

New insights on the thermodynamic barrier for nucleation in glasses: The case of lithium disilicate

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Abstract

An analysis is performed of the temperature dependence of the thermodynamic barrier to nucleation, $W^*(T)$, calculated from a fit of lithium disilicate glass data to the classical theory of nucleation. It is shown that, in order to obtain a satisfactory agreement between experimental and theoretical determinations of $W^*(T)$, lower values must be assigned to both the thermodynamic driving force and the surface energy as compared with the corresponding macroscopic values. This finding is consistent with theoretical considerations taking into account the effect that, in general, both the bulk and surface properties of the critical nuclei differ considerably from the respective properties of the newly evolving macroscopic phases. In addition, an anomalous increase of $W^*(T)$ with decreasing temperature is found near the glass transition interval. This increase is interpreted as a result of the effect of elastic strain on the thermodynamic driving force. The values of elastic strain energy estimated from the low temperature behavior of $W^*(T)$ are congruent with those calculated using the elastic constants of glass and crystal.

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1. Introduction

The investigation of glass crystallization kinetics is of great interest from both practical and theoretical points of view. In many aspects, the first stage of the process – crystal nucleation – determines the pathways of crystallization. Existing theories provide a qualitative description of both the temperature and time dependencies of the nucleation rate. However, they fail if a quantitative prediction of these dependencies is attempted. Such quantitative discrepancies arise possibly because the classical approaches do not adequately take into account several effects. Such effects may be a primary precipitation of metastable phases [1], the formation of

solid solutions with compositions unlike those of the parent glass [2], the (unknown) size or temperature dependence of the nucleus/melt surface energy, σ [3], or the effect of elastic strain energy [4]. A neglect of such possibilities may result in erroneous estimations of the thermodynamic barrier to nucleation (the work of critical nucleus formation, W^*) and, consequently, in an inaccurate description of the nucleation kinetics.

Above mentioned difficulties are partly due to the absence of direct experimental data about the properties of the critical nuclei in inorganic glass-forming melts. The absence of such data is understandable because, at high undercoolings required to enter the range of measurable nucleation rates, the size of the critical nuclei is only a few nanometers. The small sizes of these nuclei hinder the application of direct experimental methods to specify their thermodynamic properties, which are required to estimate W^* .

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For these reasons, in analyzing nucleation experiments, it is common practice to follow the classical nucleation theory (CNT). According to CNT, the properties of the critical nucleus are widely identified with those of the corresponding macro-phase. Assuming this condition, the driving force for nucleation, ΔG , can be estimated based on knowledge of the properties of the respective macroscopic phases. Therefore, in accordance with CNT, ΔG values measured for the macro-phase are usually applied to critical nuclei.

Another problem, which cannot be solved easily, is the determination of the appropriate value of the specific interfacial energy. It is well-known that existing measurements of the surface energy of macro-crystals in their own melt are confronted with serious difficulties. The problem is even more complex if one tries to determine the value of σ for a cluster of critical size. Since W^* is expressed as a combination of both ΔG and σ , any error in determining these quantities will lead to incorrect values of W^* .

However, when the theory is applied to experiment, ΔG is often determined in the manner as described above. This choice may or may not correspond to the real situation. Any inconsistency between the employed value of the thermodynamic driving force and the one corresponding to the real physical situation can be corrected – with respect to the proper determination of W^* – by choosing an appropriate value of the surface energy. In such typical approach, σ plays then the role of a fit parameter. This procedure allows one to reproduce theoretically (at least, to some extent) the correct values of the nucleation rates. However, the use of macro-properties for the specification of the properties of critical nuclei gives rise to a number of additional problems when nucleation experiments are analyzed within the framework of CNT. One of these internal contradictions is the significant difference between the values of the surface energy calculated from nucleation data on one side and from the growth rate of nuclei with sizes slightly exceeding the critical one. This problem was resolved by the reduction of the value of thermodynamic driving force as compared with the respective macroscopic samples [5].

From a more general theoretical point of view, both surface energy and thermodynamic driving force for critical and near-critical nuclei have to be considered as *unknown* quantities. Moreover, in analyzing nucleation rates, the possible effect of elastic strain (caused by the difference between the densities of melt and crystal) on the thermodynamic driving force is usually not taken into consideration. However, at high undercoolings, especially close to the glass transition region, the driving force may be diminished due to elastic strain, which, according to [6–8], can strongly diminish the nucleation rate.

In the present paper, we analyze the thermodynamic barrier for nucleation calculated from a fit (to CNT) of

both steady-state nucleation rates and induction periods in lithium disilicate glass. However, in contrast to the conventional approach, in this procedure both the thermodynamic driving force and surface energy are initially considered as unknown quantities. In addition, we estimate the elastic strain energy from the deviation between the experimentally and theoretically determined values of the thermodynamic barrier at low temperatures (close to and below the glass transition range).

2. Basic equations

According to the classical theory, the steady-state nucleation rate, I_{st} , can be written in the following general form [9]:

$$I_{st} = I_0 \exp\left(-\frac{W^* + \Delta G_D}{kT}\right), \quad (1)$$

$$W^* = g \frac{\sigma^3}{\Delta G^2}, \quad (2)$$

$$I_0 \equiv 2N_1 v_0 \left(\frac{\sigma a^2}{kT}\right)^{1/2}, \quad (3)$$

where ΔG_D is the free activation energy for the transport of a ‘structural’ unit across the nucleus/melt interface (kinetic barrier), W^* is the work of critical nucleus formation (thermodynamic barrier), ΔG is the thermodynamic driving force for the phase transition, g is a shape factor equal to $16\pi/3$ in the case of spherical nuclei, I_0 is the pre-exponential term, which is only slightly temperature-dependent, $N_1 \cong 1/a^3$ is the number of ‘structural’ units of size a in the unit volume of the melt, $v_0 \cong kT/h$ is the vibration frequency of a ‘structural’ unit, σ is the specific free energy of the nucleus/melt interface, and k and h are Boltzmann’s and Planck’s constants, respectively.

W^* can be estimated – in conjunction with ΔG_D – from a fit of experimental data for the steady-state nucleation rates, I_{st} , via Eq. (1). In order to find W^* separately, one has to know the kinetic barrier. The latter quantity can be estimated from the non-steady state time-lag in nucleation, τ_{ns} (or, equivalently, from the induction period of nucleation, t_{ind}). These parameters can be determined via the following expression [9]:

$$\tau_{ns} = \frac{16}{\pi^2} \frac{h\sigma}{\Delta G^2 a^4} \exp\left(\frac{\Delta G_D}{kT}\right), \quad t_{ind} = \frac{\pi^2}{6} \tau_{ns}. \quad (4)$$

The combination of Eqs. (1), (3) and (4) results in

$$I_{st} = K_\tau \frac{\sigma^{3/2}}{\Delta G^2 t_{ind}} \exp\left(-\frac{W^*}{kT}\right), \quad (5)$$

$$K_\tau \equiv \frac{16}{3} N_1^2 (kT)^{1/2}.$$

W^* can be calculated using experimental values of I_{st} and t_{ind} . However, since the pre-exponential term in Eq. (5) contains both ΔG and σ , certain values must be assigned to them initially. As will be shown later, the final result of W^* does not depend on the choice of these initial values.

3. Experimental data on nucleation and calculations

Fig. 1 presents our own data and data from the literature [3] on the steady-state nucleation rates (a) and induction periods of nucleation (b) in lithium disilicate glass. The values of t_{ind} are taken from a linear approximation of the dependence of $\ln(t_{ind})$ on $1/T$. Both sets of data (I_{st} and t_{ind} as functions of temperature) are then employed in our calculations.

According to X-ray diffraction experiments, in advanced stages of the transformation, the crystalline phase is lithium disilicate, $Li_2O \cdot 2SiO_2$. In the tempera-

ture interval of interest (693–803 K), the thermodynamic driving force of crystallization, measured for macroscopic $Li_2O \cdot 2SiO_2$ crystals [10], can be approximated by the following relation:

$$\Delta G_{macro} = 8.40 \times 10^8 - 540266.22T - 78.51T^2, \quad (6)$$

where ΔG is given in J/m^3 and the temperature T in K.

To a first approximation, in order to estimate W^* from experimental values of I_{st} and t_{ind} , we set $\Delta G = \Delta G_{macro}$ and $\sigma_{macro} = 0.16 J/m^2$ in the pre-exponential term of Eq. (5). The temperature dependence of W^* , calculated in this way from the set of experimentally determined values of I_{st} and t_{ind} , is shown in Fig. 2. Similar dependencies for $W^*(T)$ were also obtained for other silicate glasses [3,11]. At low temperatures, the temperature dependence of W^* , determined as described here, disagrees with the predictions of the classical theory (i.e., if classical expressions for ΔG and σ are employed in Eq. (2)). According to this classical approach, the work of critical cluster formation $W^*(T)$ has to decrease monotonically with decreasing temperature. Therefore, an explanation must be found for such a deviation.

As a reasonable explanation, one can assume that the deviation of the experimentally observed behaviour from the theoretical expectations at low temperatures results from a decrease of the thermodynamic driving force owing to elastic strain. In analyzing nucleation in glass-forming melts, both stress evolution and stress relaxation generally have to be accounted for [6]. As

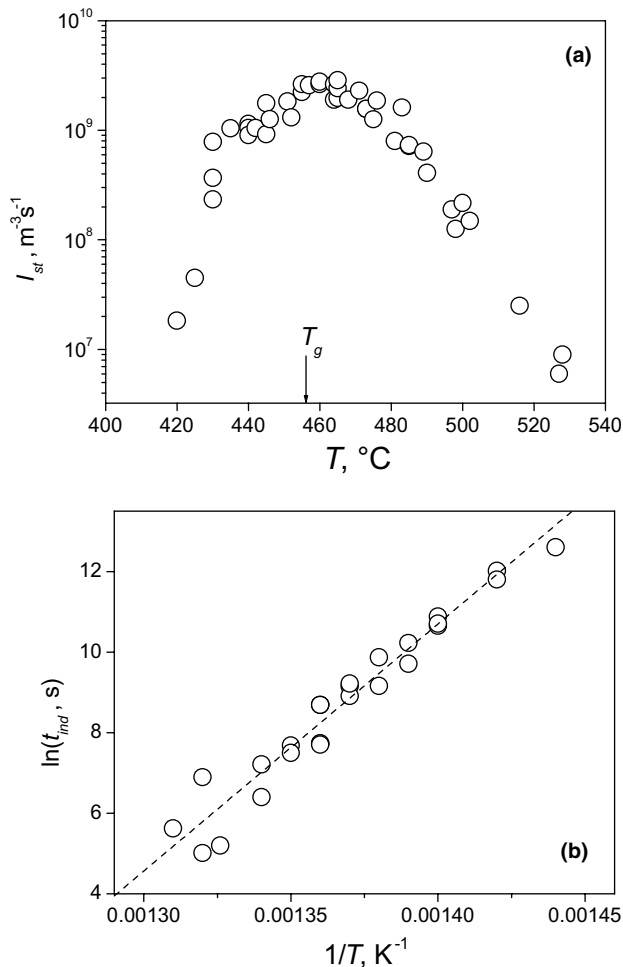


Fig. 1. Experimental steady-state nucleation rates (a), and induction periods (b) versus temperature and inverse temperature, respectively, for lithium disilicate glass [3].

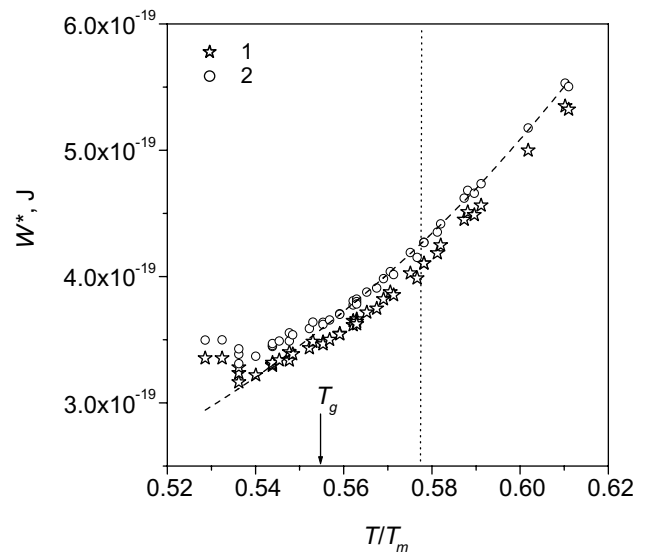


Fig. 2. Thermodynamic barrier for nucleation estimated from a fit of I_{st} and t_{ind} to Eq. (5) (1 and 2) and calculated with Eq. (2) (dashed line). See text for dotted line. The following values of σ and ΔG were used to estimate the pre-exponential term in Eq. (5): 1 – $\sigma = 0.16 J/m^2$, $\Delta G = \Delta G_{macro}$; 2 – σ and ΔG taken from Eqs. (7) and (8) with parameters P_i listed in line 3 of Table 1. Dashed line – W^* calculated by Eq. (2) with $P_1 = 0.01964$, $P_2 = 0.05738$, and $P_3 = 0.19689$.

shown in detail in Ref. [7], in the vicinity of and below the glass transition temperature, decoupling takes place between relaxation and diffusion processes. As a consequence, the effective diffusion coefficient, which is responsible for the rate of aggregation, and the viscosity coefficient, which governs relaxation, are no longer connected by the Stokes–Einstein relation. This phenomenon is not a peculiarity of the glass-forming system considered here. Decoupling of diffusion and relaxation has been shown to be a general phenomenon occurring in quite different classes of glass-forming systems [12]. As an important consequence, relaxation can be shown to have only a minor (or negligible) effect at temperatures below the glass transition temperature, T_g , and elastic stresses gain significant importance in nucleation in this temperature range [8].

At temperatures sufficiently above T_g , the glass-forming melt can be considered (to a first approximation) as a Newtonian liquid. In this temperature range, the Stokes–Einstein relation is valid. Thus, viscosity controls both phenomena – aggregation and structural relaxation – and a strong decrease of the elastic strain effect on nucleation due to the fast relaxation of stresses, should be expected here. However, as mentioned above, at and below the glass transition temperature the situation is, in general, quite different. This conclusion will be confirmed by the quantitative estimates described below.

As the first step in such quantitative analysis, we estimate σ and ΔG via a fit to Eq. (2) for W^* . Here $W^*(T)$ is determined from Eq. (5). However, in this procedure we restrict ourselves initially to temperatures $T > 758 \text{ K} > T_g = 728 \text{ K}$ (the range to the right of the vertical dotted line in Fig. 2). In agreement with above considerations, we assume that, in this high-temperature range, possible effects of elastic strain on nucleation can be neglected.

In order to determine σ and ΔG , we suppose them to be given by the following approximate equations:

$$\sigma = P_1 + P_2(T/T_m), \quad (7)$$

$$\Delta G = P_3 \Delta G_{\text{macro}}, \quad (8)$$

where P_1 , P_2 , and P_3 are initially unknown parameters. Eqs. (7) and (8) reflect the fact that the surface energy of the critical nucleus/melt interface may depend on temperature, and that the thermodynamic driving force for critical nuclei may differ from that of the corresponding macro-phase. The results of the first fitting procedure are listed in Table 1 (line 0). Hereby, to start the fitting procedure, ΔG in the pre-exponential term of Eq. (5) was identified with the classical expression given by Eq. (6), and σ was set equal to 0.16 J/m^2 to estimate W^* . As mentioned above, its final value is insensitive to the choice of these starting values. In addition, a value of P_3 close to that obtained earlier in another context was used (see Ref. [5]).

Table 1
Parameters of Eqs. (7) and (8)

N	P_1 (J/m ²)	P_2 (J/m ²)	P_3
0	0.01752	0.0606	0.19936
1	0.01956	0.05748	0.19686
2	0.01964	0.05739	0.1969
3	0.01964	0.05738	0.19689

The values of the parameters P_1 , P_2 , and P_3 obtained in the first iteration were employed in the next step to determine, in a novel way, the pre-exponential term in Eq. (5). Thus, a new determination of $W^*(T)$ was performed via Eq. (5). The new data for $W^*(T)$ were used with Eq. (2) and new values of the P -parameters were obtained.

This iteration procedure was repeated three times (see Table 1, lines 1–3) and this number of cycles proved to be sufficient to get a final (constant) result. Indeed, it is evident, from the data in Table 1, that the second and third iterations produced almost identical values of the parameters P_1 , P_2 , and P_3 .

The values of the parameters P_i were then employed to estimate the temperature dependence of W^* , including its values at temperatures below the range we started with. The results are depicted by the dashed line in Fig. 2. It should be noted that the resulting function $W^*(T)$ is only slightly dependent on the value of $\sigma^{3/2}/\Delta G^2$, which enters the pre-exponential term of Eq. (5) (see Fig. 2).

4. Driving force of transformation and interfacial energy of critical clusters

The fit to Eq. (2) of the work of critical cluster formation, $W^*(T)$, from experimental steady-state nucleation rates and induction periods, leads to the following conclusions:

- (i) The specific surface energy of the critical nuclei shows a slight *positive* temperature dependence, i.e., $\sigma = 0.020 + 0.0438 \times 10^{-3} T$; σ in J/m², T in K.
- (ii) The thermodynamic driving force for the formation of a critical nucleus is considerably *lower* than the respective value for the corresponding macro-phase ($P_3 = 0.197$).

Conclusion (i) is qualitatively in agreement with literature data for metallic [13] and silicate systems [3]. This behaviour of σ was recently discussed in detail in Ref. [3], and was interpreted as the result of an interplay of two effects. On one side, according to thermodynamic considerations [14], the specific surface energy for planar interfaces, σ_∞ , should decrease with increasing temperature. This effect, however, is coupled with a simultaneous decrease in the critical nuclei curvature.

Curvature corrections lead to a reduction of the effective value of the surface energy. Since curvature corrections lose their importance with increasing temperature (due to the increase in the critical size), the mentioned increase of σ with increasing temperature is found.

In Refs. [3,13] the respective macroscopic value of the thermodynamic driving force for critical cluster formation, ΔG_{macro} , was used in the computations. This approach differs from the present work, in which the parameter P_3 , which reflects the correction of ΔG , was obtained in conjunction with P_1 and P_2 , describing the apparent temperature dependence of the surface energy. The use of ΔG_{macro} (instead of $\Delta G = P_3 \Delta G_{\text{macro}}$), which is commonly employed in the classical approach to nucleation, leads to an overestimation of the driving force and, consequently, of the surface energy. Hence, in the classical approach, σ plays the role of a fit parameter that corrects overestimated values of the thermodynamic driving force in Eq. (2).

Indeed, the surface energy at $T = T_g$ calculated in Ref. [3] for lithium disilicate glass employing ΔG_{macro} (0.16 J/m^2) is about three times higher than the value obtained in the present work (0.05 J/m^2). One should recall that these values refer to nuclei of critical size, R^* . An approximate estimate of the corresponding values of surface energy for a planar crystal/melt interface, σ_∞ , can be made by applying, to a first approximation, the Tolman equation

$$\sigma(R) = \sigma_\infty / (1 + 2\delta/R), \quad (9)$$

where δ is the Tolman parameter. This parameter can be identified, to a first approximation, with the width of the interfacial region between the coexisting phases.

Using $\delta = 2.25 \times 10^{-10} \text{ m}$ (see Ref. [3]) and $R = R^*$, one obtains $\sigma_\infty = 0.265$ and 0.073 J/m^2 employing $\sigma(R^*)$ calculated with macroscopic and corrected values of thermodynamic driving force, respectively. The first value (0.265 J/m^2) is a factor of only 0.8 lower than the respective value for the melt/vapour surface energy, $\sigma_{\text{mv}} = 0.32 \text{ J/m}^2$, measured directly in a lithium disilicate melt [15]. However, according to Stefan's rule [9], one would expect a much lower value, i.e., $\sigma_{\text{cm}}/\sigma_{\text{mv}} \sim \Delta H_{\text{cm}}/\Delta H_{\text{mv}}$ ($\sigma_{\text{cm}} \equiv \sigma_\infty$ is the surface energy of the crystal/melt planar interface, ΔH_{cm} and ΔH_{mv} are the enthalpies of melting of the crystalline phase and of evaporation, respectively). Thus, $\sigma_\infty \approx 0.073 \text{ J/m}^2$ is more realistic than $\sigma_\infty \approx 0.265 \text{ J/m}^2$.

Another indication in favour of the values of the parameters P_1 , P_2 , and P_3 for a characterisation of the properties of the critical nucleus is the value of the critical size R^* or the number of structural units in a critical nucleus, $n^* \approx 4\pi R^{*3} N_A / 3V_M$ (N_A is Avogadro's number, and V_M is the molar volume of the crystalline phase). The number n^* is plotted in Fig. 3 as a function of temperature. The solid line is calculated using the P_i parameters listed in the last line of Table 1, and the dashed line

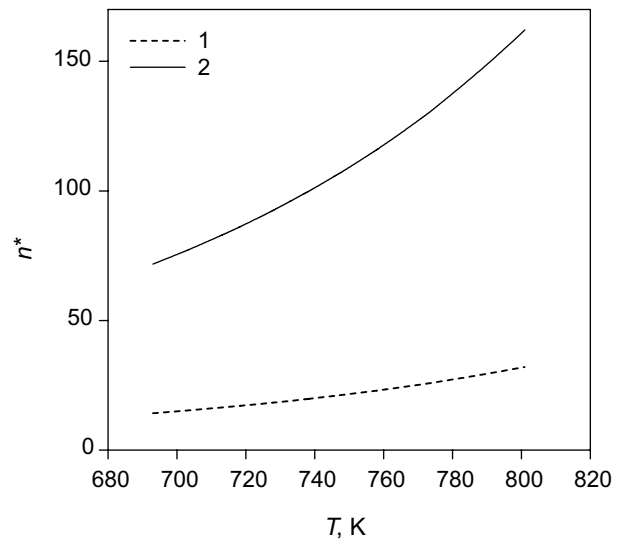


Fig. 3. Number of 'structural' units, $n^* \approx 4\pi R^{*3} N_A / 3V_M$ (see text), in the critical nucleus versus temperature. 1 – calculated with ΔG_{macro} and corresponding values of the surface energy; 2 – calculated by employing the coefficients P_1 , P_2 , and P_3 .

is determined with $\sigma = 0.058 + 0.129 \times 10^{-3} T$ (σ in J/m^2 , T in K) taken from Ref. [3] and ΔG_{macro} . The latter approximation leads to a size of the critical nucleus at T_g that corresponds to about five translations of the unit cell, while the use of the P_i parameters increases this size to about nine unit cells. The last value seems most reasonable.

Conclusion (ii) was already employed by us to estimate first the critical size and then σ_∞ and n^* . As mentioned above, the thermodynamic driving force for clusters of critical or near-critical sizes generally cannot be expected to be equal to the one for the corresponding macro-phases. According to computer simulations, a strong change of the bulk properties of critical clusters in dependence of their sizes is generally found [16]. This finding is confirmed by our conclusion (ii), according to which $\Delta G \approx 0.2 \Delta G_{\text{macro}}$ holds true.

One should recall that a similar conclusion was reached recently in Ref. [5], based on a comparison of the surface energies estimated by two independent methods. If ΔG_{macro} is used to estimate the driving force, the surface energy calculated from the growth rate of nuclei with near-critical size exceeds by about ten times the surface energy, which is calculated from a fit of nucleation rate via CNT. This discrepancy can be avoided by employing a value other than the macroscopic value of the thermodynamic driving force, i.e., a value reduced by a factor $0.19 < K < 0.23$ as compared with the macroscopic value.

This procedure also leads to a decrease in the value of surface energy to $0.05\text{--}0.06 \text{ J/m}^2$. Evidently, the value of the parameter $P_3 \approx 0.2$, obtained in the present work from a fit of W^* via CNT, is close to $0.19 < K < 0.23$,

in agreement with the estimate given in Ref. [5]. It should also be noted that the values of P_3 (or K) are average values referring to near-critical sized nuclei. It follows, from such considerations, that P_3 tends to unity when the critical nucleus size approaches macroscopic values. For such cases, which are usually not realized, the classical theory should work well, but this limiting case has never been tested.

5. Estimate of the elastic stresses effect on nucleation

A remarkable deviation of the $W^*(T)$ dependence (shown by open circles in Fig. 2) from the theoretical curve (shown by a dashed line in Fig. 2) is observed at temperatures below T_g . As mentioned earlier, this deviation can be interpreted as the result of the reduction of the thermodynamic driving force by elastic strains. These strains evolve in the course of the formation of the crystals owing to the difference between the melt and crystalline phase densities. Such a reduction of the driving force causes an increase of the thermodynamic barrier to nucleation. Therefore, the knowledge of the deviation of the respective dependencies of W^* versus T can be used to estimate the value of the elastic strain energy, G_{str} .

Let us specify the thermodynamic barrier calculated from the fit of I_{st} and t_{ind} via Eq. (5) by the subscript ‘exp’ and the one, calculated by Eqs. (2), (7) and (8) with values of P_1 , P_2 , and P_3 obtained from the high-temperature range, by the subscript ‘class’. We have then

$$W_{\text{exp}}^* = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G - G_{\text{str}})^2}, \quad (10)$$

$$W_{\text{class}}^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G^2}. \quad (11)$$

Eq. (10) reflects the fact that the thermodynamic driving force is diminished by some quantity identified by us with the elastic strain energy, while Eq. (11) neglects this effect. It is easy to show, e.g., Ref. [7], that W_{exp}^* and W_{class}^* are bound by the correlation:

$$\frac{W_{\text{class}}^*}{W_{\text{exp}}^*} = \left[1 - \frac{G_{\text{str}}}{\Delta G} \right]^2. \quad (12)$$

Hence, the elastic strain energy, G_{str} , can be determined immediately from Eq. (12) as:

$$G_{\text{str}} = \Delta G \left[1 - \left(\frac{W_{\text{class}}^*}{W_{\text{exp}}^*} \right)^{1/2} \right]. \quad (13)$$

The values of G_{str} calculated by Eq. (13) are shown as a function of temperature in Fig. 4. We will now check whether these results can be explained theoretically.

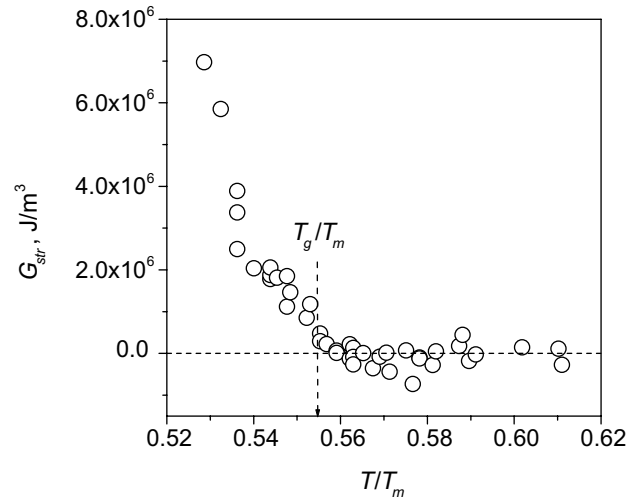


Fig. 4. Elastic strain energy versus reduced temperature calculated by Eq. (13).

In the case of a purely elastic solid, the elastic strain energy due to the formation of a unit volume of the newly evolving phase is given by [8]

$$G_{\text{str}}^0 = \frac{E_c E_m}{3[E_c(\gamma_m + 1) - 2E_m(2\gamma_c - 1)]} \zeta^2, \quad (14)$$

where E is Young’s modulus, γ is Poisson’s number and $\zeta = (\rho_c - \rho_m)/\rho_m$ is the relative density deviation between the melt and the crystal. The subscripts c and m indicate crystal and melt, respectively.

With Eq. (14), we obtain $G_{\text{str}}^0 = 22 \times 10^6 \text{ J/m}^3$ for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $64 \times 10^6 \text{ J/m}^3$ for $\text{Li}_2\text{O} \cdot \text{SiO}_2$ crystals in lithium disilicate glass. $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Li}_2\text{O} \cdot \text{SiO}_2$ crystals were chosen for this analysis because these phases are widely discussed in the literature as (possible) initially nucleated phases [1,4] in lithium disilicate glass. It appears, however, that these theoretical results are greater than the value of G_{str} determined via Eq. (13). This deviation can be explained as follows.

As the temperature approaches the glass transition range, glasses start to display viscoelastic properties. Thus, both the development and the relaxation of stress must be taken into account in order to estimate the real effect of elastic strain on the nucleation rate in glass-forming melts.

As shown in Ref. [7], a combination of these effects leads to

$$G_{\text{str}} = G_{\text{str}}^0 f(\theta), \quad (15)$$

where $f(\theta)$ is a monotonically decreasing function of

$$\theta = \frac{\tau}{\tau_{\text{rel}}}. \quad (16)$$

Here, τ is the average time interval required for the formation of a critical nucleus and τ_{rel} is the characteristic time of stress relaxation given by

$$\tau_{rel} = \frac{\eta(1 + \gamma)}{E}, \tag{17}$$

where η is the melt viscosity. The increasing effect of elastic stresses (the increase of G_{str}) with decreasing temperature can be attributed to the decrease of θ and the resulting increase of $f(\theta)$. If stress relaxation is described by the stretched exponent relaxation, the function $f(\theta)$ gets the form [7]

$$f(\theta) \cong \frac{1}{\theta} \int_0^\theta \exp \left\{ - \int_y^\theta \frac{dx}{1 + \frac{1}{q} x^p} \right\} dy, \quad q = 1 - p. \tag{18}$$

In the computations of Ref. [7], we have set $q = 0.65$. However, independently of such choice $f(\theta)$ is always less or equal to one.

Hence, as viscous relaxation must be accounted for, one always arrives at $G_{str} < G_{str}^0$. The abovementioned discrepancy can therefore be interpreted by stress relaxation. With a further decrease in temperature, the value of G_{str} can be expected to approach the value G_{str}^0 , which must be taken into account for a purely elastic solid.

Fig. 5 shows the effective thermodynamic driving force, $\Delta G = P_3 \Delta G_{macro} - G_{str}$, as a function of temperature. The unusual decrease of ΔG at low temperatures is caused by the increased effect of elastic strains. After G_{str} has reached values approaching G_{str}^0 , the effective thermodynamic driving force will increase again with a further decrease in temperature.

To estimate the value of θ and then of $f(\theta)$, τ has to be specified in Eq. (16). Alternatively, if the value of $\tau(T)$ is not known, it can be estimated approximately from $G_{str}(T)$ and G_{str}^0 obtained in the different ways described above. Here, $\theta(T)$ has to be calculated from Eq. (18), using the values $f(\theta) = G_{str}(T)/G_{str}^0$, and then $\tau(T)$ must be estimated employing Eqs. (16) and (17).

The values of τ obtained in this way are presented in Fig. 6. The upward and downward pointing triangles correspond to τ values calculated for $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot SiO_2$ crystals, respectively. The lower curve shows the temperature dependence of the relaxation time calculated by Eq. (17). The upper curve (indicated by open stars) shows the time-lag in nucleation, τ_{ns} . Taking into account our assumptions about the value of G_{str}^0 , we conclude that the resulting values of τ are quite close to τ_{ns} . This result corroborates the assumption made in [6,17], according to which τ has to be identified with τ_{ns} .

It is evident that $\tau(T)$ calculated with the value of G_{str}^0 for $Li_2O \cdot SiO_2$ crystals is slightly closer to $\tau_{ns}(T)$ than the one calculated using G_{str}^0 for $Li_2O \cdot 2SiO_2$ crystals. This result correlates with $P_3 < 1$, reflecting the fact that the properties of the nucleated phase are different to those of the $Li_2O \cdot 2SiO_2$ macro-phase. The slope of $\tau(T)$ differs from that of $\tau_{ns}(T)$. Possibly, this deviation is caused by an underestimation of the values of τ_{ns}

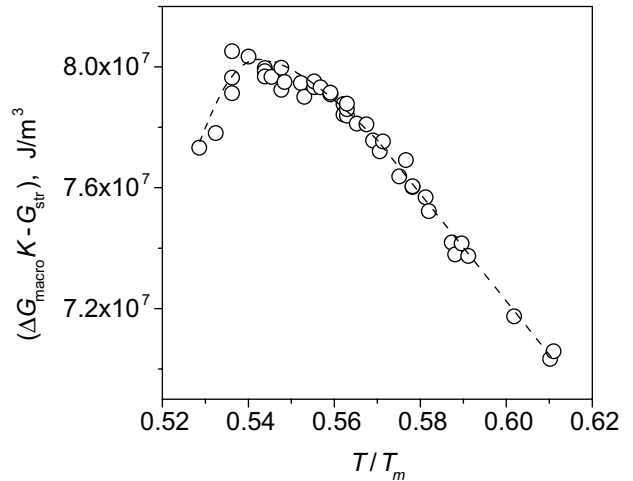


Fig. 5. Effective thermodynamic driving force versus reduced temperature. The dashed line is placed to guide the eyes.

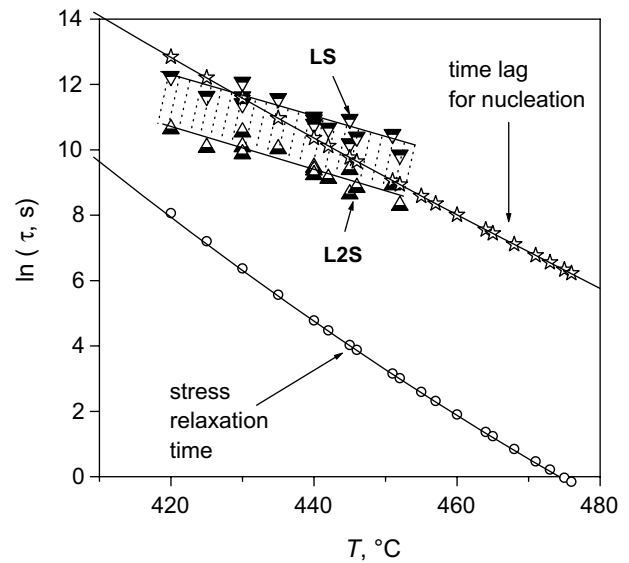


Fig. 6. Temperature dependencies of the stress relaxation time τ_{rel} (lower curve), and time τ calculated by Eqs. (15)–(18) with G_{str}^0 for $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot SiO_2$ crystals (up and down triangles correspondingly), and the time lag for nucleation τ_{ns} (stars). Lines are placed to guide the eyes.

and I_{st} at low temperatures. Therefore, we find that most of the data in the literature on nucleation at low temperatures (i.e., in the vicinity of T_g) require a careful re-examination employing, for example, the master curve ($N/I_{st}\tau_{ns}$ versus t/τ_{ns} , where N is the number of crystals nucleated at time t) derived by Collins and Kashchiev [18,19].

When analysing the data presented in Fig. 6, it is important to emphasize that the temperature dependence of $\tau_{rel}(T)$ is stronger than that of $\tau(T)$ (or $\tau_{ns}(T)$).

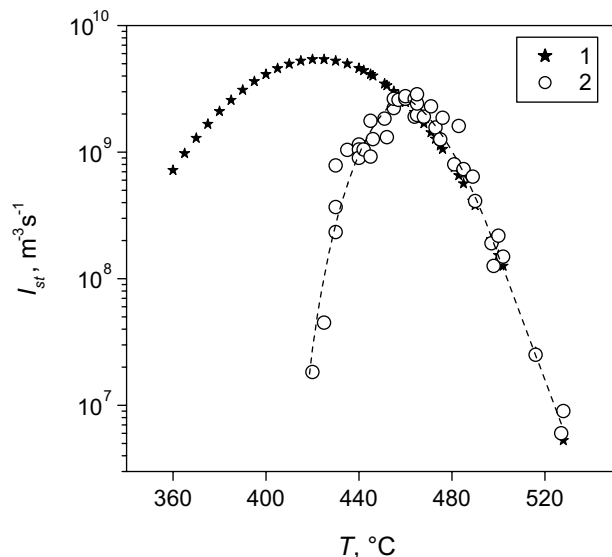


Fig. 7. Temperature dependence of the steady-state nucleation rate in lithium disilicate glass. 1 – calculated data with Eq. (5) for the case when elastic stresses do not play any role using P_i listed in last line of Table 1; 2 – experimental values. Dashed line is placed to guide the eyes.

This means that – at low temperatures, i.e., for $T < T_g$ – the process of stress development (due to critical nucleus formation) is not determined by viscous flow, as in the case of stress relaxation. We are thus likely confronted with decoupling phenomena [12], which result in a failure of the Stokes–Einstein equation at temperatures approaching T_g .

To illustrate the effects of elastic stress on nucleation, we calculated the $I_{st}(T)$ curve with Eq. (5) using the P_1 , P_2 , and P_3 parameters listed in Table 1, and extrapolated the induction period values. This curve, indicated in Fig. 7 by open stars, refers to the temperature dependence of the nucleation rate in cases where elastic stresses play no role. The open circles show experimental nucleation rate data. A comparison of experimental and calculated data shows that elastic stresses can considerably reduce the nucleation rate at low temperatures and shift the temperature of its maximum.

6. Discussion

In the present analysis, we consider two groups of results as particularly interesting for discussion. These results are: (i) the estimation of the thermodynamic properties of critical nuclei at relatively high temperatures, when the undercooled melt can be treated, to a first approximation, as a Newtonian liquid and (ii) the estimation of the effect of elastic strain on nucleation at low temperatures, when the melt reveals viscoelastic properties.

(i) According to the fit of the thermodynamic barrier values for nucleation calculated from experimental nucleation data, in the theoretical equation for W^* , both the bulk and surface properties of the critical nuclei deviate from the corresponding properties of the newly evolving macro-phase. As an initial result, the thermodynamic driving force for critical nucleus formation ends up being considerably lower than that measured for the respective macro-phase. Secondly, a simultaneous decrease of the surface energy as compared to the macroscopic values (usually employed in the classical nucleation theory) is found.

These results are corroborated by a new approach to estimate the work of critical nucleus formation, elaborated in detail in Refs. [20–22]. According to Ostwald’s generalized rule of stages formulated in Ref. [20], critical nuclei are characterized by bulk and interfacial properties that correspond to the minimal value of the thermodynamic barrier as compared with all the possible states of the critical cluster. This selection rule determines the properties of the critical clusters that nucleate first and, hence, determines the pathway of the transformation process.

One should note that, according to this approach, a minimum of the thermodynamic barrier to nucleation, and not necessarily a maximal thermodynamic driving force, is required for preferable nucleation. Hence, according to Ostwald’s generalized rule of stages, critical nuclei may have a composition, structure and properties unlike those of the macro-phase, corresponding to the final state of the phase transformation.

Further indirect experimental evidence exists supporting the above-mentioned findings. One piece of evidence is the substantial difference between the surface energies calculated from nucleation and growth rates [5]. Additional proof is given by a comparison of the values of the crystal/melt and melt/vapour surface energies. Moreover, a strong deviation between the compositions of critically sized crystals, macroscopic crystals, and the parent melt has been observed experimentally in the case of a $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glass [2]. The latter effect is apparently the reason why the application of kinetic coefficients and interfacial parameters derived from nucleation data for $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glass (parameters referring to critical nuclei), when utilized to determine macroscopic growth rates, lead to considerable differences between theory and experiment [23].

Thus, our findings indicate that, to apply the classical expression for the nucleation rate, the expression must be supplied with appropriate methods for estimating the thermodynamic driving force and surface energy for critical nuclei, being – as found here – considerably lower as compared to the respective macroscopic values.

(ii) In a previous paper [8], the effect of elastic stresses on nucleation in viscoelastic glass-forming melts was

analyzed within the framework of the original classical nucleation theory, i.e., macroscopic values of the thermodynamic driving force were applied. In contrast, lower driving force and surface energy values are employed in the present work. Accounting for this effect leads to an increase in the influence of elastic stress, since the main parameter for its estimation is the ratio between elastic stress energy and thermodynamic driving force. Indeed, we obtained a reduction of the nucleation rate at $T \sim 420$ °C (see Fig. 7) stronger than that in Ref. [8] by a factor of about two. It should also be noted that application of the corrected (diminished) values of both driving force and surface energy allows one to describe the minimum observed in the temperature dependence of the thermodynamic barrier, which was not achieved with the purely traditional approach [8]. This fact provides additional, indirect, evidence of the need to correct the properties of the critical nuclei, e.g. as performed here.

7. Conclusions

The thermodynamic driving force for the formation of critical nuclei and their specific surface energy are considerably lower than the respective quantities for the corresponding macro-phase. This fact has not been taken into account in previous analyses of crystal nucleation kinetics in glasses.

If, as suggested by different authors, at temperatures close to the glass transition, the effective diffusion coefficient (which is responsible for the rate of molecular aggregation) and the viscosity coefficient (which governs stress relaxation) are no longer connected by the Stokes–Einstein relation elastic strain evolves – owing to the difference between melt and crystal densities – and strongly suppresses nucleation. The value of elastic strain energy obtained from an analysis of the thermodynamic barrier to nucleation is in agreement with that estimated using measured values of the elastic constants of glass and crystal phases.

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