Crystal nucleation in glass-forming liquids: Variation of the size of the “structural units” with temperature

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The description of crystal nucleation rates in supercooled liquids in the framework of the classical nucleation theory (CNT) fails if one uses a fixed size of “structural units”. To reconcile the experimental data and CNT, we assumed an increase of the size of the structural units that control nucleation with decreasing temperature for temperatures below the nucleation rate maximum, \( T < T_{\text{max}} \). This hypothesis was tested for several glass-forming liquids, where crystal formation proceeds by bulk homogeneous nucleation. It can explain the temperature dependence of the nucleation rate in the range \( T < T_{\text{max}} \) where the description of nucleation rate by CNT drastically fails. The size of the structural units can be related either to the size of the cooperatively rearranging regions (CRR) or to an effective size parameter, accounting for corrections in the theoretical treatment of the kinetics of aggregation in multi-component systems via a quasi-one-dimensional description.

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1. Introduction

Crystal nucleation and growth in supercooled liquids are key phenomena in materials science, especially in glass science and engineering, because they control glass formation and the development and production of glass-ceramics [1]. Therefore, these processes have been intensively studied experimentally and theoretically in recent decades, especially for glass-forming liquids. Fortunately, due to their high viscosity, which results in relatively slow (easily measurable) kinetics, glass-forming liquids have provided a plethora of experimental data on crystallization processes, which can be employed for testing different models and theories, as we will do here.

In the theoretical interpretation of the nucleation kinetics in glass-forming melts, the classical nucleation theory (CNT), originally elaborated for one-component systems, has been predominantly employed because it allows a qualitatively correct description of the crystal nucleation processes. According to CNT, the interplay between the effective diffusion coefficient, \( D \), of the “structural units” that controls the critical nuclei formation and the thermodynamic barrier for nucleation, \( W_c(T) \), results in a maximum of the steady-state nucleation rate, \( I_{\text{st}}(T) \), at a temperature, \( T = T_{\text{max}} \), where \( W_c \) is the work of critical cluster formation. By employing certain assumptions (the main one being that the nucleus/liquid surface energy is size-dependent which can be related to the decrease of the critical nucleus size (see, e.g., [2,3,4]) with decreasing temperature) and assigning reasonable values to adjustable parameters, one can achieve a quantitative agreement between the calculated and experimental values of \( I_{\text{st}}(T) \) in the range \( T > T_{\text{max}} \). However, the theoretical and experimental curves start to diverge at \( T = T_{\text{max}} \), and the discrepancy increases for \( T < T_{\text{max}} \) [5,6].

To describe the decrease of the experimental nucleation rates occurring at higher temperatures than expected by theoretical estimates employing the standard assumptions of CNT, an anomalous increase of the thermodynamic barrier for nucleation, \( W_c(T) \), in the temperature range \( T < T_{\text{max}} \) has been assumed (Fig. 1).

However, according to the standard method of determination of the work of critical cluster formation employed in the original formulation of CNT (Eq. (4)), the thermodynamic barrier for nucleation must monotonically decrease with decreasing temperature in the range where crystal nucleation is observed [15,16].

The solid lines in Fig. 1 correspond to the reduced thermodynamic barrier estimated according to CNT by Eq. (4) using a size-dependent specific surface energy and thermodynamic driving force data determined experimentally (the difference between free energies of liquid and crystal of the same volume, see details below). At low temperatures,
Fig. 1. Reduced thermodynamic barrier for nucleation, \( W_c/k_BT \), versus the reduced temperature, \( T/T_m \), for different glasses: \( Li_2O-2SiO_2 \) (L2S) [7], \( Li_2O-2B_2O \) (L2B) [8], \( BaO-2SiO_2 \) (B2S) [9], \( Na_2O-2CaO-3SiO_2 \) (1N2C3S) [10,11,12], \( 2Na_2O-1CaO-3SiO_2 \) (2N1C3S) [13], \( 4Na_2O-5SiO_2 \) (NS) [14]. \( T_m \) is the liquidus temperature.

the values of \( W_c/k_BT \) estimated from experimental nucleation rates begin to deviate from the theoretically expected values and reveal for L2S, L2B, and 2N1C3S glasses a well-expressed minimum. Such unusual behavior of \( W_c(T) \) cannot be explained in the framework of CNT. Thus, the introduction of additional assumptions or concepts is needed to describe the low temperature part of the temperature dependence of the nucleation rates.

The abovementioned problem was first formulated in connection with the interpretation of nucleation rate data of lithium disilicate glass (see, e.g., [17]), for which crystal nucleation rates were independently measured by two groups as early as 1968 [18,19]. Since then, this glass has served as a model for testing nucleation and growth theories. The development of experimental nucleation research worldwide resulted in the accumulation of a plethora of data and broadened the knowledge concerning these processes. It thus became evident that such unusual behavior of \( W_c(T) \), first observed for lithium disilicate glass below \( T_m \), is typical for all glass-forming melts at deep undercoolings, not only for silicate glasses (see e.g. [5,20]), but also for metallic glasses (see Fig. 17 in [21]).

One reason for the increase of \( W_c(T) \) at \( T<T_m \) could consist in the reduction of the thermodynamic driving force of crystallization by the elastic stress effect, which might arise during critical nucleus formation due to the density mismatch between the melt and the crystal. To check whether elastic stresses could explain this unexpected behavior, a detailed analysis of nucleation based on a model of nucleation in viscoelastic media [22] has been performed for lithium and barium disilicate glasses [20] taking into account both the development and relaxation of stresses. These glasses differ by the values of the density mismatches and the relative locations of \( T_m \) compared with the glass transition temperature, \( T_g \). The analysis was aimed at the separation of the elastic stress effect from other possible effects in the description of the nucleation rates for \( T<T_m \). For a number of reasons (details in [20]), the calculated values overestimated the elastic stress effect. However, even with such overestimates, we demonstrated that the reduction of the thermodynamic driving force by the elastic stress energy could not explain the (assumed) increase of the calculated thermodynamic barrier for nucleation at \( T<T_m \), which would be necessary to bring the theory and experimental data into agreement [20].

In alternative attempts to resolve this paradoxical situation, such behavior of \( W_c(T) \) was interpreted as a consequence of the increase of the surface energy with decreasing temperature (see e.g., [13]). However, it is hard to provide a reasonable interpretation to such an approach. With a decreasing size of crystals, their melting enthalpy is known to decrease. By this reason, accounting in addition for the Skapski-Turnbull rule, which connects the specific surface energy and the melting enthalpy, a similar behavior is expected for the surface energy. In line with the above considerations, an increase of the specific interfacial energy with increasing temperature is normally employed in fitting CNT to experimental nucleation rate data for \( T>T_m \). Consequently, it is theoretically not consistent to assume the opposite behavior for \( T<T_m \). Thus, the problem of the deviation of the thermodynamic barrier for nucleation for \( T<T_m \) from that expected from CNT has not been resolved, and other mechanisms should be considered for its resolution.

In the present paper, we continue the analysis of the above problem by employing experimental data for several oxide glasses that reveal homogeneous internal nucleation. To reconcile experimental data and theory, we propose an increase of the size of the “structural units” with decreasing temperature in the range of \( T<T_m \). This size parameter \( d \) can be considered either i) as related to the size of the cooperatively rearranging regions (CRR) that exist in supercooled liquids (see, e.g., [23,24,25,26]) assuming that they could govern crystal nucleation; or ii) as an effective size parameter accounting for corrections of the simple kinetic model employed in CNT when the crystallization kinetics in multi-component systems is treated in terms of a more complex, quasi-one-dimensional, kinetic model. The assumption of an increasing size of the “structural units” with decreasing temperature below \( T_m \) is tested here for the mentioned glasses and allows one to reconcile theory and experiment. The agreement between experiment and theory was achieved using the standard expression for the work of critical cluster formation, \( W_c(T) \), monotonically decreasing, in line with CNT, with decreasing temperature in the whole temperature range, including \( T<T_m \).

The present paper is structured as follows. In Section 2, we outline the basic equations of CNT required for an analysis of the experimental nucleation rate data. In Sections 3 and 4, the effect of the size of the “structural units” on the nucleation rates is analyzed and interpreted. A discussion (Section 5) and a summary of the main conclusions (Section 6) complete the paper.

2. Basic equations

The main equations of CNT employed in the present work are briefly reviewed in this section. The steady-state nucleation rate, \( I_d(T) \), is described by (see, e.g. [21,27,28])

\[
I_d = c \frac{\alpha d_0^2 D}{k_B T} \exp \left( -\frac{W_c}{k_B T} \right),
\]

(1)

where \( T \) is the absolute temperature and \( D \) is the effective diffusion coefficient determining the processes of aggregation of the “structural units” on the crystal clusters. For homogeneous nucleation in one-component systems, \( c \) is the number density of the “structural units” of the ambient phase,

\[
c = 1/d_0^3.
\]

(2)

The effective size is commonly estimated via the crystalline molar volume, \( V_m \), and the Avogadro number, \( N_A \), as

\[
d_0 \approx \left( \frac{V_m}{N_A} \right)^{1/3}.
\]

(3)

\( W_c \) in Eq. (1) is the thermodynamic barrier for nucleation, that is, the increase of the free energy of a system due to the formation of a nucleus of critical size. In the simplest case of an isotropic nucleus of spherical shape, we can write

\[
W_c = \frac{16\pi \sigma c (R_c)^3}{3} \frac{1}{\Delta G_V}.
\]

(4)
\[ R_c = \frac{2\sigma}{\Delta G_V}. \]  

(5)

Here, \( R_c \) is the critical crystal radius, which is determined by the specific energy of the critical nucleus/melt interface, \( \sigma \), and the thermodynamic driving force for crystallization per unit volume of the crystal, \( \Delta G_V \). Latter parameter is determined by the change of the chemical potential per ambient phase particle, \( \Delta \mu \), in the melt to the crystal transformation as.

\[ \Delta G_V = \frac{\Delta \mu}{d_0^2}. \]  

(6)

Employing the classical Gibbs’ approach to the thermodynamic description of heterogeneous systems, it can be strictly shown that these basic relations of CNT have the same form, independent of whether the capillarity approximation is employed or a curvature dependence of the surface tensions is accounted for (e.g., \([6,29,30]\)).

The curvature correction of the specific surface energy, \( \sigma(R) \), is described here via Tolman’s equation \([31]\).

\[ \sigma = \frac{\sigma_0}{1 + \frac{2\delta}{R_c}}. \]  

(7)

resulting in

\[ R_c = \frac{2\tau_0}{\Delta G_V} - 2\delta. \]  

(8)

where \( \sigma_0 \) is the specific surface energy of a planar interface (macroscopic crystal in equilibrium with the melt), and \( \delta \) is the Tolman length, which is of the same order of magnitude as \( d_0 \). The Tolman equation can be considered as the most appropriate zeroth-order approximation of the curvature dependence of the surface tension in the whole range of critical crystal sizes \([32,33]\). It is widely employed in the treatment of curvature corrections to the specific interfacial energy, not only for condensation and boiling (as discussed originally by Tolman), but also for crystallization because it correctly reflects the decrease of the specific interfacial energy with decreasing temperature. A variety of other approximations of relations for \( \sigma(R) \), proposed by different authors, lead to a quite similar dependence \([32,33]\).

The nucleation time-lag, \( \tau \), characterizing the establishment of a stationary embryo size distribution up to the critical size, and, hence, of a steady-state nucleation rate, \( I_{ss} \), is given by

\[ \tau = \frac{16}{3} \frac{k_BT}{\Delta G_V d_0^2 D}. \]  

(9)

Nucleation time-lag data were already employed to estimate the effective diffusion coefficient \( D \), which should control both the steady-state nucleation rate, \( I_{ss} \), and the time-lag, \( \tau \). Eq. (1) can be rewritten as

\[ I_{ss} = \frac{\sigma}{3} \frac{16(k_BT)^{1/2}\Gamma^{1/2}}{\Delta G_V d_0^2} \exp \left( - \frac{W_c}{k_BT} \right). \]  

(10)

Eq. (10) allows us to determine \( W_c \) as a function of temperature using experimental data for the steady-state nucleation rates and time-lags by choosing appropriate estimates of the thermodynamic driving force and the size of the structural units. Strictly speaking, knowledge of the specific interfacial energy is also needed, but the choice of the \( \sigma \) value does not significantly affect the estimation of \( W_c \). The results obtained in this way are shown in Fig. 1.

As an example of experimental data employed in the computations, the experimental data for time-lags and steady-state nucleation rates for barium disilicate are shown in Fig. 2.

Whereas the experimentally measured nucleation rates show a well-pronounced maximum at \( T = T_{\text{max}} \) — generally with a very sharp and asymmetric shape — the nucleation time-lags are well-described by an Arrhenius-type temperature dependence and do not reveal any peculiarity at \( T_{\text{max}} \) (see, e.g., Fig. 2, where the respective data for barium disilicate are shown \([9,20]\)). Therefore, using the effective diffusion coefficient \( D \) estimated from the data for \( \tau \) (this is likely a correct procedure), the experimental nucleation rates can be correctly described in terms of CNT (using a fitted size-dependent surface energy) but only for \( T > T_{\text{max}} \). To utilize the experimentally measured time-lags in the calculations, we used a fitting function with Arrhenius form

\[ \tau(T) = \tau_0 \exp \left( \frac{E_r}{k_BT} \right). \]  

(11)

with two free parameters, \( \tau_0 \) and \( E_r \). Proper values for the studied glasses are listed in Table 1.

If experimental data on nucleation time-lags are absent, the effective diffusion coefficient is commonly estimated from viscosity data assuming the validity of the Stokes–Einstein–Eyring (SEE) equation \( \tau(T) \). We avoided such assumption by choosing for our analysis only glasses for which both nucleation rates and time-lags are available.

### 3. Estimation of the effective size of the “structural units”

As shown in one of our previous papers \([20]\), the anomalous increase of the thermodynamic barrier for nucleation, \( W_c \), at temperatures below \( T_{\text{max}} \) (which is calculated to restore agreement between theory and experiment assuming a fixed size parameter \( d = d_0 \)) cannot be explained by assuming a decrease of the thermodynamic driving force for crystallization due to elastic stresses. The effect of elastic stresses is negligibly small in the case of the nucleation of stable phases and affects only slightly the nucleation kinetics of possible metastable phases. Therefore, alternative approaches for the resolution of the mentioned problem are required.

We test, first completely neglecting the effect of elastic stresses, whether the above problem can be solved by assuming an increase of
the effective size $d_0$ of the structural units for the description of the nucleation rates for temperatures $T<T_{\text{max}}$. A direct consequence of this assumption is a decrease in the effective diffusion coefficient of the “structural units” controlling the nucleation rates and a decrease of the number of potential places for homogeneous nucleation to take place. As we will show below, the account of these effects restores agreement between the experimental nucleation rate data and CNT.

We proceed as follows. We start with Eq. (10) but employ the work of critical cluster formation given by Eqs. (4)–(7). Then, using the experimental nucleation rate and time-lag data, we rearrange Eq. (10) to determine the size parameter $d$ as

$$d = \frac{16}{3} \left( \frac{W}{kT} \right)^2 \rho \alpha^{3/2} \left( \frac{W}{kT} \right)^{1/6}. \quad (12)$$

Considering the size parameter as a variable quantity, which can change with temperature, the subscript “0” of $d$ is omitted.

To determine $d$, we use experimental values of $I_0$ and $\tau$ in Eq. (12). To employ Eq. (12), we also need the value of $W_\text{c}$ and, following Eq. (4), the knowledge of $\sigma(R)$ and $\Delta G_\text{c}(T)$. Due to the nanometric sizes of the critical nuclei, direct methods to estimate the surface energy of critical nuclei do not exist, thus $\sigma_0$ and $\delta$ are used as adjustable parameters for a description of the nucleation rate data at temperatures higher than that of the nucleation rate maximum, $T_{\text{max}}$. In this temperature range, we consider $d$ as a constant ($d = d_0$).

It should be recalled that at $T>T_{\text{max}}$, the temperature dependence $W_\text{c}(T)$, as shown in Fig. 1, does not contradict CNT, and the experimental nucleation rates can be described with only one additional assumption, i.e., a size-dependent surface energy, $\sigma(R)$. If one knows $\sigma(R_0)$ and $\Delta G_\text{c}(T)$, then the effective size, $d$, of the structural units can be estimated for $T>T_{\text{max}}$ via Eq. (12) and Eq. (4). However, as will be shown later, the temperature $T_{\text{sw}}$ of the switch from $d_0 = \text{const.}$ to $d(T)$ is somewhat higher than $T_{\text{max}}$ (see Table 1), which, in turn, is equal to or higher than the laboratory glass transition temperature, $T_g$. It is thus obvious that the $d(T)$ dependence estimated in this way results in agreement of the experimental data with the values calculated by CNT.

However, one more problem arises due to the nanometer size of the critical nuclei: the crystalline phase that nucleates is normally unknown. Therefore, to overcome this problem and to obtain a more general result, we consider nucleation of both the known stable phase and of some assumed metastable phases. Recall that the problem of metastable phases was widely discussed in connection with nucleation rate analysis (see, e.g., [6,34,35,36,37]).

For the case of stable phase formation, the values of the melting temperature, $T_m$, melting enthalpy, $\Delta H_\text{m}$, and the proper thermodynamic driving force for crystallization, $\Delta G_\text{m}$, are available. Thus, for $T>T_{\text{max}}$, Eq. (10) has only two fitting parameters, $\sigma_0$ and $\delta$, because for this temperature range, the size parameter $d$ is constant and defined by Eq. (3), that is $d = d_0$. The rationale of metastable phases employed in this work is presented in Appendix A.

The results of such a fit of the nucleation rates are shown by dashed lines in Fig. 3 for Li2O·2SiO2 (L2S) glass. Calculations are performed by Eq. (10) for the cases of nucleation of stable and metastable phases for a fixed value $d = d_0$ in the whole temperature range. The values of $\sigma_0$, $\delta$, $q$, and $T_m$ are listed in Table 1.

For an evaluation of the applicability of our work, it is important that all approximations, both for the stable ($T_m = 1307K$) and metastable phases, with the resulting fit parameters, give good agreement with experimental data [7] available for temperatures above $T_{\text{max}}$. In contrast, the values of the nucleation rates calculated at the condition of constant $d = d_0$ (dashed lines) progressively diverge from the experimental data at $T>T_{\text{max}}$ and reveal a maximum at temperatures lower than $T_{\text{max}}$ obtained in experiments (see Fig. 3).

The reduced values of $d$ versus temperature calculated by Eq. (12) for L2S glass are shown in Fig. 4. To facilitate the subsequent analysis and presentation of the results, instead of the experimental points

![Fig. 3. Nucleation rates for L2S glass versus temperature. The circles denote experimental data [7], the solid and dashed lines present a fit of the nucleation rates by Eq. (10) for stable and several metastable phases, taking into account the change of the size parameter $d$ estimated via Eq. (13) (solid lines) and using a constant value $d = d_0$ (dashed lines), respectively. $T_g$ and $T_{\text{sw}}$ are denoted by vertical dashed lines.](image-url)
estimated by Eq. (12), we will use the fitting function

\[
d = d_0 \begin{cases} 1 & \text{at } T \geq T_{sw} \\ 1 + K_d \left( \frac{T_{sw}-T}{T_{sw}(1-\beta)} \right)^\beta & \text{at } T < T_{sw} \end{cases}
\]

(13)

where \(K_d, \beta, T_{sw},\) and \(d_0\) are fit parameters for the nucleation of both stable and metastable phases in the considered glasses. They are collected in Table 1. According to Fig. 4, the values of \(d\) depend on the assumed nature of the critical nuclei only slightly. As will be shown below, such dependence is also valid for other silicate glasses.

The nucleation rates calculated by Eq. (10), taking into account the variation of the size parameter \(d\) estimated via Eq. (13) with proper fit parameters, are presented in Fig. 3 as solid lines as a function of temperature. Fig. 5 illustrates another consequence of the assumed increase of \(d\) and the lines are plotted using Eq. (13) with the proper fitting function.

Thus, in accordance with CNT, the thermodynamic barrier, \(W_c\), continues to decrease monotonically with decreasing temperature. To achieve agreement between experiment and theory, we supplement the classical interpretation for the nucleation rate maximum as resulting from the interplay of the thermodynamic barrier for nucleation and diffusion of “structural units” by an increase of \(d\). This approach results in an additional decrease of the mobility of the “structural units” with decreasing temperature. Moreover, the increase of \(d\) further decreases the nucleation rates due to a decreased number density of homogeneous nucleation sites, as shown in Fig. 5.

A treatment of nucleation data similar to that performed for lithium disilicate glass was also performed for five additional glasses: \(\text{Li}_2\text{O·2B}_2\text{O}_3\) (L2B) \([8]\), \(\text{BaO·2SiO}_2\) (B2S) \([9]\), \(\text{Na}_2\text{O·2CaO·3SiO}_2\) (1N2C3S) \([10,11,12]\), 2\(\text{Na}_2\text{O·1CaO·3SiO}_2\) (2N1C3S) \([13]\), and 4\(\text{Na}_2\text{O·5SiO}_2\) (NS) \([14]\), which reveal homogeneous internal nucleation. The calculated and measured nucleation rates, together with the effective size parameters \(d\), are presented for these glasses versus temperature in Figs. 6-10. The similarity of these results to those presented for the case of \(\text{Li}_2\text{O·2SiO}_2\) corroborates the generality of the problem of describing the nucleation rates below the maximum and the proposed methods for its resolution.

Summarizing these results, we can state that accounting for the increase of the size parameter \(d\) allows for an appropriate description of nucleation data at \(T < T_{max}\) in a variety of systems.

The elastic stresses due to the density mismatch between the crystalline and liquid phases do not noticeably affect the results of the present analysis. Fig. 11 shows the size parameter \(d\) for several glasses estimated without and with the elastic stresses based on our analysis performed in \([20]\). The elastic stresses do not change neither the temperature dependences of \(d\) nor their values (the data for \(\text{Li}_2\text{O·2B}_2\text{O}_3\) glass with and without the elastic stresses are indistinguishable and therefore are not presented here). Thus, the idea proposed in the present work permits the avoidance of the problem of anomalous behavior of the thermodynamic barrier for nucleation and quantitatively describes the nucleation rate maximum in the framework of CNT, not relying on the elastic stress effects.

Fig. 4. Reduced size of the structural units versus temperature for the crystallization of stable and metastable phases in L2S glass. The points are from calculations using Eq. (12), and the lines are plotted using Eq. (13) with the proper fit parameters collected in Table 1.

![Fig. 4](image-url)

Fig. 5. Number density of nucleation sites for homogeneous nucleation in L2S glass calculated by Eq. (2).

![Fig. 5](image-url)

Fig. 6. (a) Nucleation rates for \(\text{Li}_2\text{O·2B}_2\text{O}_3\) glass versus temperature. The circles denote experimental data \([8]\), the solid and dashed lines present a fit of the nucleation rates by Eq. (10) for stable and metastable phase, taking into account the change of the size parameter \(d\) estimated via Eq. (13) (solid lines) and using a constant value \(d=d_0\) (dashed lines), respectively. \(T_g\) and \(T_{sw}\) are denoted by vertical dashed lines. (b) Reduced size of the structural units versus temperature for the crystallization of stable and metastable phases in \(\text{Li}_2\text{O·2B}_2\text{O}_3\) glass. The points are from calculations using Eq. (12), and the lines are plotted using Eq. (13) with the proper fit parameters collected in Table 1.
4. Possible microscopic interpretations of the temperature dependence of the size-parameter

4.1. Crystal nucleation: the standard simplest model approach

The main result of the present work is the conclusion that CNT can be brought into agreement with experimental data by assuming an increase of the size of the structural units with decreasing temperature in the range of temperatures $T < T_{\text{max}}$. An increase of the size parameter by a factor of only 1.4–2.5 is sufficient to restore agreement between theory and experiment for different glasses in the temperature interval from $T_{\text{max}}$ to the lowest temperatures of the experiments. According to Eqs. (1) and (2), an increase of $d$ results in a decrease of $I_0$, for the following reasons: (i) a decrease of the number $c = 1/d^3$ of potential places for homogeneous nucleation, as illustrated in Fig. 5b, (ii) a decrease of the rate at which molecules attach to the nucleus $\nu = D/d^2$ estimated from the time-lag for nucleation via Eq. (9), and (iii) an increase of the Zeldovich factor $Z \sim \sqrt{\alpha d^2/k_B T d}$ in Eq. (1) (cf. the discussion as outlined below), but this effect is weaker than the effects (i) and (ii). We discuss how such variation of the size parameter can be given a theoretical interpretation. For that purpose, we first sketch the main assumptions employed in CNT for the derivation of the expressions for the steady-state nucleation rate and time-lag.

To quantitatively describe the whole nucleation-growth process for one-component systems consisting of certain structural units, $n$, (atoms, molecules) of a given size, a set of kinetic equations for the evolution of the cluster size distribution function, $N(n,t)$, has been formulated (e.g., [27,28]). An analytical analysis of these kinetic equations leads to the following expression for the steady-state nucleation rate.

$$ I_{\infty} = I_0 \exp \left( \frac{W_c}{k_B T} \right). $$  

Considering crystal nucleation processes, we can write in the simplest approach.

$$ I_0 \propto \omega_{n_{\infty},n+1}(n_0) \Gamma_z, \quad \omega_{n_{\infty},n+1}(n_0) = \frac{D}{d_0^4} \left( 4\pi n_0^2 \right). $$  

Here, $\omega_{n_{\infty},n+1}(n_0)$ is the aggregation coefficient to crystal cluster of critical size $R_c = n_0^{1/3} d_0$, which is equal to the number of structural units aggregating to the crystalline cluster per unit time. $c$ is the number of particles in the melt per unit volume and $d_0$ is their size. The quantity $\Gamma_z$ is commonly denoted as the Zeldovich factor. Assuming further in the derivations that the basic units in the melt and the crystal are the same and that their size parameters are of similar magnitude, the particle density in the cluster phase, $c_0$, can be set equal to the particle density in the liquid, $c$. After some straightforward transformations, we arrive at [27,28].

$$ \Gamma_z = \frac{1}{2\pi n_0 R_c^2 \sqrt{k_B T}}, $$

employed here earlier (cf. Eq. (1)).

In terms of such model, the nucleation time-lag is given by

$$ \tau = \frac{a^* k_B T}{\omega_{n_{\infty},n+1}(n_0)} \left( \frac{2\pi n_0^2 R_c^2}{\sigma} \right). $$

Variations in the parameter $a^*$ result from different approximations proposed by different authors (cf. [27]). With Eq. (5), employing the
4.2 Interpretation of the temperature dependence of $d$ in the framework of the one-component model

In a first attempt for an interpretation of the temperature dependence of $d$, we retain the one-component model assuming that: a) the "structural units" of liquid and critical nuclei are the same and b) the formation of critical nuclei occurs via aggregation of these "structural units" as a whole. However, we do not identify the "structural units" with atoms or molecules but with "units" of the melt, denoted as cooperatively rearranging regions (CRR). This concept has been widely used in the analysis of the viscosity of glass-forming melts, describing the minimal spatial sizes where a rearrangement of the liquid can be realized. Extending this concept to crystallization, we identify those units of the liquid capable of switching their state to a crystal-like structure, thus being able to be incorporated into the newly evolving crystalline aggregates. According to the Adam-Gibbs theory\cite{23}, the average sizes of the CRR increase with a decrease of temperature, giving — if the assumption is accepted — a first confirmation of the behavior of the structural units, as established in Section 3. In reality, the sizes of the CRR exhibit some distribution, but we identify the average size with the size parameter $d$. However, the average sizes of the CRR increase continuously with decreasing temperature, which differs from the present approach, where the sizes of the structural units are constant from the liquidus to $T_{\text{max}}$ and only then start to increase with decreasing temperature.

Treating the model of CRR and its switch of possible states from liquid-like to solid-like as the basic kinetic model of crystallization in detail, the kinetic equations have to be modified. However, as will be shown below in the discussion of an alternative model approach, this is not an argument to disprove this approach. We will show in the next section how a more complex case of nucleation kinetics can be treated in classical terms.

4.3 Interpretation of more complex nucleation kinetics in classical terms

The above equations are derived for the description of phase formation in one-component systems. As we have noted, the equations are widely employed also for the description of phase formation in multicomponent systems. A straightforward extension of those equations is possible and correct if the basic assumptions underlying their derivation — both phases are from the same basic units, and the transport of matter to the growing aggregates proceeds by diffusional motion of these basic units as a whole to the crystal — is fulfilled for the multicomponent systems under consideration, as we assumed in Section 4.2. However, in the general case, the formation of the new phase could proceed by a different scenario, and the question arises of how more complex aggregation kinetics can be interpreted in classical terms.

One particular example, where such a procedure can and has been performed in detail, is sketched in Appendix B. Generally, if the composition of the crystal clusters in dependence on their size is known, then one parameter (e.g., the total number of particles in a crystal cluster) fully determines its state. Moreover, the nucleation kinetics can be reduced again to the classical set of equations with a modified expression for the steady-state nucleation rate of the form

$$ I_{\text{mod}} = C \omega_{n+1} \exp \left( - \frac{W}{k_B T} \right). \quad (19) $$

In Eq. (19) $C$ is the volume density of the centers of homogeneous nucleation and $\omega_{n+1, \text{mod}}$ is the aggregation coefficient of crystal clusters of critical sizes corresponding to the particular kinetic mechanism of aggregation realized in the system.
have to assume in a correct description by Eq. (19), in terms of the classical model, we caused by the application of a one-component model. We obtain, as a

sidered in CNT as the size of structural units moving in the melt, looses its original meaning. It becomes a fit parameter compensating mistakes caused by the application of a one-component model. We obtain, as a

\[ d_0 \approx d = \left( \frac{4\pi R_c^2 D}{C_{\text{II}, n,n-1}(n_i)} \right)^{1/7}. \]  

(22)

If the classical model holds, \( d = d_0 \), if this is not the case, \( d \) may have different values compared to \( d_0 \) and may depend on temperature. However, due to the exponent \( 1/7 \) in Eq. (22), the dependence of \( d \) on such modifications of the kinetics is weak. Therefore, if \( d_0 \) is replaced by \( d \) in the expression for the nucleation time-lag, the variations for the temperatures dependence of the time-lags are also small.

5. Discussion

As was shown in Section 1, attempts to quantitatively describe the measured nucleation rates in the temperature range below the temperature \( T_{\text{max}} \) in the framework of CNT, under the conditions of a temperature-independent size parameter \( d_0 \) of “structural units”, fail. We illustrated and analyzed this problem here for the case of homogeneous internal nucleation in several silicate glasses. However, the same problem exists for different types of nucleation in different systems; hence, it is general.

To reconcile the experimental data with the theoretical description in the framework of CNT, we assumed that the average size \( d \) of the “structural units” of the liquid increases at \( T=T_{\text{max}} \). In such a way, we avoided the increase of \( W_c(T) \) at \( T=T_{\text{max}} \), strongly conflicting with CNT, resulting from the analysis when constant values \( d = d_0 \) are assumed. This increase of the size parameter was interpreted to be a consequence of modifications of the nucleation kinetics compared to the classical model. Such modifications result in different expressions for the pre-exponential term in the equation for the nucleation rate or, keeping the description in terms of CNT, in an increase of \( d \).

In Section 4, we proposed two different interpretations of the size parameter \( d \) — as the average size of diffusing particles with the composition of a crystal and as the correcting parameter in the case of more complex aggregation kinetics if the “structural units” are different in the crystal phase and in the liquid melt. Both interpretations implicitly suppose the change of liquid structure strongly affecting the nucleation kinetics when the temperature approaches the glass transition interval.

In the mentioned modifications of the crystal nucleation kinetics, we neglected the effects of the heterogeneous dynamics on crystal nucleation, similarly to the concepts such as rigid and floppy modes [39,40,41]. If nucleation suppression is supposed in the rigid regions, a decrease of the effective volume where nucleation can occur with decreasing temperature could be expected. Such effects will be analyzed in a future study.

As discussed in detail in this paper, we supposed that the thermodynamic driving force increases with decreasing temperature, in line with CNT. However, alternative developments addressing nucleation thermodynamics in contrast to the models discussed here also exist and may result in behavior of the work of critical cluster formation, as shown in Fig. 1. One method involves generalizations of the expression for the thermodynamic driving force obtained via more precise formulations of the respective expression in terms of the classical Gibbs approach and via generalizations of the Gibbs classical treatment in application to nano-particles as critical nuclei are [15]. Another thermodynamically based resolution of the problem discussed here could consist of the assumption that the evolution to the crystal phase for large undercooling does not proceed via the saddle-point of the thermodynamic potential surface but via a ridge [42,43,44,45,46].

Overall, we demonstrated that the discrepancy between the experimental data and the calculations of the nucleation rates by CNT for the temperature range below \( T_{\text{max}} \) can be restored by assuming a size parameter, \( d(T) \), that increases with decreasing temperature. Such an

\[ T_g \]

\[ T_{\text{sw}} \]

\[ T_{\text{max}} \]

\[ T \]

\[ d \]

\[ d_0 \]

\[ C_{\text{II}, n,n-1}(n_i) \]

\[ T_{\text{max}} \]

\[ T \]

\[ d \]

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\[ W_c(T) \]

\[ W_c(T_{\text{max}}) \]

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increase of size is also predicted for the CRR; hence, there could be some straight connection between these two parameters. Because CRR have some size distribution that shifts in the direction of higher sizes with decreasing temperature, we can suppose that nucleation slows in those CRR that are larger than a certain size; and they occupy an increasingly larger volume fraction of the liquid as the temperature drops, which inhibits nucleation with decreasing temperature. In this interpretation, the nucleation rate reflects the temperature evolution of the CRR. However, this interpretation requires further study.

A detailed analysis of these topics must be performed to obtain a firm answer to whether kinetic or thermodynamic factors or both are responsible for the failure of CNT to describe the temperature dependence of crystal nucleation rates for \( T < T_{\text{max}} \).

6. Conclusions

The dramatic deviation of the experimental nucleation rates from the values estimated via CNT at temperatures lower than that of the nucleation rate maximum can be explained by an increase of the effective size of the structural units of the liquid that controls nucleation with decreasing temperature at \( T < T_{\text{max}} \). Different interpretations of the meaning of the size parameter and its increase are discussed and shown to result from an interpretation of the more complex dynamics of crystal nucleation compared to the relatively simple model underlying CNT.

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Appendix A. Metastable phases

To describe the possible metastable phases, we use the following approximation of the thermodynamic driving force, \( \Delta G_V \):

\[
\Delta G_V = \Delta H_m^* (1 - T/T_m^*).
\]

This relation has been used in the past by several scientists, including Volmer, Frenkel, and Turnbull [47,48,49]. Moreover, we attributed different melting temperatures, \( T_m^* < T_m \), to the different metastable phases considered. \( T_m \) is the melting temperature of the stable phase.

To estimate the surface energy, \( \sigma_0^* \) of a macroscopic metastable crystalline phase, the semi-empirical Skapski-Turnbull equation [50,51] was used

\[
\sigma_0^* = \alpha \frac{q^*}{d_0^*},
\]

where \( \alpha \) is a constant for a given crystal/liquid interface, and \( q^* \) is the melting enthalpy per “structural unit”

\[
q^* = \Delta H_m^* d_0^*.
\]

Combining Eq. (A2) with the similar equation for the stable phase, i.e., with the set of \( \sigma_0 \) and \( \delta \), and supposing that the values of \( \alpha \) for the stable and metastable phases are equal, we can obtain the following relation between \( \sigma_0^* \) and \( \sigma_0 \):

\[
\sigma_0^* = \sigma_0 \frac{\alpha}{q^*}.
\]

Thus, in the case of the metastable phase, as well as the stable phase, we have two parameters \( \sigma_0^* \) (or \( q^* \) via Eq. (A4)) and \( \delta^* \) to achieve the best fit of experimental nucleation rates at \( T > T_{\text{max}} \).

Introducing metastable phases, we are restricted by \( T_m = 1102 \) K, which corresponds to a Tolman length \( \delta \) equal to zero. If the Tolman parameter is negative (which occurs at \( T_m < 1102 \) K, then \( \alpha \) is larger than the value for a planar interface. Therefore, it is useful to restrict the considerations to the mentioned limit. This limit is different for other compositions, as shown in Table 1.

The values of \( \delta_0, \delta, q, \) and \( T_m \) are listed in Table 1 (asterisks are omitted for simplicity of the notations).

Appendix B. Incongruent crystal nucleation: one particular model

As one of the models mentioned earlier for the aggregation kinetics, one can assume that a certain set of components moves widely independently in the glass-forming melt and aggregates into the newly evolving phase, either in a given stoichiometric composition or in a composition depending both on thermodynamic and kinetic features of the aggregation process. In latter case, one has to start the description of this process with appropriate sets of equations for the distribution function \( N(n_1, n_2, \ldots, n_k, t) \) giving the number of clusters consisting of \( n_i, \quad i = 1, 2, \ldots, k \) particles of the different components. However, this set of equations can be reduced to a quasi-one-component description if the composition of the clusters is known as a function of its size. In this case, the attachment coefficients have to be replaced by more complex relations, introducing effective diffusion coefficients, as discussed in detail in [52]. For the description of crystal nucleation, one obtains [52]

\[
\omega_{n, n-1}^{(i+)} = \frac{1}{D_{\text{eff}}^i} \sum_{i=1}^{k} \frac{1}{\sigma_{i,n_i}} \frac{v_{\text{tr}}}{n_{\text{tr}}} \left( \frac{v_{\text{tr}}}{n_{\text{tr}}} \right) \frac{1}{\sigma_{i,n_i}} = \left( \frac{x_{\text{tr}} + n_{\text{tr}} d_{\text{tr}}}{n_{\text{tr}}} \right),
\]

\[
\omega_{n, n+1}^{(i+)} = \frac{D_i}{a_i} \left( 4\pi R_i^2 \right).
\]

Here, \( D_i \) is the partial diffusion coefficient of the \( i \)-th component in the liquid, and \( a_i \) is the average size of these independently moving particles. The model aggregation coefficients can be written as

\[
\omega_{n, n-1}^{(i+)} = 4\pi a_i \left( \frac{a_i}{d_i} \right)^{2/3} D_{\text{eff}}^i \frac{1}{D_{\text{eff}}^i} \sum_{i=1}^{k} \frac{r_{\text{tr}}^2}{D_{\text{eff}}^i},
\]

where \( a_i \) is the average size per particle in the ambient phase, and \( c_i \) is the total particle concentration of the independently moving components. Using these results, the expression for the steady-state nucleation rate has the form

\[
I = C \omega_{n, n-1}^{(i+)} (n_i) \Gamma \exp \left( - \frac{W_{\text{f}}}{k_B T} \right) = c_i \prod_{i=1}^{k} (x_{ji})^{(c_i)} c_i = \frac{1}{a_i^3}
\]

or

\[
I = \left( \prod_{i=1}^{k} (x_{ji})^{(c_i)} \right) \frac{D_{\text{eff}}^i}{a_i^3} \frac{d_i}{a_i^3} \left( \frac{d_i}{a_i^3} \right) \frac{1}{2} \exp \left( - \frac{W_{\text{f}}}{k_B T} \right).
\]

In the above equation, \( C \) is the volume density of the centers of homogeneous nucleation. As evident from the above relations, the crystallization kinetics is governed by the effective diffusion coefficient, and the viscosity may not be relevant for the crystallization kinetics (cf., e.g., also [45,53,38]). In any case, employing the results for \( C \) and \( \omega_{n, n-1}^{(i+)} (n_i) \) based on Eq. (10), appropriate expressions for \( d(T) \) can be obtained provided the kinetics of crystallization is governed by this model for the system under consideration.