

A theoretical and experimental assessment of systematic errors in nucleation experiments

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Equations are derived for the fractional underestimate in the number of particles per unit volume, N_v , and in nucleation rates, I^0 , as obtained by stereological techniques from reflected light microscopy or SEM for typical cases of crystal nucleation in glasses. Three cases are considered: (i) instantaneous heterogeneous nucleation (monodispersed systems of particles); (ii) simultaneous homogeneous nucleation and growth in a single-stage heat treatment (uniform distribution of particles from the critical size to D_M , where D_M is the largest diameter); and (iii) case (ii) with a double heat treatment (uniform size distribution from D_m , the smallest diameter, to D_M). Comparison with experimental nucleation data for BaO–SiO₂ and Na₂O–CaO–SiO₂ glasses demonstrates that the equations derived predict well the observed underestimations. Typical experiments with optical microscopy lead to underestimates from 3% to 14% for case (iii) and up to 50% for case (ii). To minimize these errors one should use a high magnification objective lens with reflection or transmitted light microscopy, or electron microscopy.

1. Introduction

The kinetics of crystal nucleation in polymeric, metallic and inorganic glasses is a subject of major scientific and technological importance [1,2]. In most studies, transmission or reflection microscopy are employed for the direct determination of crystal nucleation densities and nucleation rates.

Nucleation measurements are usually performed via *two-stage* heat treatments. This method consists of heating the glass to a low temperature to produce the nuclei, followed by a high temperature heat treatment to grow the nuclei to an observable size. This procedure is required when the nucleation curve has little overlap with the growth curve. A potential disadvantage of this method is that some of the nuclei may dissolve when heated

at the growth temperature. This results from the fact that the critical radius is inversely proportional to the bulk free energy difference between crystal and liquid. The magnitude of the latter is smaller at the growth temperature, and thus the critical radius is larger at the growth temperature than at the nucleation temperature. Thus, those particles whose radii fall between these two limits will dissolve. Hence, using a two-stage heat treatment tends to underestimate the nucleation rate.

This is not a serious problem, however, if the growth rate at the nucleation temperature is significant. Thus the particles grow sufficiently rapidly at the nucleation temperature, and a *single-stage* heating suffices to determine the particle density (and nucleation rate). This procedure does not suffer from the difficulty described above. However, the single-stage heat treatment could

possibly also lead to *underestimation* of the particle number since a certain fraction of the nuclei which form will be too small to observe.

Considerable differences are expected if the measurements are carried out by transmission or reflection methods and if optical or electron microscopy is used. For the purpose of this paper the resolution limit, ϵ , will be used to distinguish optical from electron microscopy.

Transmission microscopy generally demands considerable effort on sample preparation but, if proper precautions are taken, leads to small errors in the determination of crystal nucleation densities, as recently demonstrated by Smith et al. [3]. The other, more common technique, reflected light optical microscopy, can lead to much larger errors due to the use of stereological methods, since one has to calculate volume properties (size distributions, numbers, etc.) based on statistical evaluations performed on cross-sections through the specimens.

The objective of this paper is to derive equations for the expected errors in the crystal nucleation density determined by reflected light optical microscopy or SEM for several crystallization mechanisms. Comparisons with experimental results will also be made. We will confine ourselves to the simplest cases of steady state nucleation and constant growth rates of spherical particles which lead to either monodisperse or to uniform particle size distributions.

2. Theory

According to Toshev and Gutzow [4] the number of circular intersections in a cross-section, N_s , through a random assembly of spherical particles is given by

$$N_s(\sigma) = \int_{\rho=0}^{\rho=1} \rho \, dN_v - \int_{\rho=\sigma}^{\rho=1} (\rho^2 - \sigma^2)^{1/2} \, dN_v, \quad (1)$$

where $\rho = D/D_M$ and $\rho = d/D_M$; D being the diameter of a spherical particle in the assembly, d the diameter of a circular intersection and D_M the largest diameter of the distribution. dN_v , defined

by $N_v(\rho) \, d\rho$, is the frequency distribution function (volume distribution of particles).

De Hoff and Rhines [5] have shown that the number of particles per unit volume, N_v , is related to the number of sectioned particles, N_s^0 , by

$$N_v = 2N_s^0 \bar{Z} / \pi K(q), \quad (2)$$

where $K(q)$ depends on the shape of the particles ($K(q) = 1$ for spheres), and

$$\bar{Z} = \frac{\sum_i (n_{si}/d_i)}{\sum_i n_{si}}, \quad (3)$$

where n_{si} is the number of circular intersections of diameter d_i .

If the functions $N_s(\sigma)$ and Z are known for a given system of particles it is possible to calculate the error in N_v , i.e. the fraction lost due to the limited resolution of the optical or electron microscope, normally employed in the determination of N_v . The undetectable fraction, f , is given by

$$f = \frac{N_v - N_v^m}{N_v} = 1 - (1 - f_N)(1 - f_Z), \quad (4)$$

where N_v^m is the number of particles per unit volume, as determined in the micrographs, N_v is the real value and f_N is the undetected fraction of N_s , given by

$$f_N = N_s(\sigma_1) / N_s^0, \quad (5)$$

where $\sigma_1 = \epsilon/D_M$; and f_Z is the fraction of \bar{Z} lost, given by

$$f_Z = 1 - \bar{Z}^m / \bar{Z}, \quad (6)$$

where \bar{Z}^m and \bar{Z} are the De Hoff and Rhines's factor obtained from the micrographs and the real factor, respectively. These factors are given by the following equations:

$$\bar{Z} = \int_0^1 \frac{1}{\sigma D_M} \left(\frac{dN_s}{d\sigma} \right) d\sigma / \int_0^1 \left(\frac{dN_s}{d\sigma} \right) d\sigma, \quad (7)$$

$$\bar{Z}^m = \int_{\sigma_1}^1 \frac{1}{\sigma D_M} \left(\frac{dN_s}{d\sigma} \right) d\sigma / \int_{\sigma_1}^1 \left(\frac{dN_s}{d\sigma} \right) d\sigma. \quad (8)$$

3. Application to some typical cases of crystallization

3.1. Single-stage treatment – monodispersed systems

In instantaneous heterogeneous nucleation all nuclei are rapidly formed at the temperature of study and only a linear growth occurs. A monodispersed system of crystals is predicted. For this case, it can be shown that the probability that a sphere with diameter D_M upon sectioning will reveal a circle whose diameter is equal to or less than a given value d is $1 - (1 - d^2/D_M^2)^{1/2}$. Then, the fraction of circles with diameter less than or equal to d , $N_s(d)/N_s^0$, is given by the same expression, or in terms of σ :

$$N_s(\sigma) = N_s^0 \left[1 - (1 - \sigma^2)^{1/2} \right], \quad (9)$$

where N_s^0 is the total number of particles on the cross-section.

By substituting expression (9) into eqs. (7) and (8),

$$\begin{aligned} \bar{Z} &= \int_0^1 \frac{N_s^0}{D_M(1 - \sigma^2)^{1/2}} d\sigma \bigg/ \int_0^1 \frac{\sigma N_s^0}{(1 - \sigma^2)^{1/2}} \\ &= \pi/2 D_M \end{aligned} \quad (10)$$

and

$$\bar{Z}^m = \frac{\pi/2 - \sin^{-1}\sigma_1}{D_M(1 - \sigma_1^2)^{1/2}}. \quad (11)$$

According to eqs. (6) and (5),

$$f_Z = 1 - \frac{\pi - 2\sin^{-1}\sigma_1}{\pi(1 - \sigma_1^2)^{1/2}} \quad (12)$$

and

$$f_N = \frac{N_s(\sigma_1)}{N_s^0} = 1 - (1 - \sigma_1^2)^{1/2}. \quad (13)$$

Therefore, the total fraction lost is given by eq. (4)

$$f = \frac{2}{\pi} \sin^{-1}\sigma_1. \quad (14)$$

3.2. Single-stage treatment – uniform size distribution

For simultaneous constant homogeneous crystal nucleation and growth rates, a uniform size distribution of particle diameters from zero * to D_M is expected. Therefore, according to ref. [4]

$$\frac{dN_v}{N_v^0 d\rho} = 1, \quad (15)$$

where N_v^0 is the total number of crystals in the volume considered. By substitution of dN_v into eq. (1) one obtains

$$\begin{aligned} N_s(\sigma) &= \frac{1}{2} N_s^0 \left[1 - (1 - \sigma^2)^{1/2} \right. \\ &\quad \left. + \sigma^2 \ln \left(\frac{\sigma}{1 + (1 - \sigma^2)^{1/2}} \right) \right]. \end{aligned} \quad (16)$$

In differential form (frequency distribution)

$$\begin{aligned} \frac{dN_s}{d\sigma} &= \frac{1}{2} N_s^0 \sigma \left\{ (1 - \sigma^2)^{-1/2} + 2\sigma \ln \frac{\sigma}{(1 - \sigma^2)^{1/2}} \right. \\ &\quad \left. + \sigma \left[\frac{1 + (1 - \sigma^2)^{1/2} + \frac{\sigma^2}{(1 - \sigma^2)^{1/2}}}{1 + (1 - \sigma^2)^{1/2}} \right] \right\}. \end{aligned} \quad (17)$$

Combining eqs. (7), (8) and (16) one has

$$\bar{Z} = \pi/D_M \quad (18)$$

and

$$\begin{aligned} \bar{Z}^m &= \frac{2}{D_M} \left\{ \left[\pi/2 - \sigma_1 \ln(1 + \cos \theta_1) \right. \right. \\ &\quad \left. \left. - \theta_1 + \sigma_1 \ln \sigma_1 \right] / \left[1 - N_s(\sigma_1)/N_s^0 \right] \right\}, \end{aligned} \quad (19)$$

* In actual fact the lower limit is the critical nucleus diameter instead of zero but, for all practical purposes, this is 3–4 orders of magnitude smaller than the resolution limit and can be set to zero.

where $\theta_1 = \sin^{-1}\sigma_1$ (rad) and $\sigma_1 = \epsilon/D_M$. Therefore, the total fraction lost is

$$f = \frac{2}{\pi} \left[\sigma_1 \ln \left(\frac{1 + \cos \sigma_1}{\sigma_1} \right) + 1 \right]. \quad (20)$$

3.3. Double heat treatment – uniform size distribution from D_m to D_M

This is the case when a glass with constant nucleation and growth rates has been given a second ‘development’ heat treatment to allow observation of the grown crystals under an optical microscope. A uniform size distribution of particles ranging from D_m to D_M is expected. If D_m is larger than ϵ (the resolution limit) the error would be associated exclusively with sectioning. If D_m is smaller than ϵ , in addition to sectioning errors a certain fraction of particles would be undetectable.

Employing reasoning similar to that above it can be shown that the total fraction lost is given by

$$f = 1 + \frac{2\sigma_1}{\pi(1 - \sigma_1/\sigma_2)} \left\{ \frac{1}{\sigma_1} \cos^{-1}\sigma_1 - \frac{1}{\sigma_2} \cos^{-1}\sigma_2 + \ln \left(\frac{\tan^{1/2} \sin^{-1}\sigma_1}{\tan^{1/2} \sin^{-1}\sigma_2} \right) \right\}, \quad (21)$$

where $\sigma_2 = \epsilon/D_m$. This expression is defined for $\sigma_1 < 1$ and $\sigma_2 < 1$.

4. Comparison with experiment

In fig. 1 the total fraction of N_v undetected (error in N_v) is plotted for a monodispersed system of spherical particles and for a uniform size distribution of spherical particles with diameters ranging from zero to D_M . It can be seen that for a given resolution limit, the fraction lost is smaller for a monodispersed system (typical for heterogeneous nucleation and for glasses with a very small growth rate at the nucleation temperature) than for a system having a uniform size distribution of spherical particles. The fraction lost is smaller for

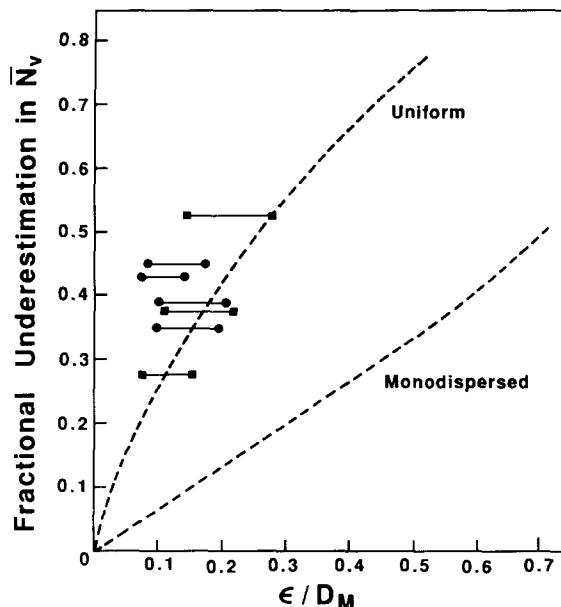


Fig. 1. Calculated underestimation in N_v as a function of the reduced resolution limit, $\sigma_1 = \epsilon/D_M$, for a monodispersed system and for a uniform particle size distribution. The experimental points indicate the measured underestimation for crystals in a glass with 29.9 BaO–70.1 SiO₂ (mol%) (■—■) and for a Na₂O·2CaO·3SiO₂ glass (●—●). The bar indicates the limits for $1 < \epsilon < 2 \mu\text{m}$.

increasingly larger particles and decreasing values of ϵ .

The experimental points shown in fig. 1 were obtained with a glass having 29.9 mol% BaO–70.1 mol% SiO₂ (■—■) heat treated at 743 or 760 °C, and with a Na₂O·2CaO·3SiO₂ (molar ratios) glass heated at 629 °C (●—●) for times long enough to allow the observation of crystals under an optical microscope. It was known from previous experimental studies [6–8] that both nucleation and growth rates of crystals in these glasses are approximately constant and therefore, a uniform size distribution of spherulites is expected. The experimental N_v' values obtained with glass specimens which had been given long single-stage heat treatments were compared with the N_v values obtained by extrapolation of the N_v vs time curves, obtained through a double-stage treatment for shorter nucleation times. For the single-stage treatments the N_v' values obtained are expected to underestimate the true values of N_v , whereas with

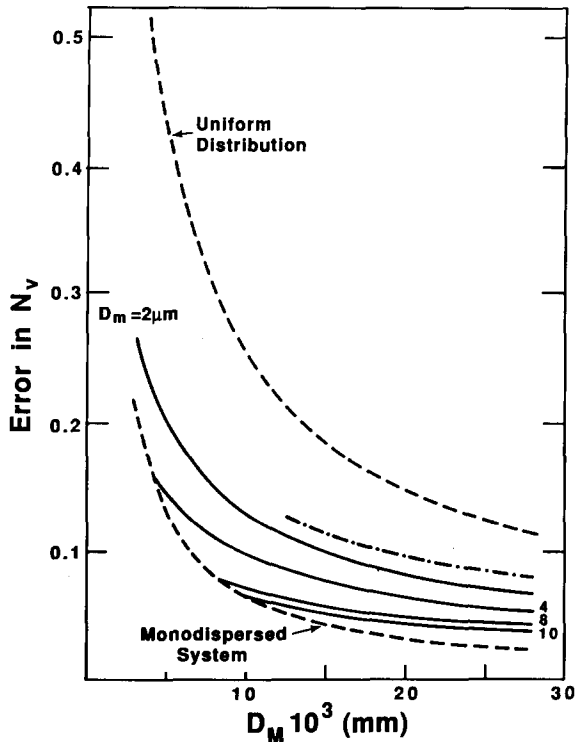


Fig. 2. Fractional error (underestimation) in N_v as a function of the maximum diameter (D_M) of the distribution for a resolution limit of $1 \mu\text{m}$. The solid lines represent the errors for a distribution of spherical particles obtained through a double-stage heat treatment, for minimum diameters of 2, 4, 8 and $10 \mu\text{m}$. The dot-dashed ($\cdot - \cdot - \cdot - \cdot$) line indicates the error when the minimum diameter of the distribution is $8 \mu\text{m}$ and the resolution limit is $2 \mu\text{m}$. The dashed curves ($---$) represent a uniform distribution of spheres with diameters from 0 to D_M ; and a monodispersed system of spheres of diameter D_M .

the double-stage treatments the results obtained are expected to be close to the actual values of N_v , since all the particles should have been 'developed' to sizes above the resolution limit. The error in N_v was then calculated by eq. (4), $f = 1 - N'_v/N_v$. It can be seen that the predicted errors are correct if the system of crystalline particles can be

described by a uniform size distribution (eq. (20)), and if the resolution limit of the microscope (for the objective lens employed) is $1-2 \mu\text{m}$. Both assumptions are very reasonable in the present case.

In fig. 2, fraction lost versus D_M curves are plotted for the three cases studied, assuming $1 \mu\text{m}$ as the resolution limit of the microscope. In the same figure there is also a family of curves for case 3.3., with minimum diameters D_m varying from 2 to $10 \mu\text{m}$ for $\epsilon = 1 \mu\text{m}$. The dash-dotted curve is for $D_m = 8 \mu\text{m}$ and resolution limit $\epsilon = 2 \mu\text{m}$. For most practical cases of nucleation studies where glass samples have been given a double-stage heat treatment, D_M varies from 10 to $30 \mu\text{m}$ and thus underestimations of 3% to 14% in N_v (and I^0) are expected. For single-stage heat treatments, underestimations of 30% to 50% are easily observed. Therefore, to minimize these stereological errors one has to use high magnification objective lenses or scanning electron microscopy.

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