

SATURATION EFFECTS IN HOMOGENEOUS AND HETEROGENEOUS CRYSTAL NUCLEATION

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Received 22 January 1988

It is known that saturation effects can occur in heterogeneous nucleation due to depletion of nucleation sites. However, in the present work additional mechanisms which could be responsible for saturation effects in both homogeneous and heterogeneous nucleation are investigated. It is demonstrated that for homogeneous nucleation, saturation effects are possible due to the reduction in volume available for nucleation as a result of crystal growth. Also, for heterogeneous nucleation an additional mechanism causing saturation is the encapsulation (ingestion) of heterogeneous nucleation sites during crystal growth. Equations are derived to describe the saturation effects in both cases, and numerical calculations are presented to compare the importance of the two means by which saturation effects can occur in heterogeneous nucleation.

1. Introduction

During the past few years there has been considerable interest in problems associated with the crystallization of glass. One source for this attention is the potential discrepancy between Classical Nucleation Theory and crystal nucleation events in glass [1–4]. Another reason for interest in this area originates in the numerous high technology applications dependent upon control and/or knowledge of glass crystallization phenomena [5–8].

A key issue in the study of internal crystal nucleation in glasses is the ability to distinguish homogeneous from heterogeneous nucleation. There have been several methods suggested for the task [9–11], none of which provides completely unambiguous results.

A second important consideration pertains to nucleation measurement. The most direct method of obtaining crystal nucleation data in glasses involves many repeated particle counting trials. This technique is tedious and slow, thus limiting the amount of nucleation data which can be

gathered in a reasonable time period. An indirect method has been used [12] to ascertain nucleation rates, which relies upon the measurement of the volume fractions transformed and crystal growth rates. This data used in conjunction with the Avrami equation [13] allows for the determination of nucleation rates. However, the implementation of this method can be difficult especially if heterogeneous nucleation is possible.

In the present work an analysis is presented which impacts both of the issues discussed above. For example, one method which has been proposed to enable one to distinguish homogeneous from heterogeneous nucleation relies upon the possibility of saturation effects for heterogeneous nucleation [9]. In the latter case nucleation can initiate at only a limited number of sites. Hence, when nucleation occurs heterogeneously after a sufficiently long time period the nucleation rate should decrease as the impurity sites are “used up.” For homogeneous nucleation, however, since nucleation can take place anywhere in the bulk, such effects will not come into play, and one would *not* anticipate saturation effects for homogeneous nucleation. However, here it will be demonstrated that a type of saturation effect can occur even for the case of homogeneous nucleation. This

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phenomenon will take place only at a late stage when nucleation is occurring in a glass which has been substantially crystallized. Furthermore, it will be demonstrated that this process occurs for heterogeneous nucleation, too. Hence, there are two competing mechanisms which may contribute to saturation effects for heterogeneous nucleation.

The physical bases for the decline in the nucleation rate at large volume fractions transformed are similar (but not identical) for the circumstances of homogeneous and heterogeneous nucleation. For homogeneous nucleation, as the volume fraction transformed (crystallized) becomes non-negligible, the volume available for nucleation declines. Although this effect is "automatically" accounted for by the Avrami equation in the computation of the volume fraction transformed, it must be explicitly considered in the determination of the nucleation rate. For heterogeneous nucleation, the nucleation rate will decline not only as a result of heterogeneous sites being "used up," but also it will decrease since heterogeneous sites may be ingested (i.e., incorporated) during crystal growth. Although both of these cases may be treated in a combined fashion, for pedagogical reasons it is desirable to consider them separately.

2. Saturation effects in homogeneous nucleation

We consider a glass sample of volume V which is nucleating homogeneously. It is assumed that V is sufficiently large so that surface and edge effects may be neglected. Also, it is assumed that transient nucleation effects are unimportant and may be ignored. Hence, if I^0 denotes the steady-state, homogeneous nucleation rate, then the number of particles nucleated, dN , in the small time period dt is given by

$$dN = I^0 V_f(t) dt. \quad (1)$$

In eq. (1) $V_f(t)$ is the part of the entire volume V which is untransformed (i.e., still glass) at time t . The actual rate of nucleation of particles at time t , denoted by I and defined as

$$I = \frac{dN}{dt} \cdot \frac{1}{V},$$

can be obtained from eq. (1). It is given as the following:

$$I = \frac{dn}{dt} = I^0(1 - x_t). \quad (2)$$

In eq. (2) x_t is the volume fraction transformed at time t and $n = N/V$. If it is assumed that spherical growth occurs at a constant growth rate, g , then use of the Avrami expression in eq. (2) lead to

$$I = \frac{dn}{dt} = I^0 \exp\left(-\frac{\pi}{3} I^0 g^3 t^4\right). \quad (3)$$

The cumulative number of particles nucleated per unit volume up until time t is obtained by integration of eq. (3).

$$n(t) = \left(\frac{3}{\pi}\right)^{1/4} \left(\frac{I^0}{g}\right)^{3/4} \int_0^{y'} dy \exp(-y^4), \quad (4)$$

with

$$y' = \left(\frac{\pi}{3} I^0 g^3\right)^{1/4} t.$$

Equation (4) may be solved numerically or the series solution

$$n(t) = \left(\frac{3}{\pi}\right)^{1/4} \left(\frac{I^0}{g}\right)^{3/4} \sum_{j=0}^{\infty} \frac{(-1)^j (x_{te})^{j+1/4}}{(4j+1)j!} \quad (5)$$

may be employed. x_{te} is the extended volume fraction transformed and defined by $x_{te} = (\pi/3)I^0 g^3 t^4$.

The reduced nucleation rate, $I(t)/I^0$, and the reduced number density, $n(t) \cdot (\pi/3)^{1/4} (g/I^0)^{3/4}$, are plotted as a function of volume fraction transformed in fig. 1. While the ordinary nucleation rate I^0 is independent of x_t , the actual nucleation rate decreases linearly with volume fraction transformed. This is a physically apparent result since the volume available for nucleation decreases as the transformation continues. Figure 1 also illustrates the difference in behavior of the reduced number density calculated from eq. (4) and that found using a constant nucleation rate. The latter number density is equal to $x_{te}^{1/4}$, and thus diverges as $x_t \rightarrow \infty$. On the other hand, the former number density approaches 0.9064 in this limit, as one may verify by setting the upper limit in the integral in eq. (4) equal to infinity. For volume

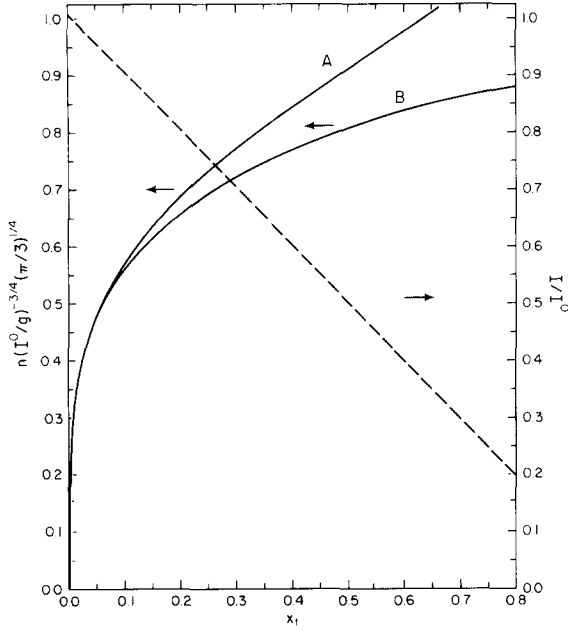


Fig. 1. Reduced density of particles nucleated and reduced nucleation rate vs. volume fraction transformed for homogeneously nucleated particles. A, particle density for constant nucleation rate; B, particle density when saturation effects are included; the dashed curve is the reduced nucleation rate.

fractions transformed of 15% or less, saturation effects have negligible effect upon the number density transformed. However, for moderate to large x_t , saturation effects significantly influence the number density. Also, it should be remembered that saturation effects produce a non-negligible reduction of the steady state nucleation rate even at small x_t .

3. Saturation effects in heterogeneous nucleation: governing equations

We now turn to a consideration of heterogeneous crystallization of glass. It will be assumed that a number density n_p^0 of identical foreign particles are present initially in the glass and that these particles serve as the sole source of crystal nucleation. Furthermore, it will be supposed that these particles are all of the same size and are randomly distributed throughout the volume of glass. It is presumed that each particle can par-

ticipate in solely a single nucleation event. The assumptions of spherical growth and neglect of transient effects in nucleation are involved once again, too.

The foreign particle density (which can serve as nucleation sites), $n_p(t)$, will decrease with time producing a time dependent nucleation rate. If, again, one denotes dn as the number of particles nucleated/(unit volume) in time dt , then

$$dn = An_p(t) dt, \quad (6a)$$

where A is yet to be determined. Thus, the nucleation rate is

$$I = \frac{dn}{dt} = An_p(t), \quad (6b)$$

and clearly $A = I_{\text{het}}^0/n_p^0$, where I_{het}^0 is the initial (unperturbed) heterogeneous nucleation rate. The nucleation rate will be determined if the time dependence of the foreign particle density is ascertained. There are two mechanisms by which this quantity is depleted. First, as particles nucleate, $n_p(t)$ decreases since sites are “used up.” This mechanism has been considered previously [14]. A second mechanism causing a decline in $n_p(t)$, which has not been taken into account previously, is due to impurity particles being ingested by growing crystals.

Thus, we consider the time interval dt and calculate the incremental change, dn_p , due to these two mechanisms. Therefore,

$$dn_p = dn_p^u + dn_p^e, \quad (7)$$

where “u” denotes the change as a result of being “used” and “e” as a result of being ingested. Clearly, dn_p^u is given as follows:

$$dn_p^u = -dn. \quad (8)$$

Next, turning to dn_p^e it is given by

$$dn_p^e = -Pn_p, \quad (9a)$$

where P is the probability of encapsulation (ingestion) and is given by

$$P = \frac{dV_{\text{trans}}}{V(t)} = \frac{dV_{\text{trans}}/V}{V(t)/V} = \frac{dx_t}{1-x_t}. \quad (9b)$$

In eq. (9) dV_{trans} is the volume crystallized in time dt , $V(t)$ is the free or available volume for

crystallization and V is the total volume. Combining eqs. (8, 9a, 9b), one obtains,

$$\frac{dn_p}{dt} = -\frac{dn}{dt} - \frac{n_p(t)}{1-x_t} \frac{dx_t}{dt}. \quad (10)$$

If one defines $f = n_p(t)/n_p^0$ and uses eq. (6b) in eq. (10), then one finds

$$\frac{df}{dt} = -Af - \frac{f}{1-x_t} \frac{dx_t}{dt}. \quad (11)$$

Use of the Avrami equation, $x_t = 1 - \exp(-x_{te})$, followed by integration, yields

$$f(t) \equiv n_p(t)/n_p^0 = \exp[-x_{te} - At] \quad (12a)$$

and

$$x_{te} = \frac{4}{3}\pi g^3 I_{het}^0 \int_0^t (t-t')^3 \exp[-At'] dt'. \quad (12b)$$

If is of utility to observe the behavior of $f(t)$ in certain limits. If the volume fraction transformed is sufficiently small so that for all times concerned $x_{te} \gg At$, then “ingestion effects” may be neglected. Here one recovers the usual expression for $n_p(t)$, i.e.,

$$n_p(t) = n_p^0 \exp(-tI_{het}^0/n_p^0). \quad (13)$$

On the other hand, for those times such that $x_{te} \gg At$,

$$n_p(t) = n_0 \exp(-x_{te}). \quad (14a)$$

Use of eq. (6b) in eq. (14a) yields

$$\frac{I}{I_{het}^0} = \exp(-x_{te}). \quad (14b)$$

The latter expression for the reduced nucleation rate, which corresponds to the limit where ingestion effects predominate, is exactly on the form found for homogeneous nucleation (i.e., eq. (2)). Therefore, ingestion of nucleation sites in the case of heterogeneous nucleation is in a sense equivalent to volume reduction in the homogeneous nucleation situation.

The extended volume x_{te} may be found ex-

plicitly by a simple integration and the result is shown below:

$$x_{te} = \left(\frac{t_u}{t_e}\right)^4 h(y) \equiv R^4 h(y), \quad (15a)$$

$$h(y) \equiv y^3 - 3y^2 + 6y - 6(1 - \exp(-y)), \quad (15b)$$

$$y \equiv At, \quad (15c)$$

$$t_e = \left(\frac{4}{3}\pi g^3 I_{het}^0\right)^{-1/4}, \quad (15d)$$

$$t_u = A^{-1} = n_p^0/I_{het}^0. \quad (15e)$$

Eqs. (15d, e) define two characteristic times which govern the relative importance of “ingestion” and using up effects and R denotes the ratio of these times (eq. (15a)). Hence, the reduced heterogeneous nucleation rate may be written as

$$I/I_{het}^0 = \exp[-y - R^4 h(y)]. \quad (16)$$

Also, the reduced crystallite density is given by eq. (17):

$$n(y)/n_p^0 = \int_0^y \exp[-y' - R^4 h(y')] dy'. \quad (17)$$

In general, the reduced crystallite density can be obtained only via numerical integration.

4. Saturation effects in heterogeneous nucleation: numerical results

The parameter R is a gauge of the relative importance of the two saturation mechanisms at various time periods. Since $R = t_u/t_e$ large values of R imply $t_u \gg t_e$ and particle ingestion will occur at short times on the t_u time scale. Contrarily, for small R , particle ingestion will not become evident until long times (on the t_u scale).

Figure 2 contains plots of the reduced heterogeneous nucleation rate, I/I_{het}^0 , as a function of reduced time, y , for several different cases. The dashed line near the top of the figure represents the reduced nucleation rate when both types of saturation effects are ignored; i.e., a constant rate. The solid lines marked $R = 1$ and $R = (90)^{1/4}$ were generated by use of eq. (16), which accounts for both depletion mechanisms. It may be noted that the decrease of the reduced nucleation rate with time is more rapid for larger R . For $R = 20$

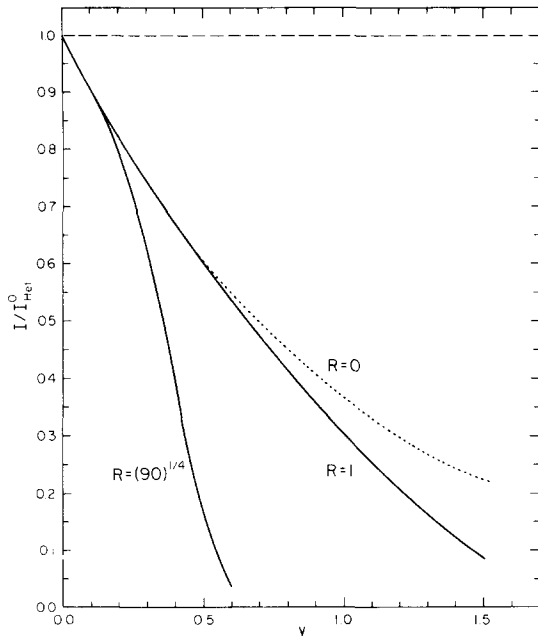


Fig. 2. Reduced heterogeneous nucleation rate vs. reduced time. The dashed line corresponds to a constant nucleation rate, while the dotted line was calculated via use of eq. (16) with $R = 0$. The solid curves were generated by use of eq. (16).

the decrease is so rapid such that it is essentially zero on the time scale shown in this figure. This type of behavior was indicated in the discussion above and corresponds to significant encapsulation effects at relatively short times. The relative importance of the two mechanisms for the reduction of the nucleation rate, for $R = 1$ and $R = (90)^{1/4}$, can be assessed by comparing the two solid curves with the dotted line. The latter curve was generated from eq. (16) with $R = 0$, and corresponds to the case where nucleation declines solely as a result of particle depletion (i.e., no ingestion effects included). It may be noted that for $R = 1$ the decline in the nucleation rate is due almost totally to heterogeneous nucleation sites being used up (except for long times where the nucleation rate is already small). On the other hand, for $R = (90)^{1/4}$ a very marked deviation from the dotted curve occurs at short times indicating that encapsulation of particles is a significant contribution to the decrease in the nucleation rate.

A somewhat different, yet very illustrative, perspective may be gained by considering I/I_{het}^0 as a function of volume fraction transformed for various values of R (see fig. 3). Here one observes that the reduced nucleation rate falls most rapidly with x_t for $R = 1$; unlike the behavior exhibited in fig. 2 which showed that $R = 1$ had the slowest decrease with time. The reason for this apparently paradoxical behavior is as follows. The larger the value of R , the shorter the time required to reach a given volume fraction transformed. In all cases at relatively small x_t (or short times) the predominant mechanism for the decrease in the nucleation rate is particle depletion. However, since the larger R corresponds to shorter times (for a fixed x_t), fewer impurities will be depleted and the nucleation rate will be relatively larger. At larger x_t , where ingestion becomes important, $(d/dx_t)(I/I_{\text{het}}^0)$ will have a larger magnitude for bigger R , and thus the nucleation curves will tend to converge for the different values of R . Since all such curves must vanish at $x_t = 1$, the values of I/I_{het}^0 for all R are similar at very large x_t (as illustrated in fig. 3).

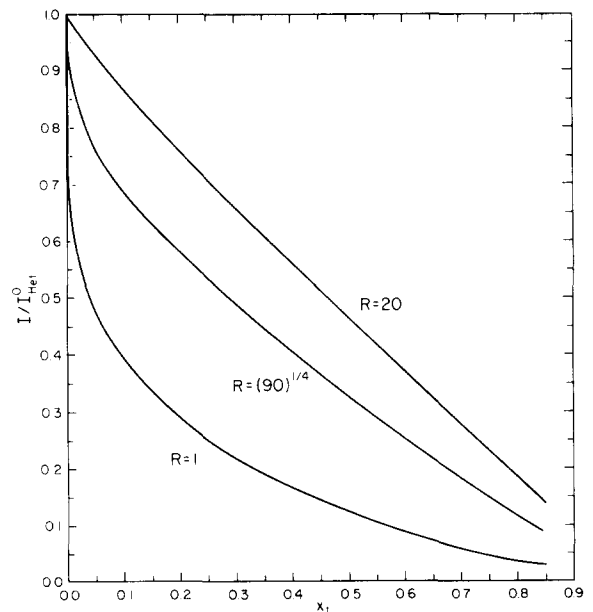


Fig. 3. Reduced heterogeneous nucleation rate vs. volume fraction transformed.

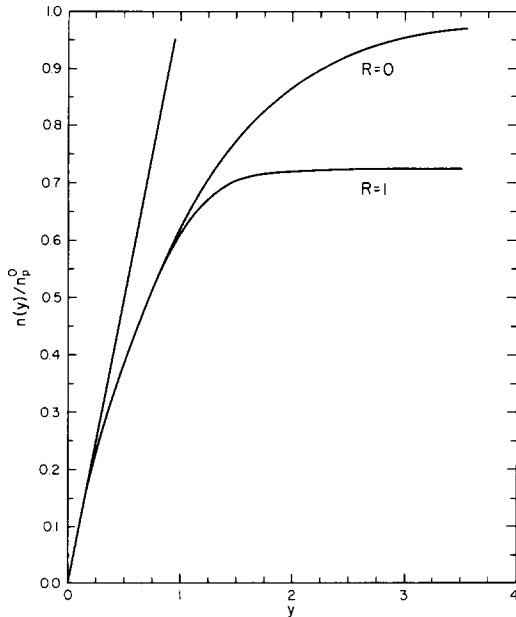


Fig. 4. Reduced particle density vs. reduced time for heterogeneous nucleation. $R=1$, calculated from eq. (17) (site depletion + ingestion); $R=0$, calculated from eq. (13) (site depletion only); the straight line corresponds to constant nucleation rate.

Now, we turn to a discussion of the behavior of the reduced nucleated particle density, $n(t)/n_p^0$. First, we consider the variation of the latter quantity with time as a function of R . This behavior is illustrated in figs. 4 and 5, for $R=1$ and $R=20$ respectively, where the reduced particle density has been plotted as a function of reduced time. For comparative purposes the reduced number densities corresponding to a constant nucleation rate and pure site depletion are shown, too. For both values of R , at the shortest times, $n(t)/n_p^0$ follow the curves found by using a constant nucleation rate. At longer times, where deviations occur and particle saturation begins, the small R and large R behavior of $n(t)/n_p^0$ differs. For the case of $R=1$, there is an intermediate time period where the particle density curve found via use of eq. (17) is fitted quite accurately by a curve in which only site depletion effects are accounted for. At somewhat longer times ingestion effects become important and complete saturation rapidly ensues. For $R=20$, however, at intermediate times, eq. (13) follows the constant nucleation curve, but

the number density computed from eq. (17) deviates from these curves since ingestion effects are significant. This difference in behavior is anticipated since particle depletion effects play a major role for small R (as discussed previously). One should also observe that the value of $n(t)/n_p^0$ at saturation is much smaller for large R than for small R . This, again, is a reflection of the fact that in the former case nucleation is reduced primarily as a result of rapid particle growth.

The variation of the reduced number density with volume fraction transformed, for several values of R , is shown in fig. 6. Several features of this figure should be noted. First, it is observed that the smaller the value of R the larger the saturation value of n/n_p^0 at $x_t=1$. In addition, the reduced number densities for small R are greater than those for larger R at all $x_t > 0$. This follows from the fact that large R corresponds to the situation where the relative growth rate to steady state nucleation rate is large. Hence, for a given x_t in the large R case there will be few particles, but of large size, while in the small R situation the same x_t will be constructed from many small particles. Hence, in the latter case $n(x_t)/n_p^0$ will be larger. Second, at very small x_t , a rapid increase in the reduced particle density seems to occur solely if R

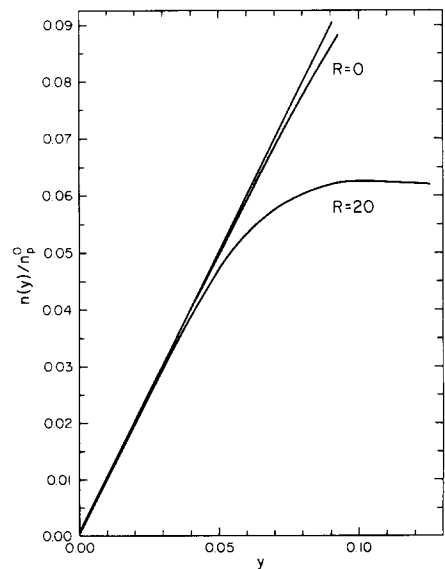


Fig. 5. Reduced particle density vs. reduced time for heterogeneous nucleation. Curves labelled as in fig. 4.

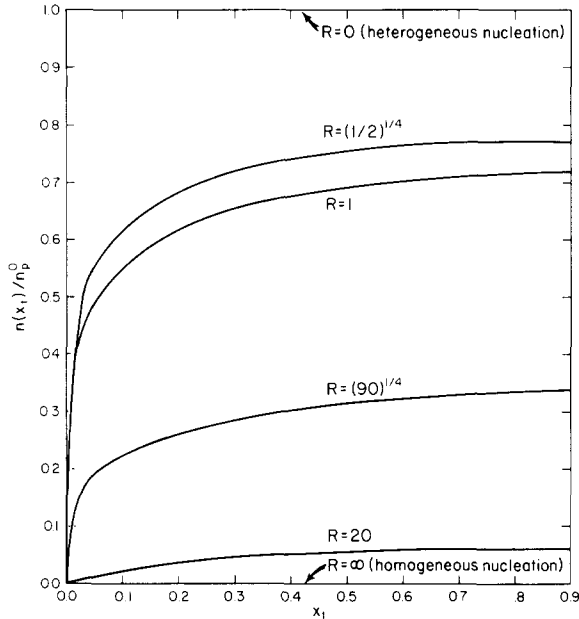


Fig. 6. Reduced particle density vs. volume fraction transformed. All curves computed from eq. (17).

is not too large. This rapid rise in $n(x_i)/n_p^0$ corresponds to the region of x_i where the reduced particle density is accurately described in terms of the constant steady state nucleation rate. It occurs for all finite values of R , but it cannot be observed in fig. 6 for large R as a result of the scale chosen for the y axis to accommodate the various curves shown simultaneously in this figure. Finally, it appears that at intermediate values of x_i (from 0.1 to 0.5) that the larger the value of R the more gradual is the change in slope of the curve. Again this feature is to a large extent a feature of scale, but there is a difference between the behavior of $n(x_i)/n_p^0$ for small and large R in the moderate x_i range. Both of the latter features are more readily discerned by an inspection and comparison of figs. 7 and 8.

Figure 7 contains plots of the reduced particle as a function of x_i , using eqs. (13) and (17) and a constant nucleation rate for the case of $R = 20$. The rapid increase of $n(x_i)/n_p^0$ for small x_i is easily observable, and it is seen that neither ingestion nor depletion effects are significant in this region. At intermediate to rather large x_i , the curve generated from eq. (13) is in substantial

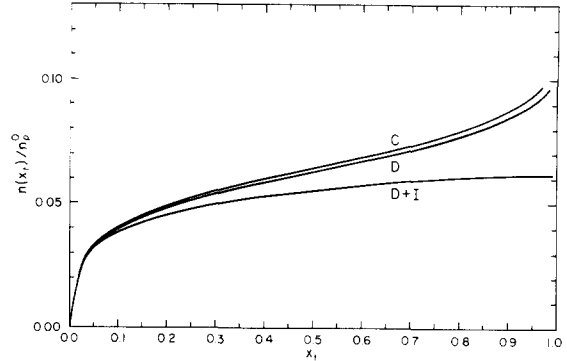


Fig. 7. Reduced particle density vs. volume fraction transformed for $R = 20$. C, D, and D+I were computed with a constant nucleation rate, solely including depletion effects, and including depletion and ingestion, respectively.

agreement with the one produced from the constant nucleation rate calculation, but the actual values of $n(x_i)/n_p^0$ deviate from the latter as a result of particle ingestion effects. Thus, for this R value it is observed that particle depletion effects have an inconsequential effect upon the reduced number density for virtually all x_i . The latter case may be contrasted with the situation when $R = 1$ (see fig. 8). Although the general shape of the reduced particle density curves shown in figs. 7 and 8 appear quite similar, it is clear that the origins of the saturation effects are quite different. The reasonably close correspondence between $n(x_i)/n_p^0$ found via use of eqs. (13) and (17)

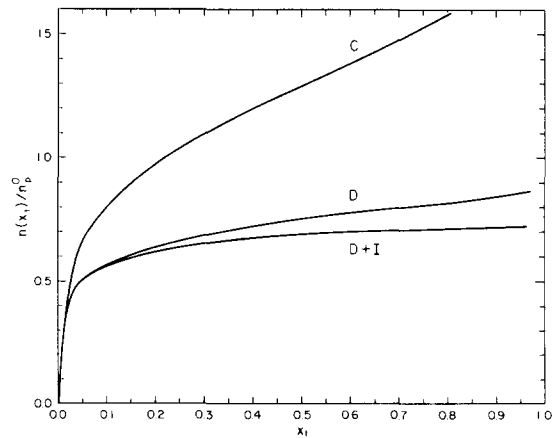


Fig. 8. Reduced particle density vs. volume fraction transformed for $R = 1$. Curves denoted as in fig. 7.

indicates that particle depletion effects are primarily responsible for saturation when $R = 1$.

5. Discussion

It is important to note that the present work is restricted to a discussion of isothermal transformations, where nucleation and growth occur simultaneously at a given temperature. For some systems [1] homogeneous nucleation and crystal growth curves (i.e. I vs. T and g vs. T) have little overlap, and hence only the small x_t region may be probed. However, other glasses [15,16] which appear to exhibit homogeneous nucleation are such that substantial overlap of $g(T)$ and $I(T)$ occur. Hence, for these systems the full range of x_t values may be reached.

As mentioned previously, the detection of saturation effects in nucleation measurements has been argued to be a telltale sign of heterogeneous nucleation. However, it has been demonstrated here that saturation effects can occur for homogeneous nucleation, too. Thus, is it possible to use the appearance of saturation effects as a sign of heterogeneous nucleation? Clearly, if the volume fraction transformed is $\approx 10\%$ or less upon completion of single stage nucleation experiments and saturation effects are in evidence, then it is safe to assume that heterogeneous nucleation has occurred. Thus, for systems such as $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ the appearance of saturation in nucleation in all probability would signal heterogeneous nucleation. On the other hand, detection of saturation effects in nucleation experiments for systems in which the volume fraction transformed was found to be greater than 10 or 15% would not necessarily indicate heterogeneous nucleation. The data would have to be analyzed making use of the equations presented here in order to determine the nature of the nucleation process.

Also, nucleation rates may be determined indirectly by measuring x_t and g and using the Avrami equation for obtaining I . However, if the volume fraction transformed is large, then it has been demonstrated here that one must account for the depression of I^0 due to reduction in volume caused by crystal growth.

When heterogeneous nucleation occurs, then saturation may occur via at least two mechanisms. The impurity particles may be used up to a significant degree or they may be encapsulated by growing crystallites. The latter mechanism is very similar to, but not exactly the same as, the one responsible for saturation in homogeneous nucleation. For the case of homogeneous nucleation the decline in the nucleation rate is produced by the continual decline in the volume available for nucleation. This decline in free volume results from crystal growth. For heterogeneous nucleation, however, the nucleation rate does not depend on the untransformed volume, but it is proportional to the number density of available active impurity sites. The latter, though, are reduced in number via crystal growth. Thus, if they are distributed randomly, crystal growth should produce equivalent effects in reducing the heterogeneous and homogeneous nucleation rates.

Finally, it is illustrative to obtain an estimate of the crystal growth rates necessary to detect ingestion phenomena as the predominant path for saturation in heterogeneous nucleation. In the previous section it has been demonstrated that for $R \geq 20$ particle depletion effects may be ignored in computing saturation. Hence, $R = 20$ will arbitrarily be selected as the limiting value. Using eqs. (15a, d, e), one finds that

$$g^3 \geq \left(20^4 (I_{\text{het}}^0)^3\right) / \left(\frac{4}{3}\pi (n_p^0)^4\right) \quad (18)$$

as the required condition. If the case of equality in eq. (18) is taken as well as a typical value of $I_{\text{het}}^0 = 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, then

$$g_c = (3.37 \times 10^{10}) / \left((n_p^0)^{4/3}\right) (\mu/s). \quad (19)$$

A plot of the log critical (minimum) growth rate, $\log(g_c)$ as a function of $\log(n_p^0)$ is presented in fig. 9. An upper limit to typical impurity particle densities of carefully prepared samples is taken to be approximately 10^9 cm^{-3} [17]. One may note that for small impurity densities ($n_p^0 \sim 10^8 - 10^9 \text{ cm}^{-3}$), growth rates of $0.1 - 1 \mu/s$ are required. This condition implies substantial overlap of the growth and the nucleation curves. However, for $n_p^0 > 10^{11} \text{ cm}^{-3}$, $g_c \leq 10 \text{ \AA/s}$. Thus, for systems

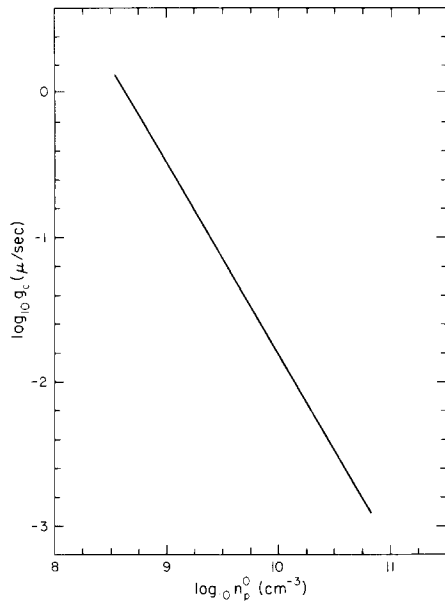


Fig. 9. Required minimum crystal growth as a function of foreign particle density for ingestion effects to be dominant. $I_{\text{het}}^0 = 10^5 \text{ cm}^{-3} \text{ s}^{-1}$.

which are intentionally heterogeneously nucleated (e.g., glass-ceramic formation) particle encapsulation probably would be the dominant mechanism producing saturation effects for nucleation.

6. Summary

A description was presented of the potential for a decline in the steady state homogeneous nucleation rate due to the reduction in untransformed volume caused by crystal growth. This effect was seen to be significant for $x_t \geq 0.15$. In order to satisfy the latter inequality it was noted that substantial overlap of the nucleation and growth curves was required.

Saturation effects in heterogeneous nucleation were considered too. It was demonstrated that the latter could occur via two processes: impurity particle depletion and particle ingestion. The former mechanism was observed to be favored by small impurity particle densities, small crystal growth rates, and large nucleation rates, while the

latter mechanism was seen to be significant for the reverse of these conditions. Furthermore, it was demonstrated that the latter three parameters could be combined into a single parameter, R , such that for small R depletion effects prevailed while for large R encapsulation effects were predominant.

Finally, a discussion was presented of the importance of a complete description of saturation effects in efforts to distinguish between homogeneous and heterogeneous nucleation and for the tailoring of crystallite densities in glass-ceramic formation.

The authors wish to express their gratitude to the Jet Propulsion Laboratory and the Division of Microgravity Science and Applications of NASA for the financial support of this work. E.D. Zanotto also acknowledges Capes/Fulbright for financial assistance. In addition, the authors are grateful to Dr. George Neilson, of the Jet Propulsion Laboratory, for his valuable comments.

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