Molecular Dynamics Investigation of Transient Nucleation in the Freezing of Clusters of SeF_6

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Although theorists have devised a number of different approaches to treat the early (transient) stages of freezing by homogeneous nucleation, no experiments of sufficient accuracy have been performed to check the theories. In the present work a computer experiment is carried out by molecular dynamics simulations in order to make such a check. A system of 2500 independent liquid clusters of SeF_6 with an average size of 545 molecules was rapidly cooled to 130 K and maintained at that temperature until each cluster froze. Nucleation times of each cluster were recorded, ordered, and plotted against the quantity $-\ln[N(t)/N_o]$ for comparison with Wu's theory of moments. Results conformed to Wu's expression. From the behavior in the transient region could be derived the reduced moment characterizing the initial, rapidly increasing rate of appearance of nuclei, and from the slope and intercept of the steady state plot could be derived the steady state nucleation rate and nucleation time lag. Although Wu provided no clue about the magnitude of the reduced moment to be expected, an earlier, more complete theory of Kashchiev did, at the expense of introducing what some had claimed to be severe approximations. Our results yielding a (dimensionless) reduced moment of 1.43(0.07) supported, to within statistical error, Kashchiev's theory which implied a moment of 1.40.

Introduction

The transient regime is the initial stage of the process of freezing before a steady state has been reached in the generation of critical nuclei.[1,2] This regime has been the subject of many theoretical treatments, treatments which introduced various approximations to make them tractable. No comparable experimental effort has been expended to test these theories. Although many studies of the kinetics of freezing have appeared, none that we are aware of have acquired enough observations of nucleation events in the transient regime to allow a definitive comparison with theory. One problem is that no purely experimental technique available has the sensitivity to detect individual nuclei directly. On the other hand, it has been found that molecular dynamics (MD) techniques, which follow the behavior of a system in molecular detail, are able to monitor the spontaneous generation of nuclei in freezing, at least in deeply supercooled liquids.[3] Therefore, MD studies of freezing with realistic potential functions offer the possibility of directly investigating what goes on in the transient regime, with observations free from possible theoretical biases about molecular behavior. Such studies, however, are so exceedingly computer-intensive that until recently it had not been practical with ordinary workstations to carry out computations on a sufficiently large set of independent spontaneous nucleation events to characterize transient nucleation.

Remarkable advances have taken place in computer technology, changing the situation considerably. Although an investigation of a fairly large number (375) of nucleation events in very small $(RbCl)_{108}$ clusters carried out on a workstation has already been described,[4] it seemed worthwhile to perform a much more computer-intensive study with the new hardware available. In the following we report the behavior observed in nucleation events taking place spontaneously in 2500 independent $(SeF_6)_n$ clusters with n ranging from 540 to 560 molecules (in subsequent sections we will take n to be 545). Simulations involved computations of nearly three orders-of-magnitude more interatomic distances than the simulations of rubidium chloride clusters. They were carried out on a distributed-array processor to be described in the next section.

Why selenium hexafluoride was chosen to be the subject of our first large-scale test of transient nucleation is somewhat accidental. Although the substance is of no particular technological importance, it offers a convenient model system. The substance is well behaved, reasonably well characterized,[5] and is composed of molecules possessing a very high symmetry. It has also been the subject of an experimental study of nucleation kinetics in this laboratory.[6] In prior MD simulations, we found it convenient to examine its behavior in several investigations of the nucleation and subsequent growth of crystals in liquid clusters.[7−11] In addition, being polyatomic, SeF_6 provides interesting orientational aspects of molecular behavior not possessed by the systems of Lennard-Jones spheres that have been the favorite subject in most other simulations. The degree to which orientations of molecules are correlated has provided a new order parameter to characterize phase changes.[11] In the present investigation, however, the recognition of phase change was made through the use of translational, not orientational order.

Procedure

Method of Moments. In our laboratory, all previous analyses of nucleation in MD simulations of sets of supercooled clusters undergoing spontaneous nucleation had been based on an oversimplified rate law. This law assumed that the decay of the population of liquid clusters followed the first-order expression

$$-\ln[N_l(t)/N_o] = K(t - t_o) \qquad (1)$$

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where

$$N_l(t) = N_o - l + 1 \tag{2}$$

is the number of clusters in the set of N_o clusters which have not yet undergone nucleation before time t of the lth nucleation event, K represents the product J_sV_c with J_s the steady state nucleation rate, V_c the volume of the clusters, $t > t_o$ the time of nucleation, and t_o the nucleation time lag. Such a rate law is the same as that for the decay of radioactive nuclei starting at time t_o but is clearly incorrect for nucleation in the transient period before a steady state is reached.

References 12 and 13 addressed the problem of how to modify eq 1 to take into account the phenomenon of transient nucleation in analyses of MD data for clusters. The most general treatment of transient nucleation that is relatively simple to incorporate into analyses is that of Wu.[14] His method of moments yields an explicit expression which he applied to nucleation in a large system of bulk matter. We modify it to apply to nucleation in a large set of clusters, obtaining

$$-\ln(N_l/N_o) = K\left\{t\left[1 - \frac{1}{2}\mathrm{erfc}(f_1)\right] - t_o\left[1 - \frac{1}{2}\mathrm{erfc}(f_2)\right]\right\} \tag{3}$$

where

$$f_1 = \left\{\frac{\ln[(t/t_o)M_R^{1/2}]}{(2\ln M_R)^{1/2}}\right\} \tag{4}$$

and

$$f_2 = \left\{\frac{\ln[(t/t_o)M_R^{-1/2}]}{(2\ln M_R)^{1/2}}\right\} \tag{5}$$

In view of the fact that the erfc function decreases rapidly when the time increases beyond t_o, it is evident that eq 3 approaches eq 1 at large times. The parameter M_R characterizing the gradual buildup of nuclei in the transient regime is a quantity we have chosen to call the "reduced moment." It is proportional to Wu's first moment M but possesses a more universal nature. Clearly, the lowest value the reduced moment can have is unity. Wu regarded his moment M as a free parameter to be derived in the analysis of experimental data.

Because the quantity $-\ln[N_l(t)/N_o]$ is known exactly in the set of nucleation events while the stochastic nucleation times are a matter of chance, it is appropriate to make the times, t, the uncertain "y" values in least-squares analyses. This requires that eq 3 be inverted. To a good approximation for the range beyond $-\ln[N_l(t)/N_o] \approx 0.03$,[12] the result is

$$t = t_o + g_l/K - t_o(1 - 0.5/M_R^{2.5})\exp[-1.82(g_l/Kt_o)^{1/2}/(M_R - 1)^{0.41}] \tag{6}$$

where g_l represents the quantity $-\ln[N_l(t)/N_o]$.

It is worthwhile to say a few words about the uncertainty to be expected for a reduced moment derived from a set of nucleation times. If the number of nucleation events is not very large, least-squares refinements of data including all three of the parameters J_s, t_o, and M_R are too ill-conditioned to be useful. Therefore, as will be discussed in a later section, refinements have been carried out including only the rate and time lag as variables while holding the reduced moment constant at one or another value in any given refinement. Having no error matrix element for the reduced moment is of no importance because it has already been shown[13] that the error matrix for a given set of data yields estimates of uncertainties in derived parameters that are far too optimistic. As described in ref 13, estimates of the true uncertainties can be deduced from histograms of J_s, t_o, and M_R derived from very large sets of nucleation times, each set generated stochastically in computer simulations. It is this source of uncertainty which will be applied in the following, not only to M_R, but also to J_s and t_o.

TABLE 1: Lennard-Jones Parameters for the Seven-Site Intermolecular Potential Function for SeF_6 Molecules[a]

atom pair	F−F	Se−Se	Se−F
σ, Å	2.92	3.78	3.322
ϵ, kJ/mol	0.213	1.38	0.5422

[a] Charges, $|e|$, for F, −0.185; for Se, 1.11.

Outline of Computational Details. For hexafluoride molecules there are many different molecular packing arrangements of roughly comparable stability, according to potential energy minimization analyses. The potential function adopted in this investigation was originally developed in order to construct molecular coordinates for the minimum energy structures of various possible phases of crystalline SeF_6. From these coordinates were calculated the characteristic diffraction powder patterns corresponding to the phases. This facilitated the identification of the several structures encountered in electron diffraction studies of crystalline clusters of SeF_6 generated in supersonic flow experiments.[6] Potential parameters for fluorine and selenium were derived by perturbation techniques from the neon and krypton Buckingham parameters published by Hill.[15] For use in MD simulations the Buckingham potential parameters were converted to Lennard-Jones parameters, and partial charges were added by Kinney,[5] based on results of charge equilibration computations carried out with the proprietary program BioGraph/PolyGraph.[16] Hence the resultant potential parameters listed in Table 1 were not developed to reproduce thermodynamic or kinetic properties. For this reason, it turns out that the corresponding enthalpy of sublimation is 24.6% too low. Nevertheless the melting point of the high-temperature solid body-centered cubic (bcc) phase is very nearly correct. Despite the fact that the potential functions yield an inexact account of the actual substance, SeF_6, they should be entirely suitable for testing the reduced moment sought here because, in the treatments reviewed by Kelton, Greer, and Thompson,[1] the moments implied are universal, independent of the exact thermodynamic properties of individual substances.

Molecular dynamics simulations were performed on a 24-node Linux cluster with individual simulations run in serial on the various nodes. The calculations were performed using two different modifications of the MD program outlined in Allen and Tildesley,[17] the second modification being a slightly more accurate version of the first.

Initially, MD simulations were performed on clusters containing 725 molecules of SeF_6, which were taken to be rigid octahedra with Se−F bond lengths of 1.67 Å.[18] Simulations were carried out at constant temperature using a seven-site intermolecular interaction function based on pairwise-additive Lennard-Jones potential functions with partial charges assigned to the atoms. Each MD simulation had a time step of 7 fs and was started from an approximately spherical cluster of 725 molecules which had been prepared in the monoclinic phase.

A set of clusters at initial temperatures of 100, 130, or 140 K were heated in at least four stages to 220 K. At each stage the clusters were equilibrated for 70 ps. During this process

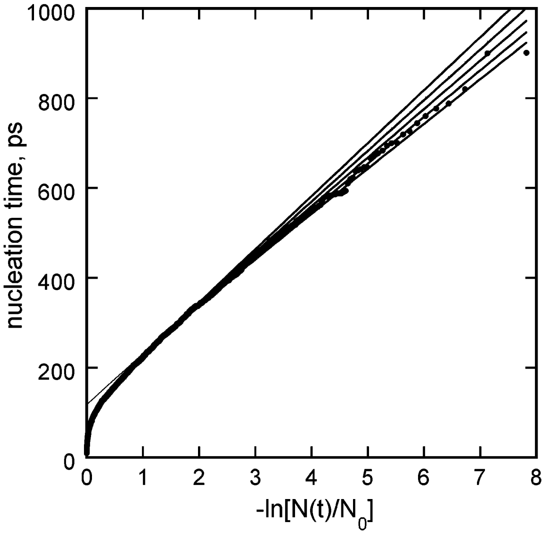

Figure 1. Nucleation times, in ps, as a function of the variable $-\ln[N_l(t)/N_o]$. The heavy dots correspond to the sorted times found for the nucleation events in 2500 independent MD simulations. The light lines correspond to the times calculated for five different reduced moments, M_R, namely with values of 1.35, 1.45, 1.55, 1.65, and 1.75. The lowest values of M_R generated the lines with the largest calculated times in the figure. The tangent to the steady state times corresponding to $M_R = 1$ intersects the time axis at the time lag $t_o = 118$ ps.

the clusters transformed from the monoclinic to the bcc phase and then melted.

The final configuration of each 725-molecule cluster at 220 K was maintained in equilibrium while 30 configurations were saved at intervals of 4.9 ps. This process resulted in 1100 new configurations which served as starting configurations for the cooling runs. During the equilibration at 220 K some evaporation took place. To ensure that the newly created clusters were comparable, each cluster was trimmed down to be approximately spherical and contain between 540 and 560 molecules. All of the 1100 clusters at 220 K were equilibrated at 200 K for 70 ps before being quenched to a temperature of 130 K for 1 ns. A subset of 600 clusters was taken from the 1100 clusters at 220 K and underwent the same equilibration at 200 K for 70 ps but with a modified version of the MD simulation program. Since the MD program had been altered to improve its internal accuracy, this resulted in trajectories that quickly diverged from the equilibration simulations performed with the original program, yielding nucleation times uncorrelated with those originally calculated. Therefore, the 600 clusters equilibrated at 200 K could be considered independent. In this new subset, the 600 clusters at 200 K were quenched to a temperature of 130 K for 1 ns. This set at 200 K was further equilibrated at 180 K for 70 ps to produce an additional set of 600 independent clusters which were then quenched to a temperature of 130 K for 1 ns. Another set of 200 was generated by a similar procedure to reach a total of 2500 clusters, each of which froze to the bcc phase during the final quench. No statistically significant differences in nucleation parameters were found in the different sets despite the differences in preparation.

Results

Determination of Kinetic Quantities. In Figures 1 and 2 are plotted the sorted nucleation times versus the quantity $-\ln[N(t)/N_o]$ for 2500 independent liquid $(SeF_6)_{545}$ clusters quenched to 130 K. From the limiting slope, intercept, and behavior in the transient regime can be determined the rate, time lag, and reduced moment in accordance with eqs 3−5. It should be noted that the irregular nucleation times plotted in Figure 1 beyond a value of 4 for the abscissa span a region in which points have become very sparse and far apart (and, hence, this region is not weighted heavily in an optimally weighted least-squares analysis). Put in a different way, 32% of the nucleation times are found within the first 5% of the range of the abscissa plotted in Figure 1, and 22% are found in the second 5%. By contrast, only 2% of the events occur in the last half of the range of the abscissa. Analyses of the entire set of times were used to derive the nucleation rate and time lag, each analysis being carried out for one member of a set of assumed reduced moments. Ideally, the reduced moment giving the best fit of the times shown in Figure 1 might be expected to correspond to the expectation value of the moment.

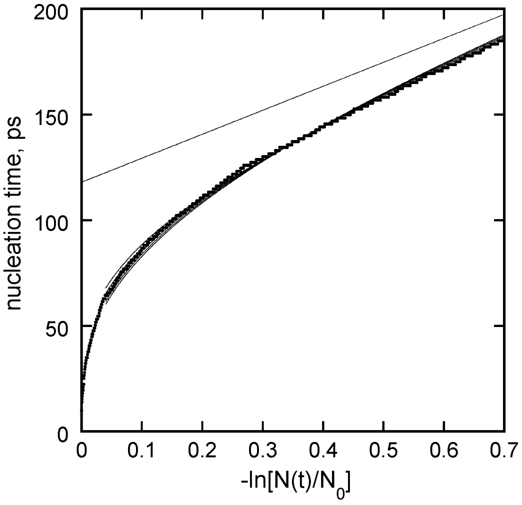

Figure 2. Same as Figure 1 except that the results are plotted for only the first 50% of the nucleation events.

In practice,[12,13] unless the optimum weight function is applied, it has been found to be more reliable to constrain the rate and time lag by fitting the *entire* set of data, as stated above, but to infer the reduced moment by finding the best fit of observed and calculated curves *in the transient region* (roughly the first 50% of the nucleation times). Such a comparison is illustrated in Figure 2 where the observed nucleation times have not quite reached their steady state values. If the optimum weighting is applied,[13] results so determined are $1.49(0.05) \times 10^{35}$ m^{-3} s^{-1} for the nucleation rate, 118(5) ps for the time lag, and 1.43-(0.07) for the (dimensionless) reduced moment, with standard deviations shown in parentheses. These parameters were derived from times of onset of nucleation found by the method listed in the Appendix.

Discussion

Comparison of the Present Results with the Results of Prior Studies. The effect of neglecting the reduced moment in earlier treatments would be expected to result in a lower rate and time lag, but such a shift tends to be masked by the large statistical uncertainty associated with the much more limited number of events involved. Moreover, statistics inferred from such an oversimplified model,[9] that is, based on the application of eq 1 instead of eq 3, give an unrealistically low estimate of uncertainties. To illustrate how sensitive results are to the number of nucleation events observed, we present results for prior MD runs on the same system. Results in m^{-3} s^{-1} that were obtained, based on eq 1, for nucleation rates in prior simulations quenched to 130 K were (with corrected uncertainties) $(2.1 \pm 0.7) \times 10^{35}$ (ref 9, 138 molecules, 15 events), $(2.2 \pm 0.7) \times 10^{35}$ (ref 11, clusters of 725 molecules, 12 nucleation events), and $(1.0 \pm 0.3) \times 10^{35}$ (ref 11, 1722 molecules, 10 events). Besides statistics, another factor which should be taken into account is that nucleation is initiated at the surface.[10] Therefore, rates calculated on the basis of critical nuclei per unit volume per unit time would be expected to be size dependent. Although this was the basis used in the present analyses of nucleation rate, it should have no effect on the derived time lag or reduced moment. It turns out that, to within statistical error, the prior results are not discernibly different from each other or from the present result of $(1.49 \pm 0.05) \times 10^{35}$ based on 2500 events. It should be noted that a treatment to account properly for the transient regime was not available in the prior studies nor was the same computer power available.

Time Lag. The spontaneous behavior of the molecules undergoing nucleation in the supercooled clusters produced fleeting structural fluctuations that resulted in a gradual buildup of embryos. As a consequence of this process, there was a time lag before a steady state of nucleation was attained. The value of the time lag derived from the MD simulations was 118 ps, as reported in the previous section. This value was based on the estimate of the reduced moment inferred from the observed nucleation times in the transient region. The duration of the derived time lag depends on the reduced moment assumed. For example, over the range of moments 1.4, 1.45, and 1.5 represented in the calculated curves of Figure 2, the corresponding least-squares time lags derived from the nucleation data were 115, 120, and 125 ps.

Reduced Moment. Finally, it is useful to comment on some aspects of the reduced moment. In a new, alternative treatment of transient nucleation by Shneidman,[19] a quantity equivalent to M_R is encountered which the author designated as q. How the reduced moment characterizes nucleation has not been discussed in the prior literature. All theoretical treatments of nucleation agree that there must be a time lag before a steady state rate in the formation of critical nuclei is attained. The reduced moment characterizes whether this lag is almost the same for all nuclei initially generated (in which case M_R is nearly unity) or whether there is a wide variation of times of formation (making M_R quite exceed unity). The reduced moment quantifies this variation. Wu,[14] in his treatment of moments, provided no guidelines about how to estimate the magnitude to be expected and simply suggested that the moment be determined by experiment. We know of no reports of such determinations by experiment. On the other hand, a 1969 treatment by Kashchiev[20] provided more specific detail than Wu's about the transient period in which nuclei materialize and disappear. Moreover, in the review of ref 1, this treatment was singled out as the best of those available. This treatment says nothing explicitly about the reduced moment, but a comparison with Wu's theory shows that the Kashchiev time behavior agrees almost exactly with Wu's when M_R is taken to be 1.40.[13] Nevertheless, in discussing alternative treatments of transient nucleation, Wu commented that Kashchiev's approach is based on rather severe approximations. Therefore, because of the so-far unknown behavior of the buildup of nuclei before the steady state, and in view of the questioned validity of the Kashchiev treatment, it is of interest that the present investigation does provide a result characterizing the transient regime. The simulations of the freezing of our $(SeF_6)_{545}$ clusters yield a value for the reduced moment of 1.43(0.07) agreeing, to within its uncertainty, with the Kashchiev value. By comparison, a reduced moment of 1.48(0.18) was found in the study of 375 nucleation events in $(RbCl)_{108}$ clusters.[4] Whether the Kashchiev result will continue to apply to systems of different sizes and compositions is currently being explored in this laboratory.

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Appendix

In MD simulations of the spontaneous freezing of clusters, no reliable criterion has been established to identify the critical nucleus. Among the problems is the fact that the size of critical nuclei is arbitrary because it depends on which order parameter is chosen to characterize the nucleus. Therefore, to provide a procedure for analyzing MD data, we adopted the following routine to recognize the times of onset of nucleation. We associated such times with the times at which critical nuclei were formed. Although our choice is somewhat arbitrary, it is presumably at least as valid as the choice adopted in experimental studies of nucleation rates, where nuclei must grow large enough to be observed.

Coordinates from each MD simulation were saved every 200 steps (1.4 ps), and each set of coordinates was analyzed with the q_6 criterion[11] to determine the number of liquid, solidlike, and bulklike molecules in the cluster, including both surface and core molecules. Initially, all the occurrences of bulklike molecules in the range 30−90 were determined. The median value of all these occurrences was used as the initial value of n, and this value was then further refined using the following criteria.

1. If the current value of n is greater than or equal to 50, then preceding values of n are examined sequentially until a value of n less than or equal to 50 is found. The value of n is set to this new value.
2. If four steps back and eight steps back n has a value which is less than the current value of n, then n is modified such that it takes the value of n from four steps back.
3. If six steps forward n has a value which is less than the current value of n by at least eight, then n is modified such that it takes the value of n from eight steps forward.
4. If 12 steps forward n has a value which is less than the current value of n, then n is modified such that it takes the value of n from 15 steps forward.

In cases 2, 3, and 4 above, if the value of n was found to be less than 20, then subsequent values of n were examined sequentially until a value of n greater than 20 was found, and the value of n was then set to this new value. If none of these criteria had been satisfied, then the value of n was rechecked against the criteria until all the criteria were satisfied or until the criteria had been checked 100 times. Since the criteria were not guaranteed to find the nucleation time for all clusters, it was necessary to limit the search to 100 checks to prevent the search from running endlessly. Once a value of n had been determined, the corresponding time was taken as the nucleation time for that cluster.

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