Transient Nucleation: Computer Simulation vs Theoretical Inference†

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A new procedure is introduced to determine the three principal parameters that characterize homogeneous nucleation, namely the "reduced moment," the time lag, and the steady-state rate. This information can be derived, in principle, by monitoring the spontaneous freezing occurring in molecular dynamics simulations of supercooled liquids. The new procedure has been applied to the set of 2500 nucleation events acquired in a prior investigation of the freezing of 2500 independent large molecular clusters of SeF_6. In this procedure the times of the first appearance of nuclei containing n molecules is determined for each cluster, considering values of n ranging from small to very large. This procedure avoids the mixing together of a large distribution of nuclear sizes that resulted from our previous algorithm based on the times of onset of nucleation. Such a superposition of sizes appears to have seriously inflated the derived reduced moment parameter characterizing transient nucleation, thereby favoring the 1969 theory of Kashchiev over the more recent treatments of Wu and Shneidman. Results of the new procedure, as interpreted by a provisional mode of analysis, reverse the assessment of the theories and provide, as well, a new method for determining the size of the critical nucleus.

Introduction

This paper represents work in progress on the problem of nucleation in the transient regime. The phase change involved is freezing. This is an area in which very little definitive experimental information exists. Advances in computer technology, however, make it feasible to carry out detailed computer experiments that can, in principle, provide significant information about the transient regime. This information should be able to afford detailed checks of results of recent developments in nucleation theory, but problems have so far stood in the way of rigorous comparisons. The computer experiments consist of molecular dynamics (MD) simulations and are very simple in concept. Molecules are given free rein in their behavior, so that when structural fluctuations in the supercooled liquid initiate nucleation, results are unbiased by any possibly subjective notions of theorists. In the computer experiments, a large number of independent spontaneous nucleation events occur. Although the experiments are simple enough in principle, their relationship to current theories of nucleation is not entirely straightforward. The laboratory experiments[1−5] to date that have been examined most closely by nucleation theorists[3,6−8] have involved the crystallization of glasses. In such experimental studies, the nucleation process takes place slowly enough to be followed readily. On the other hand, nuclei in the vicinity of the critical size formed are far too small to be detected. Only when nuclei grow large enough to be observed can data points be recorded. Therefore, the information yielded about kinetics is somewhat degraded. Moreover, and this imposes an extremely severe limitation to the determination of the parameters characterizing the transient regime, the number of nucleation events recorded in experiments we are aware of have been far too few to permit the derivation of a meaningful set of parameters. On the other hand computer experiments can provide data corresponding to thousands of nucleation events.[9]

An obstacle to the rigorous derivation of kinetic parameters from MD simulations has been the uncertainty in deciding what
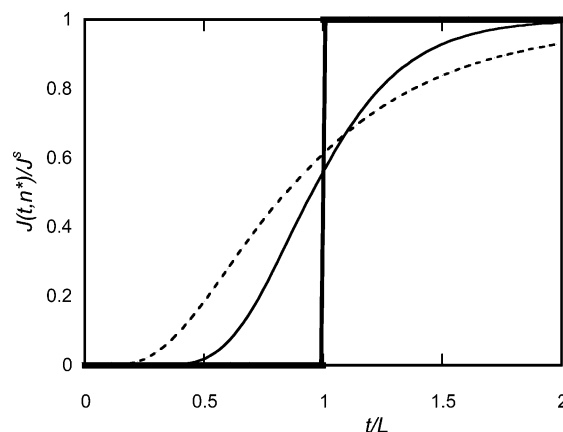
Figure 1. As illustrated above, the reduced moment parameter, M_R, describes the abruptness with which the steady state of nucleation is attained in the transient regime. The lowest value M_R can have is unity, a value leading to the step function identified by the heavy curve above. The other two curves correspond to reduced moments of 1.1 (solid) and 1.4 (dashed).

times to record as nuclei begin to form. In processing the data from thousands of runs, it is not feasible to perform detailed tests to recognize, in each run, when the nuclei become of critical size and whether they successfully pass over the free energy barrier. Instead, in prior studies in this laboratory, times of the "onset of nucleation" were recorded as determined by an algorithm documented in ref 9. Those times, when ordered and plotted vs the accumulated nuclei per volume $N(t)$ yielded quite reasonable steady-state nucleation *rates* J^s and plausible *time lags L.* Moreover, the derived $N(t)$ curve appeared to provide a well-determined value of the so-called *reduced moment* M_R,[10,11] a parameter characterizing the transient regime. The physical meaning of this parameter is conveyed in Figure 1. The mathematical definition will be given subsequently. Even though the times of "onset" must be far more closely related to times of formation of critical nuclei than are the times at which nuclei become large enough to be detected in laboratory experiments,

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we have found that our "times of onset of nucleation" seriously distorted the derived reduced moment parameter for reasons to be discussed subsequently. What is presented in the following is an alternative and, it is hoped, a more effective way of selecting the data to be recorded. Not only does the method yield a quite different, and probably more reliable, value of the reduced moment, but it also suggests a new way to estimate the size of critical nuclei.

Times of onset of nucleation derived from the MD simulations herein described, and the algorithm used to determine them, were recently published elsewhere.[9] In the following, the data from the simulations are reanalyzed and the results so obtained are compared with implications of three different theoretical formulations of nucleation theory. The present alternative treatment of data quite changes the conclusion reached about which theories provide the most satisfactory representation of the MD simulations.

Procedure

Outline of Computational Details. Because of extensive prior experience with them in this laboratory, the subject molecules were selenium hexafluoride, whose intermolecular potential function has been established reasonably well. The potential parameters associated with its seven-site function are listed in Table 1 of ref 9.

Molecular dynamics simulations were performed on a 24 node Linux array with individual simulations run in serial on the various AMD Athlon XP 1700+ nodes. Calculations were performed using one or the other of two different modifications of the MD program outlined in Allen and Tildesley.[12] The 2500 runs consumed about 5 months of continuous CPU time involving 23 nodes.

The subject molecules were taken to be rigid octahedra with Se−F bond lengths of 1.67 Å.[13] In their early history, before the liquid clusters were supercooled, they had contained 725 molecules. Before they were quenched to a low temperature, clusters were trimmed to quasi-spherical drops containing approximately 545 molecules so that the partial evaporation already suffered by many clusters would not spoil the near homogeneity of the final ensemble. Rapid quenching to 130 K was followed by a period of constant temperature, maintained until the clusters froze. This temperature was very nearly 100 deg below the freezing point of the bulk material. Simulation time steps were 7 fs.

Selection of Nucleation Times. As discussed in the Introduction, our prior algorithm[9] for selecting nucleation times has proven to be unsuitable in studies to describe the transient regime. This algorithm selected times corresponding to the formation of a wide range of nuclear sizes. Consider the time evolution of the nucleation rate, $J(t,n)$, as a function of the size, n, of the nucleus under consideration. A plot of its behavior, adapted from Figure 12 of ref 14, is shown in Figure 2 for several sizes. It is apparent that if the data analyzed happened to be a superposition of such curves, each component depending on a different value of n, the moment describing the shape of the curve of the superposition could be larger than that for any individual size. To avoid the selection of times corresponding to a distribution of sizes, and not knowing the size corresponding to the critical nucleus, we recorded the times at which a nucleus of size n first appeared in each cluster, and then, as advocated by Oxtoby,[15] eliminated that cluster from the ensemble. This was done for values of n ranging from 10 to 300. All of the curves $N(t)$ of accumulated numbers of nuclei per unit volume were qualitatively the same as the curves based on the "onset" criterion, and each could be analyzed in terms of a steady state
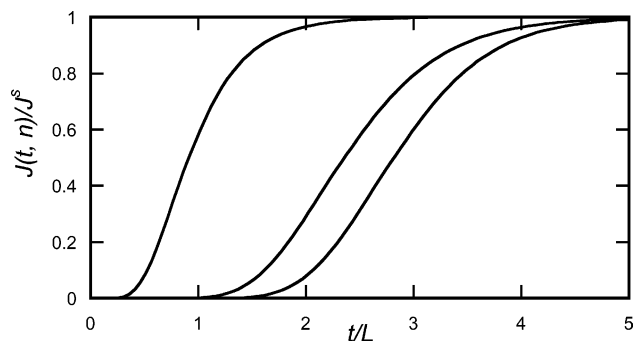
Figure 2. Temporal evolution of the nucleation rate $J(t,n)$ as a function of n, the number of molecules in the nucleus under consideration. In the figure the sizes of nuclei correspond to n^*, $2n^*$, and $3n^*$ molecules, the shortest time lag being for the smallest nucleus. Figure based on the parameters of Figure 12, ref 14.

rate at large enough times. These rates, however, differ fundamentally from those corresponding to the function $J(t,n)$ discussed above inasmuch as the $J(t,n)$ rates are based on existing populations of nuclei, not on first appearances of nuclei.

Of course, results depend on the order parameter and dividing surface adopted in the definition of n. At deep supercoolings, there appeared filaments and thin sheets of molecules identified as "solidlike" by Voronoi or Q_6 criteria, and these structures often contained many molecules. Nevertheless, such tenuous aggregates do not correlate at all closely with entities associated with nucleation. What do correlate well with nucleation are aggregates of "bulklike" solid molecules defined in ref 9. One exception to that definition introduced in the present treatment is made to include the appearance of nuclei in the surface, the most common site of nucleation. Details are given in the Appendix. How to interpret the rates of first appearances of n-molecule nuclei will be analyzed in a later section.

Nucleation Theories To Be Considered. An exact numerical treatment of the theory of freezing developed by Becker and Döring,[16] Turnbull and Fisher,[17] and Turnbull[18] can be carried out, including what happens in the transient regime, but there is utility in finding a satisfactory analytical treatment. We will consider just three different analytical treatments. The first is one introduced in 1969 by Kashchiev,[19] on the basis of an approximate solution to the Zeldovich−Frenkel continuum formulation of the nucleation problem. The second, one that was published in an excellent review by Wu[14] in 1997, is based the Becker−Döring, Turnbull−Fisher approach, which takes into account the discrete steps in the process. The third, and most recent, is an asymptotic solution to the high barrier case published in 2003 by Shneidman.[20] We will not consider possible higher-order corrections to this theory to cover low barrier cases. One reason for examining Kashchiev's theory is that in a comprehensive review by Kelton, Greer, and Thompson[7] in 1983, it was singled out as the most accurate of the various theories proposed by that time. More recently it has been criticized as being based on severe approximations, but because of the simplicity of its results, it serves as a point of comparison with the later theories.

Wu's theory is based on the attribution a log-normal form to $\rho(t)$, the time distribution of nucleation rate defined by

$$\rho(t) \equiv -\frac{\partial}{\partial t}\left(1 - \frac{J(t)}{J^s}\right) \tag{1}$$

Wu constructed a representation of $\rho(t)$ to reproduce the first two temporal moments, M_0 ($\equiv L$) and M_1, of the function $[1 - J(t,n)/J^s]$ derived from exact numerical treatments by Kelton et

al.[7,8] Wu then showed that the log-normal distribution accounted very well for the shape of the exact $J(t,n)/J^s$ function. The parameter we have chosen to call the "reduced moment," M_R, is

$$M_R \equiv 2M_1/M_0{}^2 \qquad (2)$$

It is proportional to Wu's moment M_1 but it possesses a more universal significance.

Shneidman's theory[20] introduces a parameter "q", which is defined in exactly the same way as the "reduced moment," M_R. Therefore, we will express Shneidman's theory in terms of M_R. The intention of the present work is not to assess the validity of the various theoretical approaches but simply to compare their results with the results of our computer-intensive simulations of spontaneous nucleation.

Kashchiev[19] treats the rate of production of critical nuclei (for which n is denoted as n^*). His result, expressed as a function of reduced time $J(t/L)$, is the rapidly converging series.

$$J(t/L)_{Kashchiev} = 1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp[-m^2\pi^2(t/L)/6] \quad (3)$$

The other two treatments[14,20] can be expressed as

$$J(t/L)_{Wu} = 1 - \text{erfc}\left[\frac{\ln[(t/L)\sqrt{M_R}]}{\sqrt{2\ln(M_R)}}\right] \qquad (4)$$

and

$$J(t/L)_{Shneidman} = \exp\left\{-\exp\left[-\frac{\pi}{\sqrt{6}}\frac{(t/L)-1}{\sqrt{M_R-1}}\right]-\gamma\right\} \quad (5)$$

where γ is Euler's constant (0.5772...).

Points to note are that the three functions are quite different analytically and, moreover, that both Wu's and Shneidman's expressions require an undetermined parameter, M_R, to be complete. Both authors suggest that this parameter needs to be found by experiment although Shneidman suggests an expression for the high barrier case when the nucleus is much larger than its critical size. We know of no experiment predating our computer experiment that establishes this parameter. Kashchiev's treatment is more specific in that it needs no such parameter to be adjusted. Therefore, by the rules of formal logic, it is more easily falsified than the other two treatments because it cannot be modified to accommodate facts by adjusting a parameter. As far as we are aware, Kashchiev's expression had never been tested experimentally before our computer experiment. Details of how the numbers of nucleation events as a function of time are related to integrated forms of the theoretical expressions are presented in the Appendix.

Results

Instead of encountering the time evolution $N(t)$ referred to in the foregoing, our mode of accumulation of data naturally expresses the time evolution of the quantity $-\ln(N_c(t)/N_0)$. Why this difference arises is explained in the Appendix where the quantities N_c and N_0 are defined. Sizes of nuclei selected to determine times of first appearance of nuclei were: 10, 20, 30, 40, 50, 70, 80, 90, 110, 130, 150, and 300 molecules. These times are plotted in Figure 3 as a function of $-\ln(N_c(t)/N_0)$ for n values limited in number to prevent the crowding together of the curves. The visual appearance of each of these curves is
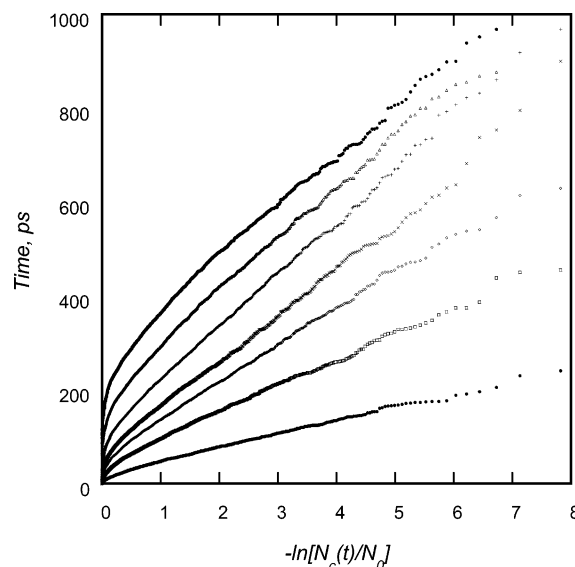

Figure 3. Times of first appearance of nuclei of size n. The plotted curves are for n-mers of 10, 20, 30, 40, 70, 150, and 300 molecules. Each curve can be described by an effective value of a time lag, a steady-state rate of appearance, $J^s_{F,n}$, and a reduced moment. Only for sizes large compared with the critical nucleus can the rate of appearance and reduced moment be interpreted as corresponding to the true nucleation rate and moment. Curves with the smallest times, of course, are for the smallest nuclei.
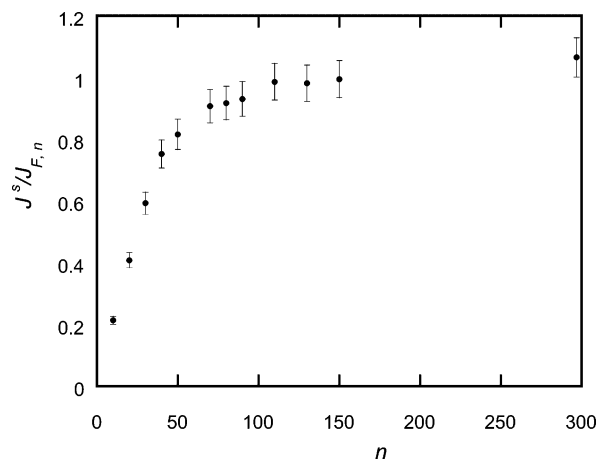
Figure 4. Reciprocal, $J^s/J^s_{F,n}$ of the steady-state rate of first appearance of n-mers as a function of n. Error bars correspond to 2σ.

qualitatively similar to our original curve[9] based on the "onset" criterion, and each curve can be analyzed in terms of the three parameters we choose to characterize nucleation, namely, the effective steady-state rate J^s, the time lag L, and the reduced moment M_R. The parameters so derived, of course, cannot all be considered to characterize the conventionally defined nucleation kinetics of freezing.

For large values of n, well beyond the critical size it is expected that the steady-state rates of first appearance of large n-mers should correspond accurately to the net steady state nucleation rate. In fact, the steady state rate of appearance of such nuclei found in this study is very close to that found in the prior study based on times of onset of nucleation. As might be expected, it was also found that the rate of first appearance is very much larger for small nuclei than for large ones. Very minor structural fluctuations can create small solidlike embryos. Because the rate was nearly proportional to the inverse of n at small n, we plot the reciprocal of the rate in Figure 4. Similarly, the apparent "reduced moment" parameter is very large at small

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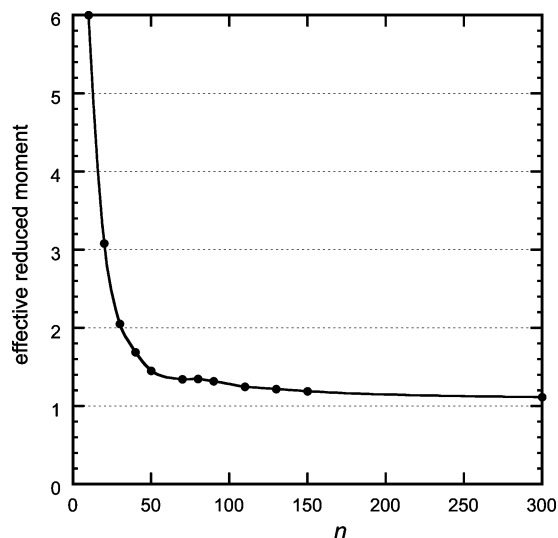
Figure 5. Effective reduced moments derived form the curves illustrated in Figure 3 as a function of size of n-mer.

n, then drops rapidly, as shown in Figure 5. What can be inferred from these quantities is discussed in the next section.

Discussion

Before attempting to derive the true steady state rate, reduced moment, and size of the critical nucleus from the results of the MD simulations, it might be helpful to make a few general remarks about the theories investigated in this study. First, it turns out that Kashchiev's theory corresponds almost exactly with Wu's theory at $n = n^*$, provided that the reduced moment is assigned the value of 1.4. In our original analysis of the MD simulations based on times of onset of nucleation,[9] we had obtained values of M_R of 1.43(0.07) by applying Wu's theory and 1.36(0.09) by applying Shneidman's theory. These results seemed to vindicate Kashchiev's theory and also indicated that a problem existed with the Shneidman high barrier asymptotic solution, eq 5. That is, for such a large value of M_R, the Shneidman distribution $\rho(t)$ protruded conspicuously into the range of negative times, times before nucleation began. Wu's $\rho(t)$, by its construction, constrained $\rho(t)$ to behave properly in this respect, a necessary but not sufficient condition for its validity. On the other hand, if the reduced moment were found to be in the range 1.1−1.2, as implied by the "exact" numerical solutions of Kelton and Greer,[7,8] the Kashchiev theory would be found to be inaccurate and the Wu and Shneidman theories would agree with each other extremely well. Even if the Kelton−Greer numerical solutions to the Becker−Döring, Turnbull−Fisher formulation were mathematically exact, however, the relations invoked to express forward and backward rates at each step might not correspond to the actual vagaries in the behavior of molecules in supercooled liquids, nor is it self-evident that such rates can be accurately lumped together and given the values corresponding to those of n^*, as is conventionally done. Therefore, it was worthwhile to consider whether the analysis of the MD data could be made sufficiently rigorous to resolve the questions just raised.

As sketched above, the new criterion for identifying nucleation times to be considered avoids the large and worrisome distribution of sizes of nuclei encountered with our prior times of "onset" of nucleation. But it is not immediately clear how the new criterion can be applied in valid comparisons with existing theories. An initial attempt to address that problem is discussed next.

Consider the treatment of homogeneous nucleation in Wu's 1997 review,[14] whose slightly unconventional notation we adopt for this section, where the rate for adding a monomer to an n-mer

$$A_1 + A_n \underset{\alpha_{n+1}}{\overset{\beta_n}{\rightleftharpoons}} A_{n+1} \tag{6}$$
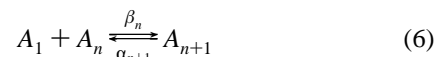
is written

$$J_{n+(1/2)} = \beta_n f_n - \alpha_{n+1} f_{n+1} \tag{7}$$

with f_k corresponding to the number of k-mers per unit volume. Now, our mode of selecting times is to record the time of first appearance of an n-mer in each cluster, then sort the N_0 times and plot them against $-\ln(N_c(t)/N_0)$. From the steady-state rates we observe for each n, we conclude we have found the steady-state rates of production of n-mers from $(n - 1)$-mers and associate this rate with the component $\beta_n f_n$ of eq 7. We discard the $\alpha_{n+1} f_{n+1}$ term because f_{n+1} is zero, inasmuch as there were no nuclei present containing more than n molecules in our clusters. Still, our population f_n is not the same as the existing population during a steady-state production of n-mers. Neglecting this complication for now, let us call our present steady-state rate $J_{F,n}^s$, the subscript signifying "first appearance" of n-mers. Now, using Wu's notation, we write the net steady-state nucleation rate, (which is the same for all $n \geq 2$ [14]) as

$$J^s = f_1 \beta^* Z e^{-G^*/kT} \tag{8}$$

where Z is the Zeldovich factor.[21] This assumes (as usual) an inexhaustible supply of monomers. Let us consider the ratio $J_{F,n}^s/J^s$. For $n = n^*$ it is

$$
\begin{aligned}
J_{F,n^*}^s/J^s &= \frac{\beta^* f_{n^*}}{\beta^* f_1 Z e^{-G^*/kT}} \\
&= \frac{\beta^* (f_{n^*}/z_{n^*}) z_{n^*}}{\beta^* f_1 Z e^{-G^*/kT}}
\end{aligned} \tag{9}
$$

where z_n is the hypothetical equilibrium concentration of n-mers, given by

$$z_n = f_1 e^{-G_n/kT} \tag{10}$$

Moreover, as suggested in the review by Kelton, Greer, and Thompson[7] (who verify this aspect of Kashchiev's 1969 treatment[19]), the actual concentration of n^*-mers compared with the hypothetical equilibrium concentration at n^* is $f_{n^*}/z_{n^*} \approx 1/2$. This result, inserted into eq 9 gives the ratio $J_{F,n^*}^s/J^s$ the value of

$$J_{F,n^*}^s/J^s \approx 1/2Z \tag{11}$$

Even if the classical nucleation theory (CNT) in its usual approximation is a very crude one, the Zeldovich factor can be estimated by using the CNT physical parameters ΔG_v (corresponding to the bulk free energy per unit volume of freezing at the temperature of supercooling) and σ_{sl} (mean interfacial excess free energy of the liquid−solid interface) just as long as the latter is adjusted to make the value of G^* be that which yields the correct MD rate J^s. The nucleation barrier G^* enters Wu's expression representing Z.[14] An error in ΔG_v is compensated for, to some extent, by the correlated error in the σ_{sl} value adjusted to yield the proper G^* value. Actually, the value of

G^* needed to yield the measured rate, J^s, depends also on the prefactor, and we believe the "classical prefactor" tends to be too small. Because a small change in G^* can give a large change in J^s for a given prefactor, the smallness of the classical prefactor is not likely to introduce a very large error in G^* or Z. Our data for SeF_6 indicate that $1/2Z$ is approximately 3.0. This suggests that we can estimate the size of the critical nucleus by finding at what n value $J^s_{F,n^*}/J^s$ is about 3. Applying this result to the data in Figure 4, we find n^* to be about 17 "bulklike solid molecules" (based on order parameter Q_6). This value is much smaller than the size estimated subjectively in ref 22. Of course, as stated in the foregoing, the value of n attributed to a given nucleus depends on the choice of order parameter invoked as well as upon the Gibbs dividing surface adopted. We are in the process of investigating the effect of applying different choices.

In any event, the estimated size n^*, based on Q_6, an order parameter characterizing the translational order, is roughly the size derived from the CNT but including, in addition, a partially ordered liquid layer clinging to the solid nucleus, conforming as well as possible to the surface. Such an ordered liquid layer was first postulated by Turnbull.[23] Density functional theory yields a closely related result,[24] making the radii of nuclei reckoned from the density (true crystal) smaller than radii computed from the translational order.

What can be said about the reduced moment M_R? Values of this parameter derived from the shapes of the curves of times of first appearance vs $- \ln(N_c(t)/N_0)$ shown in Figure 5 are very large at small n, fall rapidly to a value much larger than 1.4 in the vicinity of $n = n^*$, and continue to drop. When n is well beyond n^*, they decrease to the vicinity of 1.2 to 1.1, namely, to the range of values predicted by the Kelton–Greer exact numerical solutions[7,8] of Becker–Döring theory. What, then, can be inferred about the physically meaningful value of M_R? It might be argued that this reduced moment applies only to those curves for which the true steady-state nucleation rate has been reached in the limiting slopes associated with $J^s_{F,n}$. Because the curves of t vs $- \ln(N_c(t)/N_0)$ do not reach this rate until n is well beyond n^*, we conclude that the Kashchiev-like value of 1.4 inferred from our original "times of onset of nucleation" criterion was an artifact of our criterion. Furthermore, the Wu and Shneidman treatments indicate that the reduced moments corresponding to the functions $J(t,n)/J^s$ continue to fall as n increases. There is a distinct suggestion of that trend in our data.

It seems clear that our new procedure to record times of nucleation is an improvement over our prior procedure, and that, in contrast to the prior procedure, it implies that the more modern analytical theories are a distinct improvement over those reviewed in 1983.[7] It will be important to develop a more rigorous analysis of the steady-state rate of first appearance of n-mers. Meanwhile, we are reinvestigating the data by a more conventional approach, that of finding the accumulation of n-mers, namely $N(t,n)$, the function whose time derivative is $J(t,n)$. The rise time of $J(t,n)$ is a direct measure of the reduced moment, the parameter most definitively differentiating between the various proposed theories of transient nucleation.

Concluding Comments

After this manuscript was submitted, new evidence surfaced that is worth noting. First, in private communications, both Wu and Shneidman pointed out that when $n = n^*$, the ratio $J^s_{F,n}/J^s$ should be 2, not 3, as we crudely estimated. This increases n^* to over 20 molecules for our system but does not materially

alter the substance of our discussion. The more rigorous result of Wu and Shneidman, however, is based on the classical (bulk plus surface) form of the function $G(n)$. Considerations of size effects suggest a modified form yielding a ratio somewhat larger than 2 but probably not as large as 3. Moreover, the simulated first appearance rates hint at a deviation of $G(n)$ from the classical form.

Also, the promised more conventional analysis based on $N(t,n)$ has been carried out. The behavior of this variable confirms that the rate at steady state, $J(n)$, is indeed the same for all n, unlike the result for the rates of first appearance. What is remarkable is that the reduced moments derived from the conventional rates depend on n in virtually the same way as those derived from the rates of first appearance (Figure 5). Therefore, our data do not support the Kashchiev value for the reduced moment even in the vicinity of n^*. To what extent the strong dependence of M_R on n shown in our results is universal is now under investigation.

Perhaps the most significant result of applying an analysis of times of first appearance of nuclei of various sizes is that such analyses yield information about the size of critical nuclei.

Appendix

Mode of Expressing the Accumulation of Nuclei. In conventional theories, the quantity treated is $N(t)$, the accumulated number of nuclei of size n per unit volume in a system such that the appearance of one nucleus has no effect on the probability of formation of another nucleus. This quantity is

$$N(t) = \int_0^t J(t',n) \, dt' \qquad (12)$$

In our system of clusters of modest size, however, the formation of the first nucleus may significantly influence the probability of the next nucleation event, even if the system is maintained to be nominally isothermal while the heat of fusion is evolving. Our procedure is simply to remove a cluster from the system once it has nucleated. Therefore, instead of following the quantity $N(t)$ as in the conventional theoretical treatment, we must take into account the decreasing volume available for nucleation. We consider the number of clusters to be large enough to make a continuum approximation satisfactory, as follows. The rate per unit volume of producing nuclei is, by definition,

$$J(t,n) = (dN/dt)/V \qquad (13)$$

where, for our system, the volume is $N_c V_c$, the number of clusters times the volume per cluster. After removing N clusters from consideration, the number of clusters left is $N_c = N_0 - N$, making the expression for the nucleation rate

$$J(t,N) = -\frac{dN_c(t)/N_c}{V_c \, dt} \qquad (14)$$

Hence the decay in the number of clusters which have not yet nucleated is given by

$$- \ln(N_c(t)/N_0) = V_c \int_0^t J(t',n) \, dt' \qquad (15)$$

An explicit expression for the integral in Wu's theory is given

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in refs 10 and 14. At large times, the slope of $-\ln(N_c(t)/N_0)$ has become constant and eq 15 reduces to

$$-\ln(N_c/N_0) = V_c J^s(t - L) \quad (16)$$

The actual number of points in the data set is $N_0 + 1$ because, in addition to the number of nucleation events observed, at $-\ln(N_c(t)/N_0) = 0$, the rate is known to be zero.

Because the quantity $-\ln(N_c(t)/N_0)$ is known exactly and the nucleation times are a matter of chance, we have chosen to treat the times as the uncertain "y" variable in least squares analyses, and $-\ln(N_c(t)/N_0)$ as the known "x" variable. This means that the equation expressing N_c as a function of t, namely eq 15, must be inverted. The approximate result of this inversion for Wu's theory is given in ref 9 where the approximation is stated to be good down to $-\ln(N_c(t)/N_0) \approx 0.03$. This was an unduly pessimistic assessment. The approximation is quite good down to about 0.002. Because the Kashchiev expression agrees almost perfectly with the Wu expression for $n = n^*$ when M_R is taken to be 1.4, a separate inversion of the Kashchiev rate is not needed. When M_R is as large as 1.4, the Wu and Shneidman expressions differ appreciably but, in the range of 1.1 to 1.2, they are so nearly identical that no distinction need be made when analyzing experimental data.

Modification of the Definition of Bulklike Molecules. Because this work introduces a new procedure, it is necessary to specify exactly how the times of first appearance of n-mers were determined. The analysis of kinetic parameters from the accumulation of data stored after the runs were finished, is somewhat complex.

The translational bond order parameter (based on the Q_6 criterion) has been used in our prior work to identify regions of crystalline SeF_6 in liquid clusters.[22] In the current work the definition of "bulklike" molecules has been modified to take into account nuclei that form on the surface of a cluster. Surface nucleation is more common than nucleation in the interior. We now define solidlike molecules that are on the surface of a cluster to be bulklike if they have at least 7 solidlike neighbors. All interior solidlike molecules require at least 12 solidlike neighbors to be identified as bulklike. In each case, once a bulklike molecule has been identified, the neighboring solidlike molecules are considered to be bulklike also. This means that the minimum size of a bulklike region at the surface is now 8 molecules whereas the minimum size of a bulklike region in the interior of the cluster remains at 13 molecules.

To identify molecules that are on the surface of a cluster, the following technique was used. A cube is constructed such that it completely encloses the cluster. Onto each face of this cube is superimposed a 2-dimensional grid with adjacent grid points separated by 1 Å. Each SeF_6 molecule in the cluster is represented by a sphere assigned a radius that is slightly larger than the van der Waals radius of the molecule. This slight increase in radius is added to reduce the possibility of molecules in layers below the surface layer being identified as on the surface. A surface molecule is then defined to be the molecule possessing the shortest distance, normal to the face of the cube, from a grid point on that face. Each point on each face of the cube is used to identify surface molecules across the whole cluster.

Calculation of the Time of Nucleation of a Nucleus of Size n. A bulklike n-mer is defined as a contiguous group of bulklike molecules where no bulklike molecule is separated from any neighboring bulklike molecule by more than 7.2 Å.

The time t, at which a nucleus of size n first appears in a supercooled cluster undergoing nucleation was calculated using

the following approach. During the simulation, cluster configuration snapshots are stored at regular intervals (usually 1.4 ps) and these were analyzed to determine the time of nucleation after the simulation had finished. Initially, each configurational snapshot was examined to find the first snapshot (S) that contained a contiguous region of bulklike molecules that was greater than n. The actual number of bulklike molecules in that region was then the upper limit (n_S). The simulation time t_S was the time at which snapshot S was taken.

Next, the previous configurational snapshot ($S - 1$) was examined and if a region of bulklike molecules in that snapshot was found to be contiguous with the molecules in snapshot S, then the number of molecules in that region was regarded as the lower limit (n_{S-1}). If there were no bulklike molecules in snapshot $S - 1$ contiguous with those in snapshot S then n_{S-1} was set to zero. The simulation time t_{S-1} was the time at which the snapshot $S - 1$ was taken .

The time t, at which a nucleus of n appears was then calculated by using

$$R = \frac{n - n_{S-1}}{n_S - n_{S-1}} \quad (17)$$

$$t = t_{S-1} + R(t_S - t_{S-1}) \quad (18)$$

Using this method, it was possible to interpolate linearly to obtain t even for sizes of n that (by definition) were below the 13 molecule minimum size associated with a bulklike region in the interior of the cluster or the 8 molecule minimum associated with a bulklike region at the surface.

The times of first appearance of n-mers so calculated were determined for each of the 2500 clusters for a range of sizes, n. The reasons for carrying out such a procedure are outlined in the foregoing text.

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