

On the thermodynamic driving force for interpretation of nucleation experiments

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ABSTRACT

According to the Classical Nucleation Theory (CNT), the volume and surface thermodynamic properties of the nuclei of a new (nucleating) phase are considered to be size independent and hence equal to the respective values of the corresponding macroscopic crystals. However, this assumption leads (if one also considers in addition σ as temperature independent) to a dramatic underestimation of steady-state nucleation rates. In this paper, we propose as a resolution of these problems that one should employ a value of the thermodynamic driving force that is equal to that for formation of macroscopic crystals, but reduced by a constant value. This approach leads to a considerable decrease in the thermodynamic barrier for nucleation. This choice of the thermodynamic driving force for the analysis of nucleation rate data employing the classical equation results in a self-consistent description that allows one not only to obtain the theoretically expected value of the size of the structural units and of the pre-exponential term in the steady-state nucleation rate equation, but also to obtain a more reliable (reduced) value of the crystal/melt interfacial energy than that estimated in the framework of currently utilized CNT approximations.

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1. Introduction

Despite new developments on the theoretical understanding and description of nucleation phenomena, crystal nucleation data are most often interpreted using the Classical Nucleation Theory (CNT) [1,2]. According to the CNT, the volume and surface thermodynamic properties of the nuclei of the new phase are considered to be *size independent* and equal to the respective values of the corresponding macroscopic crystals. This is why the thermodynamic driving force for growth of macro-crystals, ΔG_{vU} , and their specific interfacial energy, σ , are usually attributed to the (nano-sized) critical nuclei. Under this (strong) assumption the main parameters of CNT can, in principle, be independently determined. However, when comparing experimental results and theoretical predictions, it turns out that the mentioned assumption about the size independence of the cluster's properties leads to a dramatic *underestimation* of steady-state nucleation rates (if one also considers σ as temperature independent) [3]. The discrepancy between calculated and experimental values of nucleation rates can be removed if one assumes a slight increase of the specific interfacial energy with increasing temperature. Such increase can be interpreted as a consequence of the change of the critical nucleus size and hence its curvature with temperature [4]. However, if one tries to overcome the mentioned problem by only taking the size and temperature dependence of the interfacial energy into account, the

obtained values of the specific interfacial energy are very close to the experimental value for the respective (macroscopic) liquid/vapor interfacial energy. But this result is in conflict with Stefan's rule, which connects the specific interfacial energy with the enthalpy of the respective phase transformation [5] (in our case, with the melting/crystallization and evaporation/condensation enthalpies).

The main objective of the present analysis is to show that it is possible to resolve this serious problem of CNT in application to the interpretation of experimental data by keeping the specific interfacial energy temperature independent but utilizing for the determination of the parameters of the critical clusters a reduced thermodynamic driving force for nucleation as compared to that for macro-crystallization, by a constant, temperature independent value. As will be shown later, this procedure also leads to a reduction of the specific interfacial energy, leading to more realistic estimates of its value. This reduction of the thermodynamic driving force for nucleation can be qualitatively interpreted as a consequence of the difference in the bulk properties of critical (or near-critical) nuclei and the corresponding crystalline macro-phase. This finding is supported both by theoretical considerations [6–8] and experimental evidence [9–11].

The existence of such finite temperature independent correcting term can be quantitatively explained as follows. The range of significant (measurable) homogeneous nucleation rates corresponds to large under-coolings and is usually narrow. By this reason one can assume that the change of the thermodynamic driving force for the critical clusters as well as for the respective macroscopic phase is not high as compared with its mean value in the considered temperature

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range. In this case the constant difference between thermodynamic driving forces for critical clusters and macroscopic phase can be indeed expected.

In order to substantiate the above sketched approach, we start with a brief reconsideration of the classical expressions for the steady-state nucleation and growth rates. Both nucleation and growth rates are determined, at least partly, by the effective diffusion coefficients. In the analysis of experimental nucleation rates for some chosen glasses we use two different ways to estimate the diffusion coefficient from experimental data: (i) via the crystal growth rate and (ii) via the time-lag for nucleation. In the first case, we assume that the effective diffusion coefficients determining the rate of aggregation are independent of cluster sizes and, hence, they must be equal for the nucleation (nano-sized clusters) and growth (micron-sized clusters) processes, i.e., we employ the values of the diffusion coefficients measured for aggregates of macroscopic sizes also for the description of nucleation. The second way to estimate the diffusion coefficient – via time-lag data – does not have the above-mentioned limitation and is commonly employed in studies of nucleation phenomena.

As will be shown, by taking into account the change of the driving force, we can not only reconcile experimental data and calculated values for the nucleation rate, but we may also obtain reasonable estimates for the effective size of the basic building units that participate in the formation of the crystalline phase.

2. Basic equations and methods of determination of the effective diffusion coefficients

2.1. Determination via macroscopic growth rates

The steady-state nucleation rate can be written as [1,2]

$$I_{st} = D_I \frac{1}{d_{ol}^4} \sqrt{\frac{\sigma}{kT}} \exp\left(-\frac{W_*}{kT}\right), \quad (1)$$

where

$$W_* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_{vl}^2} \quad (2)$$

is the so-called thermodynamic barrier for nucleation or the work of critical cluster formation. W_* is determined by the specific surface energy of the interface between critical nucleus and surrounding liquid, σ , and the thermodynamic driving force for nucleation, ΔG_{vl} . The latter quantity is the difference of the Gibbs free energy between the liquid and crystal phase per unit volume of the melt. In Eq. (2), σ and ΔG_{vl} are considered as size independent. D_I is the effective diffusion coefficient determining the rate of aggregation of new structural units to the critical cluster via the nucleus/liquid interface, and d_{ol} is the characteristic diameter of the structural units of melt. The subscripts “I” (for nucleation) and “U” (for growth) in some of the quantities are added to specify that the respective parameters may have different values for nucleation and growth kinetics, respectively [10].

For the most typical Normal growth and Screw Dislocation growth models, the crystal growth rate, U , can be written in the following form [1,2]

$$U = D_U f \frac{1}{4d_{oU}} \left[1 - \exp\left(-\frac{\Delta\mu}{kT}\right) \right], \quad (3)$$

where D_U is the effective diffusion coefficient determining the rate of aggregation of structural units with size d_{oU} to the crystal/liquid interface, and $f < 1$ is a dimensionless parameter having different values for different growth models. For the Normal growth mechanism, which we shall assume in the present analysis to govern the

growth, f is about one. $\Delta\mu$ is the difference in the chemical potentials per structural unit of liquid and crystalline phases. $\Delta\mu$ is connected with the thermodynamic driving force for growth of macro-crystals, ΔG_{vU} , by

$$\Delta\mu = \Delta G_{vU} \frac{d_{oU}^3}{2}. \quad (4)$$

In the general case, the diffusion coefficient governing growth and the diffusion coefficient governing nucleation are expected to be different. Such difference could be caused by possible disagreement in the composition of critical nucleus and the evolving macro-crystals, or by the variation of the properties of the interface with crystal size. The problem, whether such variations take place or not and which kind of variations occurs, must be analyzed separately. If one supposes that the relationship

$$D_U = D_I \quad (5)$$

holds, then the combination of Eqs. (1) and (3) leads to the following equation

$$\frac{I}{U} \frac{T^{1/2}}{4} f \left[1 - \exp\left(-\frac{\Delta\mu}{kT}\right) \right] = \sqrt{\frac{\sigma}{k}} d_{oU} \frac{1}{d_{ol}^4} \exp\left(-\frac{W_*}{kT}\right) \quad (6)$$

or, equivalently, to

$$\ln \left\{ \frac{I}{U} \frac{T^{1/2}}{4} f \left[1 - \exp\left(-\frac{\Delta\mu}{kT}\right) \right] \right\} = \ln \left(\sqrt{\frac{\sigma}{k}} d_{oU} \right) - 4 \ln(d_{ol}) - \frac{16\pi}{3k} \sigma^3 \frac{1}{\Delta G_{vl}^2 T}. \quad (7)$$

By knowing the left hand side of Eq. (7) as a function of temperature and the size parameter d_{oU} (that governs the growth of macro-crystals), one can plot the left hand side of Eq. (7) versus $1/\Delta G_{vl}^2 T$ and estimate d_{ol} and σ from the intersection of the linear fit with the ordinate axis and the slope, respectively. In such procedure, a constant specific interfacial energy has to be assumed. Then the value of d_{ol} obtained in such computation can be used for testing CNT because d_{ol} determines to a large extent the pre-exponential term I_o in the equation for steady-state nucleation rate. This equation can be written in the following simple form

$$I = I_o \exp\left(-\frac{W_* + \Delta G_D}{kT}\right), \quad (8)$$

where ΔG_D is the activation free energy of diffusion, the so called kinetic barrier for nucleation and

$$I_o \approx \frac{2}{d_{ol}^3} \frac{kT}{h}. \quad (9)$$

The value of I_o for nucleation of a solid phase in under-cooled liquids varies from 10^{41} to $10^{43} \text{ m}^{-3} \text{ s}^{-1}$ [1]. In more precise expressions for the nucleation rate the pre-exponential term differs by not more than one order of magnitude. Thus, our test of CNT consists in the analysis of the value of the size of the basic structural units d_{ol} estimated via Eq. (7). Such test is equivalent to a comparison of I_o estimated from experimental nucleation data and theoretically calculated values of I_o .

2.2. Determination via time-lag data

Another way to analyze nucleation rates is based on values of the diffusion coefficient D_I estimated from experimental data of nucleation time-lag. This way is basically correct since the same diffusion coefficient should determine steady-state nucleation rates and time-lags for nucleation. Hence, here there is no need to assume the validity

of Eq. (5). According to [12,13], the time-lag for critical cluster formation can be written as

$$\tau_{s-s} = \frac{80}{3} \frac{kT\sigma}{\Delta G_{vl}^2 d_{ol}^2 D_l} \quad (10)$$

Combining Eqs. (1) and (10) one obtains

$$I = \frac{80}{3} \frac{\sqrt{kT}\sigma^{3/2}}{\Delta G_{vl}^2 d_{ol}^6 \tau_{s-s}} \exp\left(-\frac{W_*}{kT}\right) \quad (11)$$

or

$$\ln\left(\frac{I\tau_{s-s}\Delta G_{vl}^2}{T^{1/2}}\right) = \ln\left(\frac{80}{3}k^{1/2}\sigma^{3/2}d_{ol}^{-6}\right) - \frac{16\pi\sigma^3}{3k} \frac{1}{\Delta G_{vl}^2 T} \quad (12)$$

Similar to Eq. (7), Eq. (12) allows one to estimate the size parameter d_{ol} together with σ if the thermodynamic driving force for nucleation is known. The choice of the σ -value in the first term of the right-hand side of Eq. (12), as in the case of Eq. (7), practically does not affect the result.

3. Method of calculation and applications

3.1. Method of computation

It follows from the above considerations that the main problem for the application of Eqs. (7) and (12) to the analysis of nucleation experiments consists in the correct determination of the thermodynamic driving force, which in turn determines the value of the specific interfacial energy. Indeed, according to Gibbs's classical theory, the work of critical cluster formation can be written as

$$W_* = \frac{1}{3}4\pi R_c^2 \sigma, \quad (13)$$

$$R_c = \frac{2\sigma}{\Delta G_{vl}}$$

where R_c is the critical size. Eq. (13), directly results from Eq. (2).

The thermodynamic driving force of nucleation is the difference between the free energies of an equivalent of the critical size amount of the liquid and critical-sized nucleus. In the classical approach, it is assumed that the bulk properties of the nano-sized clusters are equal to the respective parameters of the macroscopic phase. Consequently, the problem of determination of the driving force for nucleation and growth is in such approach actually reduced to the determination of thermodynamic properties of the macroscopic liquid and crystalline phases as a function of under-cooling.

Commonly, deviations between theory and experiment are attempted to be removed by the introduction of a curvature or size-dependence of the specific interfacial energy, e.g., via an expansion of the form [14,15]

$$\sigma(R_c) = \sigma_\infty \left(1 + \sigma_1/R_c + \sigma_2/R_c^2 + \dots\right), \quad (14)$$

where the coefficients in the expansion may depend on pressure and temperature, but not on curvature. To a first approximation, Eq. (14) gives a Tolman-like correction. However, as it turns out, in a number of systems the Tolman correction may be too small [14,15] and the curvature dependence of the interfacial energy is governed not by the first, but by the second term in the expansion, as was shown e.g. for regular solutions [16,17]. In such cases, Eqs. (13) and (14) yield

$$W_* = W_*^{CNT} + \sigma_\infty \frac{4\pi}{3} \sigma_2 \quad (15)$$

resulting in a nearly constant correction (reduction) to the classical value of the work of critical cluster formation (where the capillarity approximation is involved) [18].

Employing the concept of a temperature dependent interfacial tension, a number of problems arise, however. Possible ways of resolution of these problems are discussed in detail in Refs. [11,19], however, they are far from being convincing. By this reason, the formulation of alternative approaches to reconcile theory and experiment is highly desirable. One of them, which we are going to analyze here, consists of the introduction of a size-dependence not only of the specific interfacial energy but also of the driving force for cluster nucleation and growth [6–8,10].

Indeed, it has been frequently discussed whether the parameters of the critical clusters are similar, in general, to the parameters of the evolving macroscopic phases or not. Assuming that the critical clusters have different bulk properties (structure, density and/or composition) as compared with the newly evolving macroscopic phases, then one can explain drastic discrepancies between experimental and theoretically expected values of the pre-exponential factor I_0 and some other striking examples of failure of the CNT for a quantitative interpretation of experimental data in two ways: either as the formation of a small aggregate with properties of a phase which may exist, at least, in a metastable form also for macroscopic systems or, in a more general approach, to consider the bulk state of critical clusters as transient states which may not be realized at all in macroscopic form. In both cases, the evolution to the new phase will follow these alternative evolution paths, as a rule, only if the work of critical cluster formation is smaller as compared with the values corresponding to the formation of similar aggregates with properties of the newly evolving macroscopic phase.

The thermodynamic driving force for growth processes, ΔG_{vU} , on the other hand, is equal to the driving force of formation of a unit volume of the evolving macroscopic phase. Substituting this value into the expression for the work of critical cluster formation would imply that one neglects possible changes of the state parameters of the critical clusters. As was shown recently [7], such neglect leads, as a rule, to an overestimation of the work of critical cluster formation. By this reason, we can state that the account of changes of the cluster properties results in a decrease of the work of critical cluster formation as compared with the respective value obtained by classical theory (involving the capillarity approximation).

Since calorimetric data are only available for the calculation of the thermodynamic driving force for crystallization of the most stable phase, ΔG_{vU} , the thermodynamic driving force for other thermodynamically possible phases, and particularly for the nucleating phase, is not known but must be smaller than ΔG_{vU} . To take into account in the present analysis the possible deviation of the properties of the nucleating phase from the most stable phase we suppose that the following relationship holds between ΔG_{vl} and ΔG_{vU} .

$$\Delta G_{vl} = \Delta G_{vU} - \Delta G, \quad (16)$$

where it is assumed that ΔG has some constant value in the temperature range where nucleation processes are experimentally observed. This situation is sketched in Fig. 1. Then, analyzing Eqs. (7) and (12), we will use ΔG as a fitting parameter and determine it in such a way that a reasonable value of d_{ol} and, hence, the expected value of I_0 is obtained.

3.2. Application to $Li_2O \cdot 2SiO_2$ glass

In Ref. [20] we have shown that if one employs the thermodynamic driving force for crystallization of macroscopic lithium disilicate (the most stable phase), the value of D_l (estimated from nucleation time-lag data) considerably differs from D_U (estimated from macroscopic crystal growth rates). By analyzing those results we concluded that

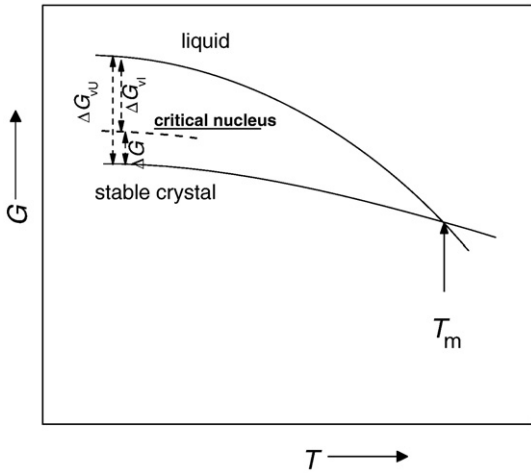


Fig. 1. Hypothetical Gibbs free energy of liquid, metastable or transient (representing the critical nucleus) and stable crystalline phases versus temperature.

the composition and/or structure of the critical clusters deviate from that of lithium disilicate crystal and, therefore, the thermodynamic driving force for critical cluster formation should be smaller than the driving force for macroscopic crystal growth. This reduction could be estimated only for the special case when $D_l = D_U$ holds, i.e. for the case when D_l is not strongly affected by the composition of the critical nucleus or if the critical nucleus is a polymorphic form of the stable lithium disilicate. For this special case of lithium disilicate glass, we analyzed nucleation and growth rates measured in the same temperature interval via Eq. (7) assuming the Normal growth mechanism ($f = 1$) and a temperature independent interfacial energy. One should recall that Eq. (7) was derived with the condition that Eq. (5) is valid. A plot of the left-hand side of Eq. (7) versus $1/((\Delta G_{vU} - \Delta G)^2 T)$ was approximated by a linear function as shown in Fig. 2 (we excluded temperatures below the nucleation rate maximum at which, as shown in [11,21], elastic stresses result in a decrease of thermodynamic driving force for nucleation and hence of the nucleation rate). The intersection of this straight line with the ordinate allows us to estimate d_{ol} , and by its slope, the specific interfacial energy, σ . By this procedure we employed in the first term on the right-hand side of Eq. (7) the following estimated values: $\sigma = 0.2 \text{ J/m}^2$ and $d_{oU} = 5.88 \times 10^{-10} \text{ m}$ evaluated as $d_{oU} = \sqrt[3]{2 \frac{V_M}{N_A}}$, where V_M is molar volume, N_A is Avogadro's number. A similar procedure with σ was

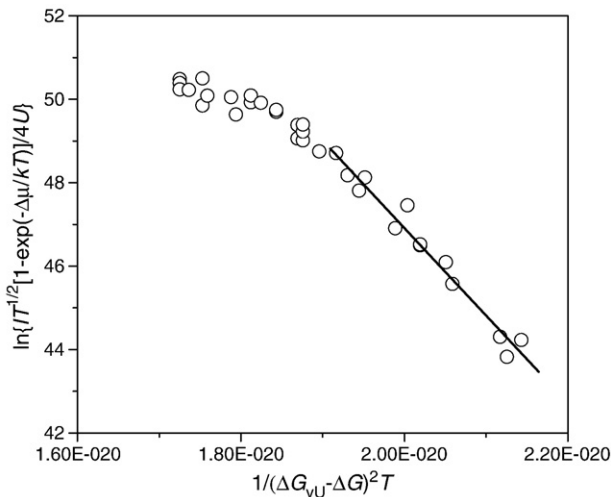


Fig. 2. Plot of $\ln \{I_{st} T^{1/2} [1 - \exp(-\Delta\mu/kT)] / 4U\}$ versus $1 / (\Delta G_{vU} - \Delta G)^2 T$ for lithium disilicate glass, where $\Delta G = 1.3 \cdot 10^8 \text{ J/m}^3$.

also employed in the application of Eq. (12), when D_l was determined via nucleation time-lag data.

Figs. 3 and 4 show the results of calculations obtained by these two different ways (via Eqs. (7) and (12)). As it is evident, the values of d_{ol} and σ depend on the value of the correction term ΔG . If we set $\Delta G = 0$, supposing that the difference of the bulk properties of the clusters and the respective macroscopic phase is equal to zero, i.e. that $\Delta G_{vU} = \Delta G_{vU}$ holds, the values of d_{ol} estimated via Eqs. (7) and (12) are equal to $6 \times 10^{-4} \text{ \AA}$ and $4 \times 10^{-4} \text{ \AA}$, respectively (see Table 1). Such sizes of structural units do not have any physical meaning. They correspond to a value of $I_0 \approx 10^{63} \text{ m}^{-3} \text{ s}^{-1}$, while the theoretically expected value of I_0 is about $10^{41} - 10^{43} \text{ m}^{-3} \text{ s}^{-1}$. To resolve this problem, finite values of ΔG must be assumed.

According to Figs. 3 and 4 the reduction of ΔG_{vU} by ΔG leads to an increase of d_{ol} and to a decrease of σ . Since realistic values of d_{ol} almost do not differ from that of d_{oU} , we employ the latter (see horizontal dotted line in Fig. 3) to estimate the proper values of ΔG corresponding to $d_{ol} = 5.88 \text{ \AA}$. It is seen that a significant decrease of ΔG_{vU} (by 1.28×10^8 or by $1.78 \times 10^8 \text{ J/m}^3$) leads to an increase of d_{ol} from $4 \times 10^{-4} \text{ \AA}$ to 5.88 \AA , the latter value corresponds to $I_0 = 1.4 \times 10^{41} \text{ m}^{-3} \text{ s}^{-1}$. The average value of ΔG_{vU} in the considered temperature range is about $3.85 \times 10^8 \text{ J/m}^3$. Hence, in order to arrive at a self-consistent description of the crystallization process, the thermodynamic driving force for the nucleating phase must be significantly lower than that of the stable macroscopic phase. This result qualitatively corroborates the conclusions previously derived in Refs. [11,20,22] based on the analysis of other independent experiments, where the reduction of the thermodynamic driving force for nucleation was performed via the introduction of a coefficient smaller than one.

The reduction of the thermodynamic driving force by ΔG , corresponding to $d_{ol} = 5.88 \text{ \AA}$, leads to a decrease of the specific interfacial energy (see Fig. 4) from about 0.20 J/m^2 ($\Delta G = 0$) to 0.12 and 0.10 J/m^2 estimated via Eqs. (7) and (12), respectively. One should recall that these values of interfacial energy refer to critical-sized nuclei. Therefore for comparison with the surface energy of planar liquid/vapor interfaces one has to recalculate their value, e.g. via Tolman's equation. The value 0.20 J/m^2 recalculated in such a way is lower than the experimental value of the specific interfacial energy of a planar liquid/vapor interface only by a factor of 0.8 and seems to strongly overestimate its real magnitude (see more details in Ref.

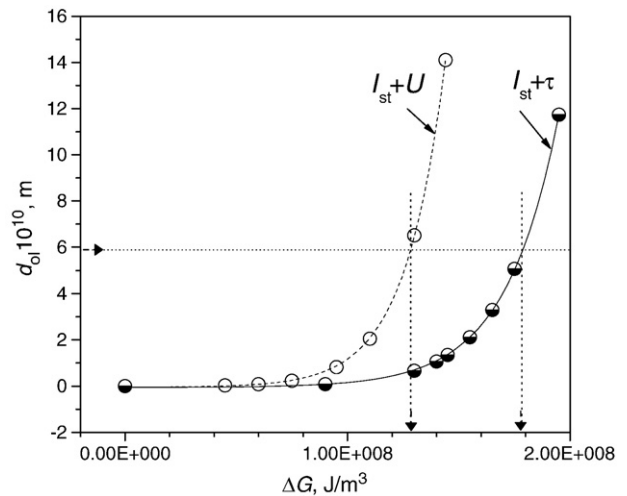


Fig. 3. Size parameter for nucleation d_{ol} as a function of the difference between thermodynamic driving force for formation of the stable crystalline phase (lithium disilicate) and that of the critical crystal. The dotted horizontal line corresponds to $d_{ol} = 5.88 \times 10^{-10} \text{ m}$. The plots on the left and right hands correspond to analyses using the growth rate (given by Eq. (7)) and time-lag for nucleation (given by Eq. (12)), respectively.

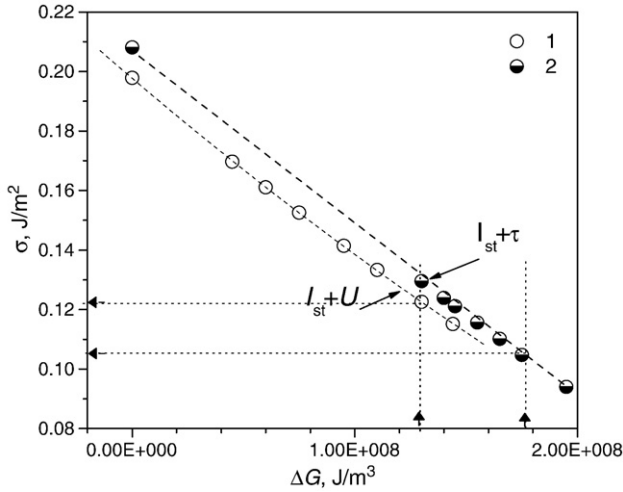


Fig. 4. Specific interfacial energy as a function of the difference between thermodynamic driving force for formation of the stable crystalline phase (lithium disilicate) and that of the critical nucleus. The horizontal dotted lines show the values of σ corresponding to the values of ΔG using $d_{ol} = 5.88 \times 10^{-10}$ m (see Fig. 3). 1 – calculated by Eq. (7); 2 – calculated by Eq. (12).

[22]). Thus a decrease of the specific interfacial energy by a factor of about 2 due to the reduction of the thermodynamic driving force is reasonable.

A combination of the reduction of the thermodynamic driving force by ΔG with the corresponding reduction of the critical nucleus/liquid interfacial energy results in a strong decrease of the thermodynamic barrier for nucleation as compared with that obtained by the classical theory employing the assumption that the properties of the newly evolving phase do not depend on its size. These results are illustrated on Fig. 5. It should be noted that the difference between the corrected thermodynamic barrier, W , and the classical, W^{CNT} , corresponding to $\Delta G = 0$ practically does not depend on temperature. That is, we arrived at a result that could be obtained when only the specific interface energy is changed in a way indicated by Eq. (14).

3.3. Application to $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass

As shown in Refs. [9,23], the formation of crystals of stoichiometric composition $Na_2O \cdot 2CaO \cdot 3SiO_2$ ($N_1C_2S_3$) in a glass of the same composition occurs via nucleation of a solid solution, which is enriched in sodium, with a composition close to $Na_2O \cdot CaO \cdot 2SiO_2$ ($N_1C_1S_2$). But this shifted composition remains more or less constant during the initial stage of the phase transformation to which crystal

Table 1
Some parameters employed in the computations shown in Figs. 3 and 6.

$\Delta G, J/m^3$	$d_{ol} 10^{10}, m$	$\sigma, J/m^2$
<i>Li₂O2SiO₂</i>		
<i>I_{st}</i> and <i>U</i> ; $d_{oU} = 5.88, d_{ol}$		
0	6.09483E-4	0.198
1.3E8	5.88	0.122
<i>I_{st}</i> and τ ; d_{ol}		
0	4.02031E-4	0.208
1.78E8	5.88	0.105
<i>Na₂O2CaO3SiO₂</i>		
<i>I_{st}</i> and <i>U</i> ; $d_{ol} = d_{oU}$		
0	2.5841E-14	0.162
1.075E8	7.35	0.064
<i>I_{st}</i> and τ ; $d_{ol} = d_{oU}$		
0	3.08882E-13	0.190
1.37E8	7.35	0.050

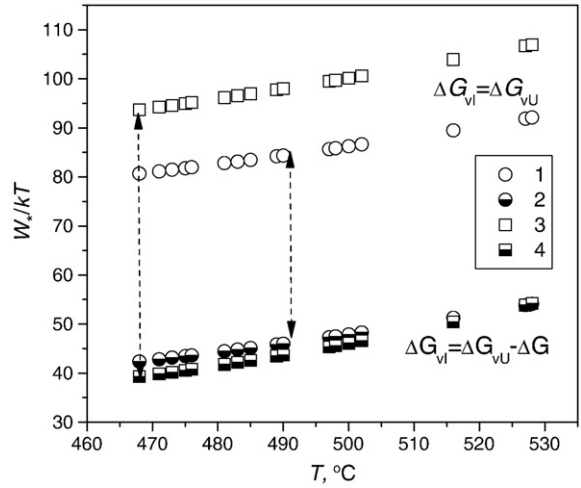


Fig. 5. Reduced thermodynamic barrier for nucleation, (W_v/kT), versus temperature estimated at $\Delta G_{vl} = \Delta G_{vl}$ ($\Delta G = 0$) (1, 3) and $\Delta G_{vl} = \Delta G_{vl} - \Delta G$, (ΔG corresponds to $d_o = 5.88 \times 10^{-10}$ m) (2,4). Curves 1, 2 and 3, 4 are obtained employing σ estimated from an analysis of Eqs. (7) and (12), respectively.

growth measurements commonly refer. This experimental fact implies that the growth rate refers to crystals with a similar composition as the critical crystals and those both nucleating and growing crystals differ from those of the stable phase. Hence, in this case, it can be assumed that the application of Eq. (7) is more founded than in the case of lithium disilicate glass. Taking into account these features of $N_1C_2S_3$ glass crystallization, we can rewrite for this system Eq. (16) as

$$\Delta G_{vl} = \Delta G_{vU} = \Delta G_v - \Delta G, \tag{17}$$

where ΔG_v is the thermodynamic driving force estimated via melting enthalpy and difference in the specific heats of $N_1C_2S_3$ crystals and the liquid of the same composition (in the case of lithium disilicate glass, $\Delta G_{vU} \equiv \Delta G_v$ holds). Also we can expect that

$$d_{oU} = d_{ol} \equiv d_o \tag{18}$$

is fulfilled. Thus, for the case considered Eqs. (4) and (7) can be rewritten as

$$\Delta \mu = (\Delta G_v - \Delta G) \frac{d_o^3}{2} \tag{19}$$

$$\ln \left\{ \frac{1}{U} T^{1/2} f \left[1 - \exp \left(- \frac{\Delta \mu}{kT} \right) \right] \right\} = \ln \left(\sqrt{\frac{\sigma}{k}} \right) - 3 \ln(d_o) - \frac{16\pi}{3k} \sigma^3 \frac{1}{(\Delta G_v - \Delta G)^2 T} \tag{20}$$

Eq. (12) remains valid in the case of $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass since it does not include the parameters referring to the crystal growth stage.

Figs. 6 and 7 show the results of computations of the parameters d_o and σ , respectively, versus ΔG . As in the case of lithium disilicate glass, the values of d_o obtained with $\Delta G = 0$ (i.e. with $\Delta G_{vl} = \Delta G_{vU} = \Delta G_v$) are extremely small, equal to 1×10^{-10} Å and 3×10^{-13} Å, employing Eqs. (20) and (12) for their determination, respectively. The horizontal dotted line in Fig. 6 marks the value $d_o = 7.35$ Å corresponding to $N_1C_1S_2$, i.e. to the nucleating phase and to the crystals for which the crystal growth measurements were performed. Intersections with this dotted line correspond to the values of ΔG required to obtain $d_o = 7.35$ Å and a reasonable value of $I_o = 5 \times 10^{41} m^{-3} s^{-1}$. These values of ΔG (1.1×10^8 and $1.4 \times 10^8 J/m^3$) are comparable to ΔG_v

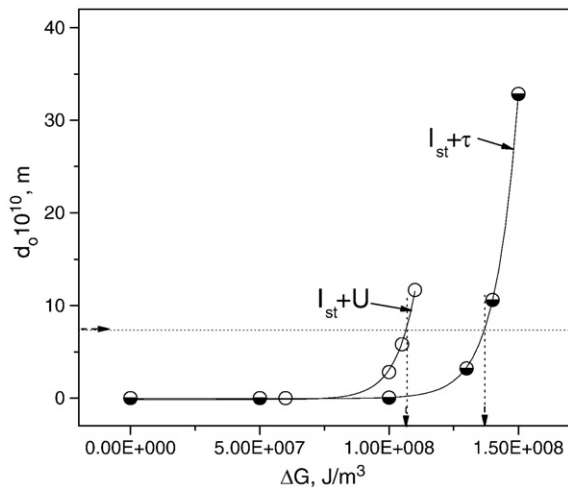


Fig. 6. Size parameter for nucleation, d_0 , as a function of the difference between thermodynamic driving force for formation of the stable crystalline phase $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ and that of the critical crystal being a solid solution. The dotted horizontal line corresponds to $d_0 = 7.35 \times 10^{-10}$ m. The plots on the left and right hand correspond to results of analyses employing the growth rate (Eq. (20) and time-lag for nucleation (Eq. (12), respectively.

whose average value in the considered temperature range is about 2×10^8 J/m³. The reduction of the thermodynamic driving force by ΔG also leads to a decrease of specific interfacial energy (see Fig. 7) and to a strong decrease of the thermodynamic barrier for nucleation. Fig. 8 shows the values of the thermodynamic barrier versus temperature estimated for $\Delta G = 0$ (classical approach) and for ΔG equal to 1.1×10^8 and 1.4×10^8 J/m³, respectively, which correspond to $d_0 = 7.35$ Å ($I_0 = 5 \times 10^{41}$ m⁻³ s⁻¹).

4. Discussion

The analysis of the nucleation-growth kinetics performed for two model glasses of stoichiometric compositions, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$, but that undergo a quite different course of phase transformation, yields quantitatively similar results. The analysis of the results shows that the assignment to the critical nuclei of a strongly reduced value of the thermodynamic driving force (as compared with the value governing growth of stable

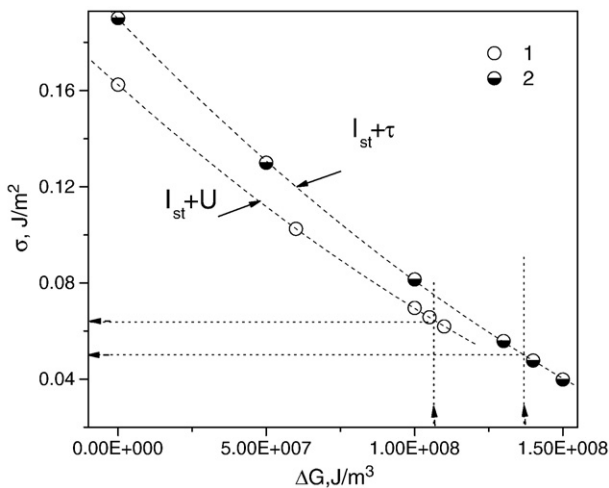


Fig. 7. Specific interfacial energy as a function of the difference between the thermodynamic driving force for formation of the stable crystalline phase ($\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$) and that of the critical nucleus. The horizontal dotted lines show the values of σ corresponding to the values of ΔG using $d_0 = 7.35 \times 10^{-10}$ m (see Fig. 6). 1 – calculated by Eq. (20); 2 – calculated by Eq. (12).

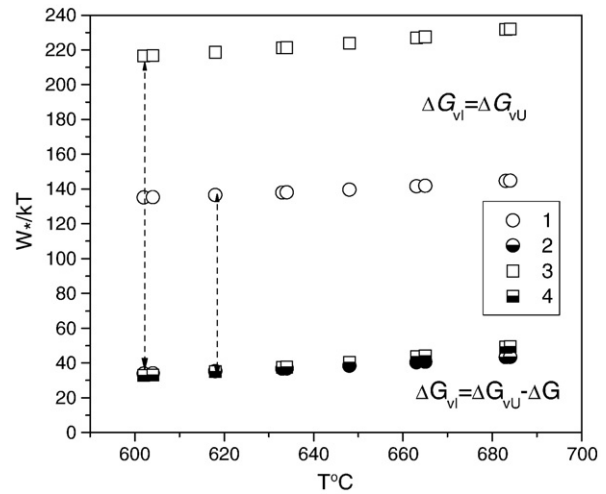


Fig. 8. Reduced thermodynamic barrier for nucleation, (W^*/kT) , versus temperature estimated at $\Delta G_{vl} = \Delta G_{vU} = \Delta G_v$ ($\Delta G = 0$) (1, 3) and $\Delta G_{vl} = \Delta G_{vU} = \Delta G_v - \Delta G$, (ΔG corresponds to $d_0 = 7.35 \times 10^{-10}$ m) (2,4). Curves 1, 2 and 3, 4 are obtained employing σ estimated from the analysis of Eqs. (20) and (12), respectively.

macroscopic crystals used in CNT) by a constant value, leads to the theoretically expected value of the pre-exponential term in equation for the steady-state nucleation rate. This pre-exponential value together with the reduced thermodynamic barrier for nucleation – due to the simultaneous decrease of the thermodynamic driving force and specific surface energy – allows one to quantitatively describe the nucleation rate curve. Two independent approaches to estimate the diffusion coefficient were employed in the present analysis leading to qualitatively similar results.

Proceeding in such way, we obtain a self-consistent picture of the nucleation-growth process and the set of parameters, governing them, i.e. the thermodynamic driving force for critical nucleus formation and the surface energy. The results correspond to the theoretically expected value of I_0 and experimental values of steady-state nucleation rates. Moreover, this procedure results in a reduction of specific interface energy making its value more reliable, while the consideration only of its size-dependence does not resolve this problem.

Despite that the present analysis was performed only for two silicate glasses, it seems that the reduction of the thermodynamic driving force for nucleation could resolve the discrepancy between the theoretically expected and experimental nucleation rates which arises in the analysis of nucleation data for many other glasses. The conclusions about size-dependent volume and surface properties of the critical nuclei agree with the generalized Gibbs approach to the description not only of nucleation but also of growth and dissolution processes taking into account changes of the bulk and surface state parameters of clusters as a function of supersaturation and size [10,24,25].

Finally, it should be noted that in the present analysis the way used for the reduction of the thermodynamic driving force is of vital importance. The correction of the thermodynamic driving force simply by multiplying it by some coefficient $K < 1$ – as it was performed in Refs. [20,22] – does not result into a consistent description (compare the solid and dotted curves in Fig. 9), while the decrease of ΔG_{vU} by a constant value (dashed line) causes a strong reduction of the point of intersection with the ordinate and, hence, increases the parameter d_0 . It should be noted that the use of the latter way to reduce the thermodynamic driving force in methods proposed in [20,22] to describe the experimental nucleation and growth data does not change the main results of above papers.

Thus it is likely that the reduction of the thermodynamic driving force by a temperature independent value ($\Delta G_{vU} - \Delta G$) is more

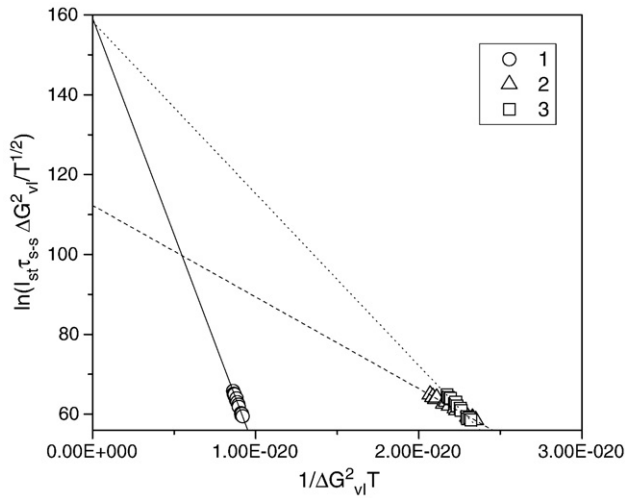


Fig. 9. Plots $\ln(I_{st}\tau_{s-s}\Delta G_{vl}^2/T^{1/2})$ versus $1/\Delta G_{vl}^2T$ for lithium disilicate glass at different sets of thermodynamic driving force for nucleation. 1 – $\Delta G_{vl} = \Delta G_{vl}$; 2 – $\Delta G_{vl} = \Delta G_{vl} - 1.4 \times 10^8$ J/m³; 3 – $\Delta G_{vl} = \Delta G_{vl} \cdot 0.63$. The reduction of thermodynamic driving force for curve 2 is close to that for curve 3. The lines are linear fits.

appropriate than the reduction by some coefficient $K < 1$ ($K\Delta G_{vl}$), at least, in the relative narrow temperature interval where measurable nucleation rates are found in experiment.

5. Conclusions

In the analysis of nucleation rate data utilizing the classical equations (CNT), we propose that one should employ a value of the thermodynamic driving force that is equal to that for formation of macroscopic crystals, but reduced by a constant value, ΔG . This new approach (using a reduced thermodynamic driving force) leads to a considerable decrease in the thermodynamic barrier for nucleation. In addition, a proper choice of ΔG results in a quantitatively self-consistent description that allows one not only to obtain the theoretically expected value of the size of the structural units and of the pre-exponential term in the steady-state nucleation rate equation, but also to obtain a more reliable (reduced) value of the crystal/melt interfacial energy than that estimated in the framework of current CNT approximations. This procedure allows one to arrive at a self-consistent qualitatively correct description not only of the steady-state nucleation rate curve but also of a variety of other parameters

describing the critical clusters and, hence, gives an indirect evidence for the existence of a difference between the properties of the critical nuclei and the evolving macro-phase.

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