Analyses of Nucleation Rates from Molecular Dynamics Simulations†

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The goal of this research is to develop a reliable method to derive nucleation rates and time lags from times of nucleation observed in sets of molecular dynamics simulations of supercooled clusters undergoing spontaneous freezing. What is taken explicitly into account, which was missing in prior analyses, is the kinetics of transient nucleation. Failure to consider this aspect of nucleation has led to substantially larger errors than the statistical errors associated with the stochastic process. It is found that analyses simultaneously including the transient nucleation parameter as well as the nucleation time lag and the steady-state nucleation rate are too ill-conditioned to yield satisfactory results. A procedure to circumvent this problem and to estimate uncertainties is formulated.

Introduction

In a previous paper,[1] the derivation of nucleation rates from molecular dynamics (MD) simulations of freezing in sets of supercooled clusters was discussed. In particular, the statistical errors to be expected when nucleation events are few, were analyzed. Although steady-state nucleation in clusters obeys a first-order rate law, the problem differs from the somewhat analogous problem of radioactive decay rates. For one thing, at least two parameters must be derived, not only the rate constant, but also the nucleation time-lag, which does not apply to radioactive decay. Complicating the problem is the phenomenon of transient nucleation, which, as it turns out, adds a third parameter.[2] In addition, in MD simulations, the total number, N_o, of clusters in the set is known exactly, and the number n, having undergone at least one nucleation event, is also known exactly, whereas the stochastically determined times are very much a matter of chance and can vary widely from set to set. Therefore, it seemed appropriate consider the times as the uncertain "y" variable in least squares analyses and the variable $\ln(N_n/N_o)$ to be the accurately known "x" variable, where N_n is the number of clusters not to have experienced the formation of a critical nucleus *before* the n^{th} nucleation.[1] The recommended weights and standard deviations to be expected for such an analysis were correctly determined in a previous paper, provided that the decay of unfrozen clusters obeyed the first-order law

$$\ln[N_n(t)/N_o] = -K(t - t_o) \tag{1}$$

where 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. In real processes, this analysis is wrong because the period of transient nucleation is ignored. This leads to a large systematic error in eq 1 at short nucleation times.[1] How this neglect can remedied is described in the following.

Procedure

First, let us examine the effect of transient nucleation on the decay curve for a system of unfrozen clusters. The most general treatment of transient nucleation that is relatively simple to incorporate into an analysis of cluster data is that of Wu.[2] His method of moments yields an explicit expression for the ratio $R(t)$ in the development of nucleation rate $J(t)$, where

$$J(t)/J_s \equiv R(t) \tag{2}$$

with the ratio expressed in Wu's notation as

$$R(t) = 1 - \frac{1}{2}\,\mathrm{erfc}\left[\frac{\ln(t/t_o) - a}{\sqrt{2b^2}}\right] \tag{3}$$

This ratio differs from unity during the time it takes for the buildup of precursors that ultimately leads to a steady-state rate J_s of production of critical nuclei. Wu then integrates eq 2 to obtain a relation for the accumulated number of critical nuclei, $N(t)$, in the freezing of a fixed volume, V_l, of supercooled liquid or glass, or

$$N(t)/J_sV_l = \int_o^t R(t)dt \equiv S(t) = t\left(1 - \frac{1}{2}\,\mathrm{erfc}\left[\frac{\ln(t/t_o) - a}{\sqrt{2b^2}}\right]\right) - t_o\left(1 - \frac{1}{2}\,\mathrm{erfc}\left[\frac{\ln(t/t_o) + a}{\sqrt{2b^2}}\right]\right) \tag{4}$$

assuming that the nuclei formed do not significantly deplete the volume V_l accessible to further nucleation. Wu's parameters a and b are defined by

$$a = -\frac{1}{2}\ln(2M/t_o^{\,2}) \tag{5}$$

$$b^2 = \ln(2M/t_o^{\,2}) \tag{6}$$

with M corresponding to the first moment of a distribution of embryos encountered. Moment M is a quantity Wu regards as a free parameter to be derived in the analysis of experimental data. It is evident that the lowest value the moment can have is for $2M/t_o^2$ to be unity. If the moment were to possess that value, eq 4 would reduce to

$$N(t)/K = 0,\ t < t_o \tag{7a}$$

and

$$N(t)/K = t - t_o,\ t > t_o \tag{7b}$$

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making the time dependence of eq 1 valid. It is convenient to introduce the reduced moment

$$M_R \equiv 2M/t_o^2 \tag{8}$$

to characterize transient nucleation. Reasonable values for this parameter will be discussed subsequently.

Now consider a set of N_o supercooled clusters, each with volume V_c, making N_oV_c the total volume available for nucleation. Each time a critical nucleus appears in one of the clusters, let us remove it from the set, leaving N_l clusters which have not experienced a nucleation and, therefore, leaving a total volume of N_lV_c. For this convention, the rate of change in N_l is no longer given by eqs 2−4 but rather by

$$\frac{J(t)}{J_s} = \frac{1}{J_s}\frac{dN/dt}{N_lV_c} = \frac{-(dN_l/N_l)/dt}{K} \tag{9}$$

so that

$$-\ln(N_l/N_o) = K\int_o^t R(t)dt = KS(t) \tag{10}$$

This expression reduces to eq 1 when $b^2 = -2a = \ln M_R$ when M_R approaches unity. Equation 1 has been used to date in all of our analyses of data from MD runs, but is rigorously applicable only in the case for which the moment M has its minimum value. Such conditions are unrealistic.

The above relation 10 is obviously appropriate for small clusters which, in accord with Kashchiev's criterion, [3] exhibit mononuclear freezing. For larger clusters, several critical nuclei may form before the clusters completely freeze.[4] In MD simulations, it is not a simple matter to establish the times of nucleation for nuclei later than the first, making the convention of the previous paragraph a convenient and particularly simple way to handle the problem when polynuclear freezing occurs.

Inversion of the Equation for $N(t)$. To carry out least squares analyses in which times, not numbers of clusters in which nucleation has occurred, are taken to be the uncertain "y" variable, it is necessary to invert eq to the form $t(N_l/N_o)$. In view of the complexity of eq 10, it is much simpler to fit the inverse empirically than to carry out the inversion analytically. The result for the reduced nucleation time, t/t_o, can be expressed, as expected from the form of eq 10, in terms of the variable

$$g(t) = N(t)/J_sV_lt_o \tag{11a}$$

in Wu's case, or

$$g(t) = -\ln(N_n/N_o)/Kt_o \tag{11b}$$

in the case of clusters, and the fitting parameter M_R of eq 8. A satisfactory representation is given by

$$t/t_o \approx 1 + g - (1 - 0.5/M_R^{2.5})\exp[-1.82g^{1/2}/(M_R - 1)^{0.41}] \tag{12}$$

How well this representation agrees with Wu's result, eq 4, is illustrated in Figure 1 for several representative values of M_R. Over the range of physically significant moments the representation is entirely adequate for our purposes. If M_R is given its minimum (but unrealistic) value, unity, then the result is equivalent to eq 1.

Practical Derivation of J_s and t_o. Insofar as the author is aware, there are no simple rules for estimating the value of the parameter M_R characterizing transient nucleation. In the well-known treatment of Greer and Kelton[5] numerically simulating the crystallization of the glass lithium disilicate, the result can be represented quite well with M_R in the range of 1.1 to 1.2. Another treatment frequently cited[6] is that of Kashchiev[7] whose expression for $J(t)/J_s$ can be approximated by assigning the value of approximately 1.4 to M_R. Figure 1 compares Kashchiev's representation with those of Wu for several different values of M_R.

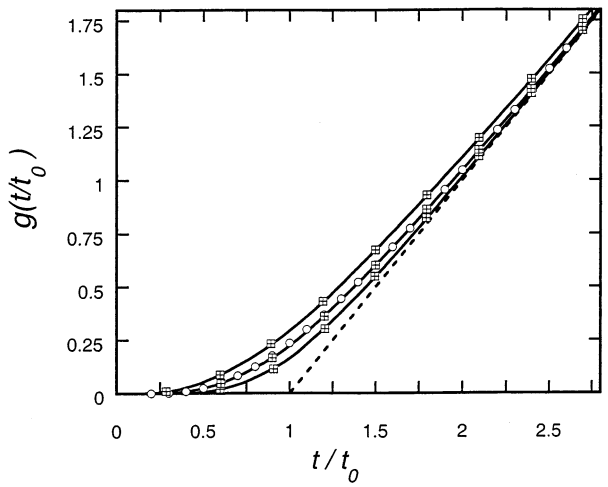

Figure 1. Time development of integrated nucleation function $g(t)$, cf. eq 7−12 of text, for reduced moments of 1 (dashed line) and 1.2, 1.4, and 1.8 (from lower to higher curves). Wu theory, solid lines; representation of eq 12, decorated squares; Kashchiev theory, circles closely following the Wu curve for $M_R = 1.4$.

Although Wu[2] suggested determining M_R by letting it be a free variable in analyses of experimental data, it is found that when J_s, t_o, and M_R are all varied freely, the solution tends to be extremely ill-conditioned. It is more reasonable to constrain M_R to a plausible value. To get some idea of errors arising because of uncertainty in the parameter M_R, it would be reasonable to carry out analyses assigning values to M_R in the range of, say, 1.1 to 1.4, or perhaps a little higher in successive analyses. The variation in results for nucleation rate and time-lag should give some idea of the magnitudes of uncertainties in the derived kinetic quantities. Certainly, the results taking into account transient nucleation should be more reliable than those of analyses based solely on eq 1.

We consider two options for analyzing nucleation rates from the nucleation times found in sets of molecular dynamics runs, namely:

Option 1: Adopt a reasonable value for M_R, adjust the parameters J_s and t_o in eq 12 by least squares to fit the observed MD nucleation times t.

Option 2: Derive the parameters J_s and t_o by least squares, using eq 1 as the fitting function, and then correct for systematic errors involved in the neglect of M_R.

Although Option 1 appears to be the more reasonable and straightforward, in some respects Option 2 is superior in practice. How this conclusion was reached is described next. To determine the relative effectiveness of the two options, to find the systematic errors and establish the statistical uncertainties in the parameters J_s and t_o for data sets with small numbers of nucleation events, it is simplest to carry out model calculations. First, many realistic sets of N_o stochastic times are generated, each set to correspond to nucleation times in a collection of N_o clusters. Such a set of times can be created by dividing times from 0 to ∞ into a large number, N_B, of equally probable time bins, that is, into bins for which the probability of nucleation

in each is $1/N_B$. A given bin i is associated with a time t_i. Therefore, a set of N_o times can be generated using a random number generator to select a set of N_o independent bins. Times are then treated as they would be in an experiment or an MD simulation, and analyzed by a least squares procedure to derive the parameters J_s and t_o corresponding to an assumed value of M_R.

In our previous paper,[1] such an analysis was based on eq 1, and consequently neglected the period of transient nucleation. It was found that results were very insensitive to whether the number of bins, N_B, was 100 or 100 000. In the present work with a more complex set of time bins, accurate results require N_B to be much larger than 100. We took N_B to be 10 000. When eq 1 is the basis, it is elementary to relate t_i to the bin number i analytically. When transient nucleation is taken into account, however, the construction of equally probable time bins is more complicated. Consider a set of bins, 1, 2, ..., i, ...N_B, each of which represents a time between t_i and $t_i + \Delta t_i$ with $t_1 = 0$ and $t_{N_B} + \Delta t_{N_B} = \infty$. For each of the N_B bins, the probability $\int_{ti}^{t_i+\Delta t_i} P(t)dt$ of a nucleation event is $1/N_B$, where

$$P(t) = \frac{-dN_l}{N_o dt} = R(t)\frac{N_l}{N_o} = R(t)\exp[-KS(t)] \qquad (13)$$

As defined above, t_i is the initial time for a bin i. Finding the time t_i associated with bin number i can be done by numerically carrying out the integration

$$\int_o^{t_i} P(t)dt = \int_{t_1}^{t_2} P(t)dt + \int_{t_2}^{t_3} P(t)dt + ... = \sum_{j=1}^{i-1}\int_{t_j}^{t_{j+1}} P(t)dt = \sum_{j=1}^{i-1} 1/N_B = (i-1)/N_B \quad (14)$$

for a given value of M_R. As long as N_B is a large number, bin i corresponds to time t_i, the upper limit of the integral, and it makes little difference whether t_i is the initial or some intermediate time in the bin. To implement the stochastic generation of times by random selections of time bins, one can form a table of t(i) from the results of eq 14, a procedure taking only a few seconds on today's PC computers. When i becomes large, say beyond about 0.7 N_B, the erfc functions contributing to $R(t)$ and $S(t)$ nearly vanish so that the asymptotic solution to eq 14 is

$$t_i = t_o - (1/K)\ln[1 - (i-1)/N_B] \qquad (15)$$

For each set of events, times are sorted and subjected to a least-squares analysis to determine the parameters J_s and t_o. Inasmuch as the original values of J_s and t_o fed into the treatment at the outset are known, the systematic errors and standard deviations from the mean of the parameters in an ensemble of N_s sets of results (each set involving N_o stochastic times) are readily determined. Least squares calculations can be carried out with various weight functions, $w(t)$ for each option. In our prior analysis based on eq 1, the optimum weight function was found to be reasonably well represented by[1]

$$w(t_i) = \arctan(1/Kt_i) \qquad (16)$$

expressing the fact that stochastically selected time bins get considerably wider, the greater the time. In the present analysis, the optimum weight function was not determined. It was found, however, that for option 1, when unit weights were chosen instead of the weights of eq 16, smaller standard errors in J_s and t_o were obtained. On the other hand, the opposite was true for option 2. Therefore, in results reported in the following, unit weights were used in analyses based on Option 1 and the arctangent weight for Option 2.

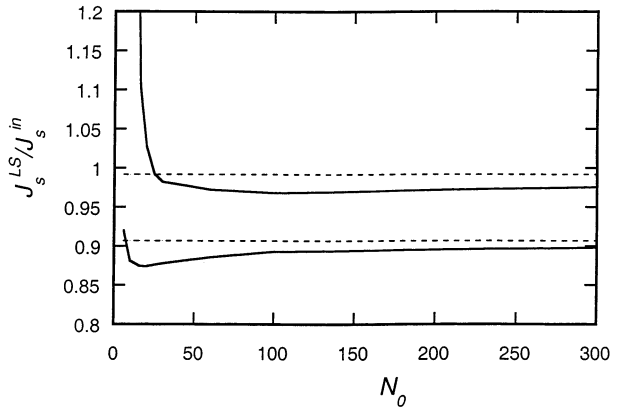

Figure 2. Dependence of the mean nucleation rate J_s^{LS} derived by least-squares analysis, upon N_o, the number of clusters in a set, where J_s^{in} is the nucleation rate from which the numerous sets of stochastic times were generated. Upper curve, Option 1, the result of fitting times by a Wu function. Lower curve, Option 2, fitting times by a straight line. A reduced moment of 1.2 was assumed in generating times and in the Wu function. Horizontal dashed lines represent the limiting rate for very large N_o.

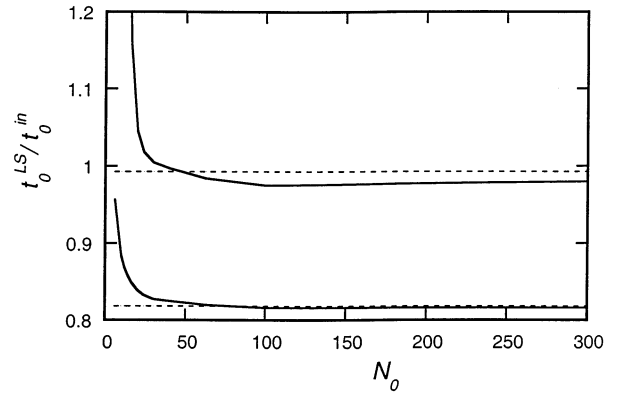

Figure 3. Dependence of the mean nucleation time lag t_o^{LS} derived by least-squares analysis, upon N_o, the number of clusters in a set, where t_o^{in} is the time lag from which the sets of stochastic times were generated. Upper curve, Option 1, the result of fitting times by a Wu function. Lower curve, Option 2, fitting times by a straight line. A reduced moment of 1.2 was assumed in generating times and in the Wu function. Horizontal dashed lines represent the limiting time lag for very large N_o.

Results

Obviously, the accuracy of the rates and time lags derived from stochastically generated times of nucleation events depends on the number of nucleation events available in the analyses. Illustrative results showing this dependence for both of the options are presented in Figures 2 and 3. The corresponding statistical uncertainties are plotted in Figures 4 and 5. In these figures the reduced moment adopted was 1.2. For reasons stated in the previous section, a unit weight function was incorporated into Option 1, and the arctangent function of eq 16, into Option 2. When analyzing sets with no more than $N_o = 50$ clusters, runs of at least 30 000 independent sets were carried out to establish parameter means and variances. For sets with a larger number of clusters, fewer runs were needed to achieve comparable statistical accuracy.

Note that the asymptotic values of the rates and time lags for sets with very large numbers of clusters (large N_o) are

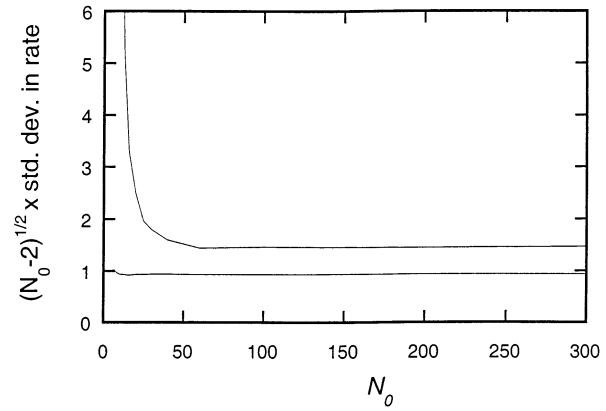

Figure 4. Dependence upon N_o of the standard deviation from the mean of J_s^{LS}/J_s^{in}, amplified by the factor $(N_o - 2)^{1/2}$. A horizontal line would indicate the result for statistically distributed errors and uncorrelated parameters (rate and time lag). Upper curve, for Option 1, where stochastically generated times were fitted by a Wu function. Lower curve, for Option 2, fitting times by a straight line. A reduced moment of 1.2 was assumed in generating times and in the Wu function. Option 2, although giving a poorer representation of the nucleation times, gives a substantially smaller spread in the derived rates.

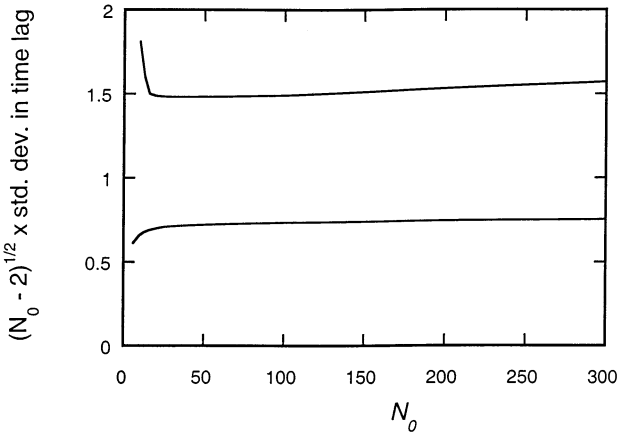

Figure 5. Dependence upon N_o of the standard deviation from the mean of t_o^{LS}/t_o^{in} on the number of clusters in a set, amplified by the factor $(N_o - 2)^{1/2}$ discussed in caption 4 along with conditions of analyses. Upper curve, for Option 1, where stochastically generated times were fitted by a Wu function. Lower curve, for Option 2, fitting times by a straight line. Option 2, although giving a poorer representation of the nucleation times, gives a substantially smaller spread in the derived time lags.

indicated by the dashed lines. For Option 2 the deviations from unity in Figures 2 and 3 are real. For Option 1, the small deviations from unity were caused by minor imperfections in the numerical integration of eq 14 and/or in the empirical representation of eq 12.

From inspection of Figures 2 and 3, it can be seen that the fitting of the (curved) g(t) data with a function specifically representing the effect of transient nucleation, namely Option 1, does indeed yield better values of rates and time lags, on average, than does Option 2 which fits the curve as well as possible with a straight line. There is a price to be paid for this greater apparent accuracy yielded by Option 1, however, because it comes at the cost of larger standard errors, as revealed in Figures 4 and 5. Therefore, if analyses based on Option 2 are corrected for systematic errors of the sort displayed in Figures 2 and 3, they may give more accurate results than those of Option 1. Of course, if the set of nucleating particles were extremely large, the uncertainties would decrease to the point of being of little concern. Figures 4 and 5 demonstrate that, at intermediate to large N_o, the statistical errors do decrease as expected for the derivation of two independent parameters from N_o measurements. Table 1 indicates that the uncertainties can be very large, particularly in the case of nucleation rates. Indeed, the uncertainty when N_o is small can be larger than the correct (input) value of the parameter. In such a case, it is important to note that the effective "3σ" error limit of the nucleation rate is *not* simply three times the *rms* deviation from the mean. This is because of the extreme skewness of the probability distribution in the derived rate, as discussed in the appendix.

TABLE 1: Illustrative Examples of Mean Systematic Errors in Derived Parameters and in the Corresponding Standard Deviations for Various Combinations of Reduced Moments

M_R^{in}	M_R^{LS}	J_s^{LS}/J_s^{in}	σ_{Js}/J_s^{in}	t_o^{LS}/t_o^{in}	σ_{to}/t_o^{in}
1.0	1.0	0.978[a]	0.266	1.020[a]	0.132
1.2	1.0	0.875	0.229	0.839	0.164
1.2	1.2	1.028[a]	0.501	1.045[a]	0.354
1.2	1.4	1.221	0.997	1.245	0.564
1.4	1.0	0.833	0.196	0.728	0.174
1.4	1.2	0.946	0.380	0.905	0.338
1.4	1.4	1.056[a]	0.650	1.056[a]	0.488

M_R^{in} is the moment applying to the stochastic generation of nucleation times and M_R^{LS} is the moment adopted in the least squares analyses of nucleation times. in all cases, the number of clusters in a set was 20, a typical number in published studies. [a] Results converged to unity, within numerical error, in the limit of very large N_o.

Finally, it is necessary to get some idea of how large the errors in derived parameters might be if the reduced moment M_R assumed in a least-squares analysis differs from the actual moment, the moment upon which the nucleation times are based. Unfortunately, little is known about how M_R depends on the composition or the preparation of the system. Table 1 shows effects of various combinations of assumed vs actual moments, using ranges of values discussed in the foregoing. For most of the tabulated combinations, the statistical uncertainty in the nucleation rate is substantially greater than that in the time lag.

Discussion

It is intuitively obvious that the compromise fitting of the curved shape of time vs $-\ln(N_n/N_o)$ (cf. Figure 1) with a straight line (i.e., the use of Option 2) must yield values for the slope (rate) and intercept, (time lag) that are too small. Therefore, the results in Figures 2 and 3 for Option 2 are readily accounted for, qualitatively. What is less obvious is why the nucleation rates for Option 1 depend as observed upon N_o, the number of clusters in a set of runs. A little reflection helps to account for the decrease in the derived J_s as N_o decreases from large values. This is due to the fact that the maximum stochastic time is unlimited because the time bins randomly selected bear no explicit relation to N_o. In contrast, the maximum value of $-\ln(N_n/N_o)$ *is* limited. Its upper limit is $-\ln(1/N_o)$, which is smaller with smaller values of N_o. This imbalance biases the derived slope J_s to be smaller than the slope that was fed into the generation of stochastic times. This having been said, it is true, nevertheless, that the larger the number N_o, the greater the number of random selections, and hence, the greater the chance that the maximum time will be large.

These considerations do not explain the very sharp increase in the derived J_s as N_o decreases below about 16. What can be said about the behavior of sets with very few clusters is that the chance distribution of the scant number of nucleation times in a given set does not give a reliable portrayal of the functions of eqs 10−12. Accordingly, the uncertainty in the derived J_s becomes *very* large, larger even than J_s itself, and because J_s

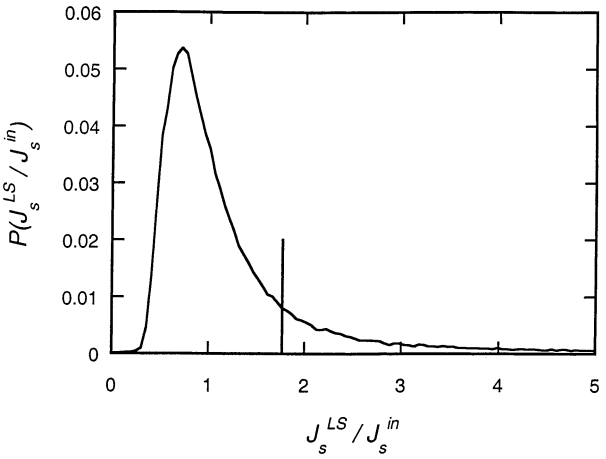

Figure 6. Highly skewed probability distribution of nucleation rates derived from nucleation times for sets of clusters when the number of clusters in each set is only $N_o = 10$. The data were acquired in 60 000 independent sets of least squares determinations of rates using Option 1 with $M_R = 1.2$. The heavy vertical line far to the right of the probability maximum is the mean rate which, itself, is 77% higher than the rate used to generate the sets of stochastic nucleation times that were fed into the least squares analyses. Moreover, the standard deviation from the mean is twice the value of the mean, illustrating the effect of the extremely long tail of the distribution. As the number of clusters in a set increases, the distribution narrows and becomes less skewed as shown in Figure 7.

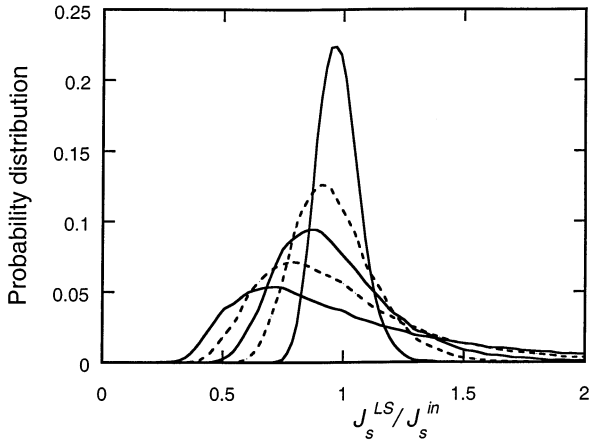

Figure 7. Probability distributions in nucleation rates from least squares analyses of sets of 10, 20, 40, 80, and 320 clusters per set with $M_R = 1.2$, with curves for 20 and 80 dashed to help distinguish between the long tails. Distributions were based on at least 30 000 independent least squares analyses for each curve except for 320. They closely resemble log-normal distributions, approaching more closely, the greater is N_o.

cannot be negative, the mean of this wide distribution must be at a value larger than the correct (input) value of J_s. This is strikingly illustrated in the distribution functions in the appendix.

Why the option yielding more accurate values of the rate and time lag (Option 1) also gives greater statistical uncertainties is due to the strong correlation between the derived parameters J_s and t_o in the least-squares fits of Option 1. This correlation arises from the form of $g(t)$ implied by eqs 10−12. A similar but weaker correlation exists in Option 2.

As noted in the foregoing, it is evident why the derived parameters yielded by Option 2 are smaller than those based on Option 1. A rationale for the results in Table 1 follows the same line of reasoning. If the true value of M_R is greater than the value adopted for the least-squares analysis, the situation is analogous to a comparison of Option 1 ($M_R > 1$) with Option 2 ($M_R = 1$) and the derived J_s and t_o will be too small. If the situation is reversed, the results will be reversed.

Although the results found in this study can be understood qualitatively, a statistical analysis was necessary to establish quantitatively the magnitudes of the uncertainties and the corrections for systematic errors. Errors assessed in previous analyses of molecular dynamics investigations of spontaneous nucleation neglected to take transient nucleation properly into account and therefore overestimated the reliability of the derived results.

Appendix

A few words should be said about the interpretation of the standard deviations in the figures and in Table 1. Figure 6 shows how extraordinarily skewed the probability distribution of least squares values of nucleation rates can be for a case for which there are only a few nucleation events available for analysis. In the particular case illustrated, 60 000 sets of $N_o = 10$ events were analyzed via Option 1 with M_R taken to be 1.2. Inspection of the figure shows how misleading our typical notion can be about the meaning of the standard deviation in such cases. For the illustrated case, the standard deviation from the mean is *twice* the mean value of the rate and nearly *4-fold* greater than the rate adopted in the generation of the sets of stochastic times analyzed by least squares. Obviously, if σ is taken as the square root of the variance, the notion of $\pm 3\sigma$ as a measure of the limit of error is totally meaningless. It is somewhat surprising to see the actual mean value identified by the vertical line in Figure 6 so far from the value of the rate from which the stochastic times were based. What leads to the problem, of course, is the extremely slow decay of the very long tail of the probability function. What would correspond to error limits comparable to the 3σ limits of a Gaussian distribution, for example, would be to equate the area of the probability distribution function bounded by the very asymmetric integration limits (from the mean value to the mean value plus or minus the "effective 3σ limit") to the same area as that corresponding to a Gaussian distribution between the mean and the $\pm 3\sigma$ limits. Clearly, subtracting three times the actual standard deviation from the mean leads to a negative rate, an absurd result, and adding the same quantity falls far short of the true upper limit of error. The way to avoid such enormous and complicated uncertainties is to use larger samples of nucleation events. By the time the horizontal portions of the curves in Figures 4 and 5 have been reached, error analyses become more straightforward. Figure 7 shows how the probability distribution narrows and becomes less skewed as the number of nucleation events is increased. It also suggests how the mean rate can drop below the input rate for intermediate sizes of sets of clusters.

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