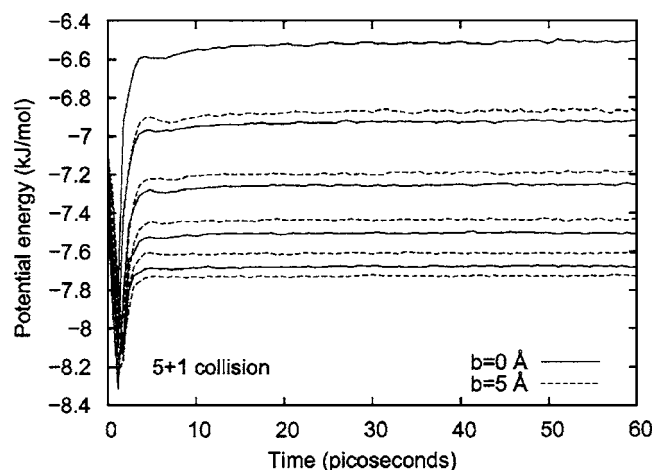


FIG. 2. Potential energy of the cluster after 5+1 collisions. Impact parameters  $b=0 \text{ \AA}$  and  $b=5 \text{ \AA}$  are compared. The solid lines correspond to those in the upper panel of Fig. 1, with monomer velocity increasing with increasing potential energy.

limiting value in a very early stage, which is reasonable because a monomer is not able to disturb a large cluster as easily as a small one. Also, the initial compression is virtually nonexistent. The mixing of the colliding atom, however, lasts about as long as in the case of a five-atom target cluster.

We also made simulations where the monomer collides obliquely with the cluster (impact parameter  $b=5 \text{ \AA}$  in 5+1 collisions and  $b=6 \text{ \AA}$  in 10+1 collisions). The radii reproduce the results of Fig. 1 almost exactly, with the only exception of a somewhat faster relaxation of  $R_{\max}$ . A molecule aimed to the edge of the cluster is likely to cause less disturbance in the target cluster than a head-on collision.

## B. Energetics

The potential energy of the cluster after collision follows the trends of maximal radius  $R_{\max}$ . Figure 2 shows the evolution of potential energy for 5+1 collisions and impact parameters  $b=0 \text{ \AA}$  and  $b=5 \text{ \AA}$ . Upon entering the cluster, the kinetic energy of the monomer is quickly converted to potential energy, as revealed by a dip in the curves, and shortly after that is partly converted back to kinetic energy on recoil. The relaxation in terms of potential energy is similar to  $R_{\max}$ .

Because there is a rapid transformation between kinetic and potential energies during the first few picoseconds after the collision, changes in the speed distribution of the cluster atoms are expected. Figure 3 shows the speed distribution at five different instances after the 5+1 collision with the monomer velocity of 200 m/s, corresponding to the middle line in the upper panel of Fig. 1. At 1.43 ps after collision, the potential energy is at minimum and the speed distribution is very distorted, even chaotic. Compared to later instances, the distribution is shifted to the right because the initial velocity of the monomer is higher than the average velocity of the target cluster atoms. At 3.13 ps the cluster has started to recoil; the corresponding distribution seems Maxwellian but continues to lean toward higher velocities. Small changes are still seen around the maximum radius at 4.81 ps, but the last

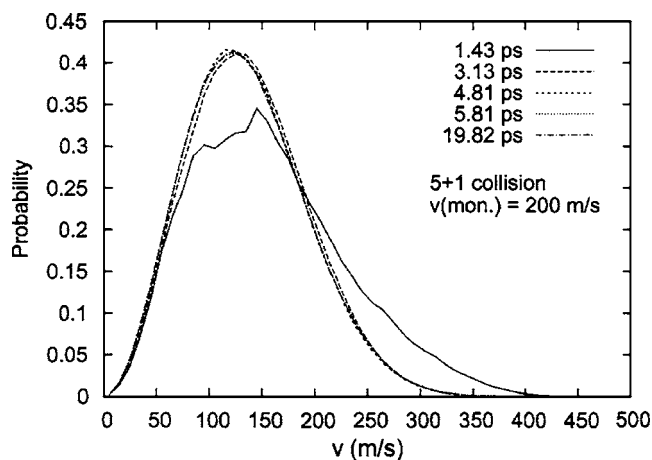


FIG. 3. Speed distribution of a six-atom cluster at different times after the collision.

two distributions at 5.81 and 19.82 ps are practically identical. Maxwellian distribution of speeds are thus obtained in less than 6 ps after the cluster formation.

Figure 2 shows that an oblique collision leaves the cluster to a lower state in the potential well. Because the total energy of the cluster is constant (when the velocity of the monomer is constant), the kinetic energy must be higher after an oblique collision. The kinetic energy of a cluster consisting of particles without internal structure can be divided into three parts:<sup>13</sup>

$$E_{\text{kin}} = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}}. \quad (4)$$

Here  $E_{\text{trans}}$  is the translational kinetic energy of the cluster CM,  $E_{\text{vib}}$  is the internal vibrational energy of the cluster, and  $E_{\text{rot}}$  is the rotational energy expressed as<sup>14</sup>

$$E_{\text{rot}} = \frac{1}{2} m \sum_i [\omega_i^2 r_i^2 - (\boldsymbol{\omega}_i \cdot \mathbf{r}_i)^2], \quad (5)$$

where  $\mathbf{r}_i$  and  $\boldsymbol{\omega}_i$  are the position and angular velocity of the atom  $i$ , respectively, and  $m$  is the mass of the atom.

An oblique collision increases the rotational energy of the cluster quite a lot, as shown in Fig. 4 for 10+1 collisions. A prominent feature in Fig. 4 is the very slow relaxation;

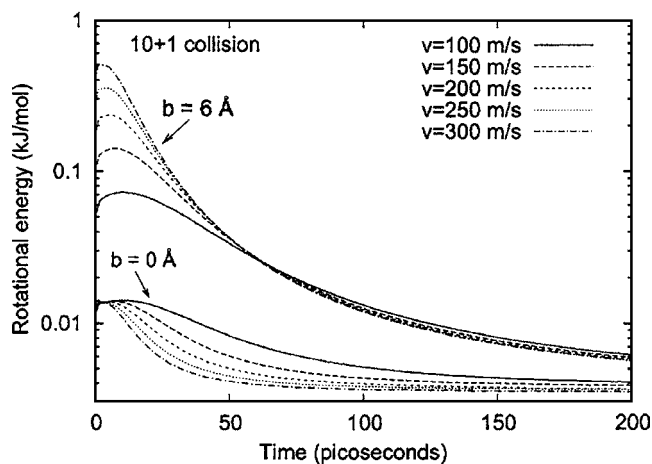


FIG. 4. Rotational kinetic energy of clusters resulting from 10+1 collisions. Impact parameters  $b=0 \text{ \AA}$  and  $b=6 \text{ \AA}$  are compared.

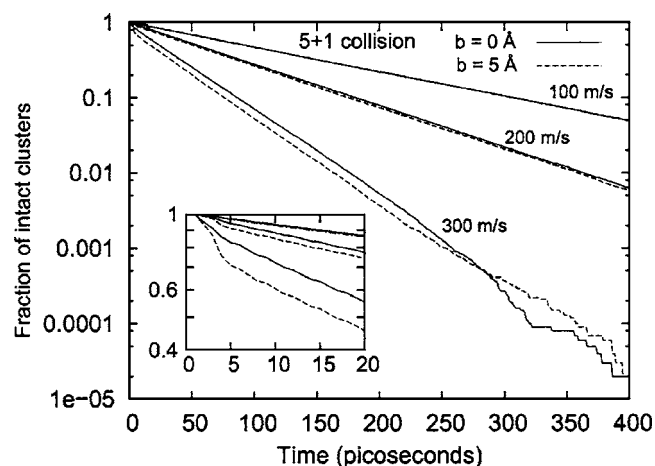


FIG. 5. Fraction of clusters remaining intact after 10+1 collisions as a function of simulation time. Impact parameters  $b=0$  Å and  $b=6$  Å are compared. The inset shows the first 20 ps in greater detail.

even at 200 ps the rotational energy can be far from the final value. Note that the meager increase in rotational energy in collisions with  $b=0$  Å also relaxes rather slowly. Rotational energy is clearly not converted to potential energy because potential energy relaxes rapidly (Fig. 2). Then, because total energy is a conserved quantity, rotational energy must be transformed to internal vibration of the cluster. This transfer, however, is not reflected in the cluster radius.

### C. Cluster decay

The results of the previous section have shown that the relaxation time of a cluster after collision depends on the property chosen to indicate relaxation. These considerations, however, do not tell how much the actual nucleation rates are affected. To gain information more pertinent to nucleation we must investigate the evaporation behavior of clusters in various stages of relaxation and the condensation of monomers on unrelaxed target clusters.

Figure 5 shows the fraction of six-atom clusters remaining intact after the cluster formation. After the first few picoseconds the curves are straight lines on logarithmic scale, indicating Poissonian law of cluster decay. This means that if clusters are compared, for example, at 50 and 200 ps, they have the same average lifetime, and the evaporation coefficients determined from the properties of the clusters at these two instances are equal. The linearity of the curves, however, does not extend to the very first moments after the cluster birth. Especially, if the velocity of the monomer is high and the collision is aimed to the cluster edge, a considerable amount of the clusters are disrupted before 5 ps. As this seems to happen during the compression and recoil period (see Fig. 1), we can conclude that the clusters are especially prone to decay during the initial disturbance. It is worth noticing here that even the monomers aimed to the edge of the target cluster result in successful collision in the sense that the monomer enters deep in the potential well of the cluster. There are practically no encounters where the monomer comes close to the target cluster, joins it (according to the

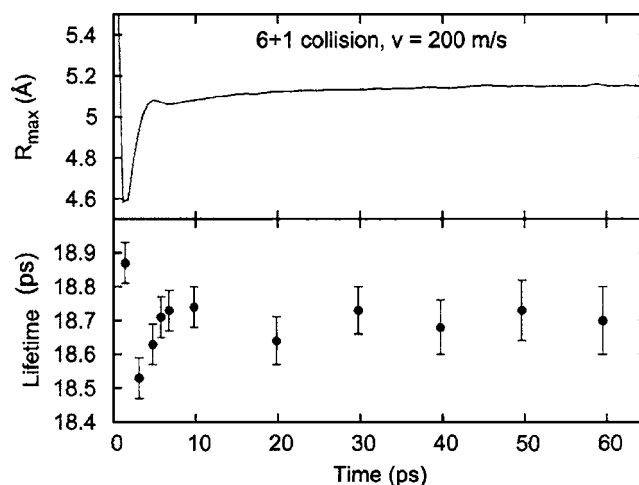


FIG. 6. The average lifetime of clusters resulting from 6+1 collisions with unrelaxed target clusters. Upper panel: the maximum radius of the six-atom target cluster (same as the middle line in the upper panel of Fig. 1). Lower panel: the average lifetime of clusters resulting from 6+1 collisions. The horizontal axis indicates the time since the formation of the target cluster. Standard deviation is shown as error bars.

cluster definition), and then departs. The short-lived clusters can be considered properly formed, but they are by no means equilibrated.

Variations in cluster radius affect the condensation rate by causing changes in collision cross section. One can then assume that the condensation rate is smaller for clusters in the compressed state at the beginning of the cluster formation (see Fig. 1). This hardly changes nucleation rate because a monomer collision is very rarely followed by a second one in a few picoseconds. On the other hand, if the monomer is required to be a part of the cluster for some time, which means that sticking probability is included in the definition of condensation rate,<sup>10,15</sup> the lifetime of the cluster must be taken into account. The obvious question is then how the unrelaxed state of the target cluster changes the lifetime of the cluster resulting from the collision. Simulation results presented above cannot answer that because the target clusters were prepared to a relaxed state.

For a proper assessment of cluster lifetimes we simulated reaction



where the starting configurations of the six-atom target clusters were taken from the simulations discussed in the previous two sections and recorded when the six-atom cluster was born according to the cluster definition ( $10^5$  configurations in total). To ensure that the vapor monomer collided with the cluster at a given time, the monomer was placed at a fixed initial distance from the cluster. Of course, cases where the target decayed before the collision were not taken into account.

The lower panel of Fig. 6 shows the average lifetime of the seven-atom cluster when the velocity of the monomer is 200 m/s and the impact parameter  $b=0$  Å. For comparison  $R_{\text{max}}$  of the six-atom target cluster is shown in the upper panel (the same as the middle line in the upper panel of Fig. 1). The horizontal axis indicates time passed since the for-

mation of the target cluster. Figure 6 indicates that the lifetime of the cluster is shorter only when the target cluster is expanding after the previous collision, and even then the decrease is small. It is obvious that the state of the target cluster has negligible effect on the lifetime of the cluster resulting from the collision.

#### IV. DISCUSSION AND CONCLUSIONS

We have performed molecular-dynamics simulations of atom-cluster collisions to assess the role of unrelaxed cluster states on cluster properties and gas-liquid nucleation in LJ argon systems. Our results indicate that variations in cluster radius and potential energy take a relatively short time to reach a final value, while rotational energy relaxes very slowly. Time-dependent decay rates and non-Maxwellian distribution of molecular speeds are observed only at the very beginning of cluster formation. A slight decrease in the cluster lifetime is seen if the monomer collision takes place a few picoseconds after the formation of the target cluster.

The simulation results must be put into proper perspective before we can make any conclusions concerning nucleation. In supersaturated argon vapors collisions between free atoms and clusters are expected to occur every 50–500 ps.<sup>10,12</sup> A study of monomer collisions on clusters at different stages of relaxation then suggests that in typical nucleation conditions practically all vapor atoms collide with clusters which are relaxed in terms of evaporation behavior. For the monomer-cluster collisions to happen more often than every 10 ps on average, the vapor should be close to spinodal conditions or even in the unstable region. We can therefore conclude that the internal equilibration of clusters is fast enough for the transient effects not to have serious effects on rate coefficients and, consequently, on nucleation rates.

Although interesting phenomena and topics are well worth a further study, changes in the cluster radius and internal transformations between different kinetic-energy contributions have little value from the nucleation point of view. For example, a cluster may still have quite a lot of rotational kinetic energy long after the cluster formation, but this has no effect at all on evaporation rates. Evaporation seems to be controlled by kinetic energy as a whole, not by the partitioning of kinetic energy into vibrational and rotational contributions.

Nucleation rates can be assumed to decrease if there are fewer target clusters than expected. This may indeed be the case because with certain collision geometries and high-speed monomers the decay rate immediately after the collision is faster than in later times, and thus the cluster distributions are affected. To fully gauge this effect on nucleation rates would require very extensive simulations.

Our results show that in 5+1 collisions the cluster atoms attain the Maxwellian distribution of speeds in a few picoseconds. The relaxation period is likely to shorten with increasing cluster size. The initial period with distorted speed distribution means that the temperature of the cluster is not well defined. While temperature can always be calculated from the kinetic energy of the molecules and clusters as

small as four molecules can be viewed to have a canonical temperature,<sup>16</sup> a cluster cannot be regarded as having a temperature during the first moments of cluster formation. This has consequences to nucleation kinetics if the clusters and rate coefficients are discussed in terms of temperature rather than energy.<sup>17</sup> Comparing the results for cluster energetics (Fig. 2) and decay (Fig. 5) with speed distributions reveals that the distributions are distorted where there is a significant conversion between kinetic and potential forms of energy and fast decay is observed.

Some doubts can be raised whether the non-Markovian effects (for example, in Fig. 5) might in fact be caused by monomers passing and attaching the cluster in geometrical sense but not actually becoming bound members of the cluster. This is not likely the case in our simulations. The chosen impact parameters are such that the monomer inevitably interacts with two or more cluster atoms, not just with one atom at the edge of the cluster. Furthermore, potential energy has a minimum at approximately 2 ps after the cluster definition is satisfied, which means that the cluster is tightly bound. On the other hand, anomalous decay is observed up to 5 ps.

We have limited our simulations to target cluster sizes of five and ten molecules. In typical nucleation conditions these are rather small clusters and are undoubtedly in the precritical range. It is quite obvious that small clusters are mostly disturbed by the collision, and the effects found in this study would mostly disappear as the critical cluster size is approached.

We have also omitted carrier gas from the simulations. A nucleating cluster typically experiences much more frequent collisions with the carrier gas molecules than with the vapor molecules of the nucleating substance. Carrier gas collisions may cause the cluster to be in a continued unrelaxed state, which could cause greater changes in nucleation rates than suggested by the present study.

The results and conclusions presented here apply to simple molecules or atoms with no internal structure. It is conceivable, for example, that much of the kinetic energy of the incident molecule could be efficiently converted to the internal vibrational degrees of freedom of more complicated cluster molecules, and could thus speed up the relaxation process. Similar speculation might also apply to the rotation of the cluster molecules. These effects are left for future study.

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