



## Predicting homogeneous nucleation rates in silicate glass-formers

Alexander S. Abyzov<sup>a,b,\*</sup>, Vladimir M. Fokin<sup>a,c</sup>, Edgar D. Zanotto<sup>a</sup>

<sup>a</sup> Vitreous Materials Laboratory - DEMa, Federal University of São Carlos, Brazil

<sup>b</sup> National Science Center Kharkov Institute of Physics and Technology, Kharkov, Ukraine

<sup>c</sup> Vavilov State Optical Institute, St. Petersburg, Russia



### ARTICLE INFO

#### Keywords:

Glass  
Nucleation rate  
Glass transition temperature

### ABSTRACT

We employed the Classical Nucleation Theory using a characteristic value of the pre-exponential constant and an average (temperature dependent) interfacial energy and derived an expression to estimate the maximum nucleation rates,  $I_{\max}$ , as a function of the reduced glass transition temperatures,  $T_{gr} \equiv T_g/T_m$  ( $T_g$  is the laboratory glass transition temperature and  $T_m$  is the melting point or *liquidus* temperature). The theoretical predictions were surprisingly good for 51 out of 54 silicate glass-formers tested and describe well the experimental trend that  $I_{\max}$  strongly decreases with increasing  $T_{gr}$ . This trend, in turn, explains the well-known fact that only silicate glasses having a relatively low  $T_{gr}$ ,  $T_{gr} < 0.6$ , show internal homogeneous nucleation in laboratory time/sample-size scales.

### 1. Introduction

The objective of materials science is to *understand*, *describe* and *predict* (a very demanding endeavor) all the physical and chemical phenomena related to the structure, dynamic processes and properties of materials. This short article deals with the ability of the Classical Nucleation Theory (CNT) to describe and predict the crystal nucleation rates in silicate glass-forming substances.

In previous publications [1, 2], some of us made the first attempts to tackle this important problem. In ref. [1], we used CNT and successfully confirmed the (experimental) trend that the homogeneous nucleation rates maximum,  $I_{\max}$ , of silicate glasses decrease with increasing values of the reduced glass transition temperature,  $T_{gr} \equiv T_g/T_m$ , where  $T_g$  is the glass transition temperature and  $T_m$  is the melting point of the respective crystal phase or the *liquidus* temperature of non-stoichiometric compositions. In the other publication, [2], some of us have shown that the temperatures of maximum nucleation rates,  $T_{\max}$ , are shifted below the respective  $T_g$  of each glass forming system as their  $T_{gr}$  increases; which results in longer nucleation time-lags and smaller nucleation rates.

However, in the calculations performed in both articles, we used a constant (average) value of the nucleus/liquid interfacial energy. In this way, the predictions of ref. [1] yielded the correct trend, but underestimated the strong variation of  $I_{\max}$  with  $T_{gr}$ . The objective of this short article is to revisit ref. [1], propose and test an improved expression to estimate the  $I_{\max}(T_{gr})$  dependence. For this purpose, we will

use a *temperature dependent* interfacial energy (which restores agreement between theory and experimental data), rather than the constant value used in [1].

### 2. Governing equations

The steady-state rate of homogeneous nucleation is given by (see, e.g. [3])

$$I_{st} = c \frac{D}{d_0^2} Z \exp\left(-\frac{W^*}{k_B T}\right), \quad Z = \sqrt{\frac{\sigma d_0^2}{k_B T}} \quad (1)$$

where  $D$  is the effective diffusion coefficient that controls the aggregation of the “structural units” of size  $d_0$  to the clusters,  $Z$  is the Zeldovich factor,  $\sigma$  is the critical nucleus/liquid interfacial energy,  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature. For homogeneous nucleation,  $c$  is the number density of the “structural units” of the ambient phase,

$$c = d_0^{-3} \quad (2)$$

The size of the “structural units”,  $d_0$ , is commonly estimated as

$$d_0 \approx (V_M/N_A)^{1/3} \quad (3)$$

where  $V_M$  is the crystalline molar volume, and  $N_A$  is Avogadro's number.

The thermodynamic barrier for nucleation of spherical nuclei,  $W^*$ , is given by

\* Corresponding author at: Vitreous Materials Laboratory - DEMa, Federal University of São Carlos, Brazil.

E-mail address: [abyzov@kipt.kharkov.ua](mailto:abyzov@kipt.kharkov.ua) (A.S. Abyzov).

$$W^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_V^2} \quad (4)$$

where  $\Delta G_V$  is the thermodynamic driving force, i.e., the Gibbs free energy difference between the supercooled liquid and the critical nucleus.

It is quite difficult to measure the diffusion coefficient,  $D$ , of the (unknown) structural units in Eq. (1), hence it is often replaced by the Newtonian viscosity,  $\eta$ , of the supercooled liquid via the Stokes-Einstein-Eyring equation

$$D = \frac{k_B T}{\eta d_0} \quad (5)$$

Therefore, Eq. (1) may be rewritten as

$$I_{st} = \frac{k_B T}{\eta d_0^6} Z \exp\left(-\frac{W^*}{k_B T}\right) \quad (6)$$

A plethora of experimental evidence indicates that the position of the maximum homogeneous nucleation rate,  $T_{max}$ , is close to the laboratory glass transition temperature,  $T_g$  [1].

For example, for 34 silicate liquids that display homogeneous nucleation,  $T_{max} - T_g$  varies from approximately  $-15$  to  $+35^\circ\text{C}$ , which correlates to a viscosity variation of approximately  $10^{14.5}$  to  $10^9\text{Pa s}$ . Hence, for an *estimate*, one could take the laboratory  $T_g$  as a characteristic value of  $T_{max}$ . This is a convenient choice because the viscosity has a defined value,  $\eta \approx 10^{12}\text{Pa s}$ , at  $T_g$ . It then follows that a reasonable value of the pre-exponential term in Eq. (6) could be used for different glass-forming melts. Therefore, to a good approximation, we have the following equation for the maximum nucleation rate:

$$I_{max} = I_c \exp\left(-\frac{W^*}{k_B T_g}\right),$$

$$I_c \equiv \frac{k_B T_g}{10^{12} d_0^6} Z \approx 10^{24} \text{m}^{-3} \text{s}^{-1} \quad (7)$$

where this value of  $I_c$  is typical for silicate glasses. For example, for lithium disilicate,  $T_g = 727\text{K}$ ,  $d_0 = 0.48\text{nm}$ ,  $Z = 1.855$  and  $I_c \approx 1.5 \cdot 10^{24} \text{m}^{-3} \text{s}^{-1}$ .

We should note here that, unlike ref. [2], in our new approach we estimate the nucleation rate only at the glass transition temperature because it is close to the position of the maximum homogeneous nucleation rate,  $T_{max}$ . Thus, in this way we avoid the serious and still not resolved discrepancy between the predictions of CNT and the experimental nucleation rates at temperatures below  $T_{max}$  [4–7].

Therefore, using this reasonable average value for the pre-exponential term, the maxima of the homogeneous nucleation rates of different glass-forming liquids are determined mainly by their thermodynamic barriers,  $W^*/k_B T$ . To estimate this property for different systems, we use the crystal/melt interfacial energy,  $\sigma$ , and the thermodynamic driving force,  $\Delta G_V$ , which are given by the Stefan–Skapski–Turnbull relation [1, 8].

$$\sigma = \alpha \frac{\Delta H_m}{V_m} d_0 \quad (8)$$

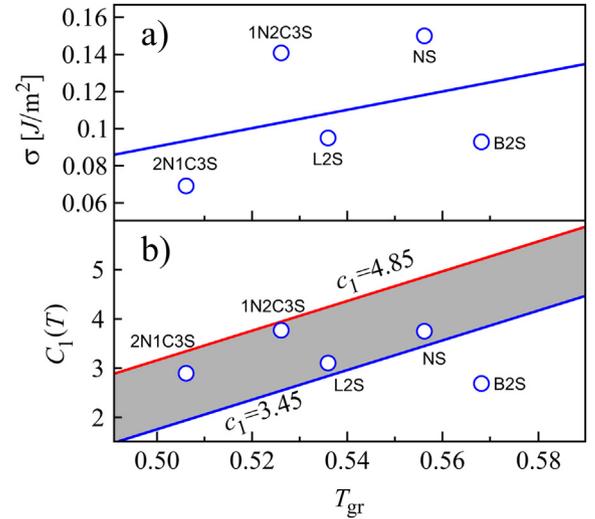
and the Turnbull relation

$$\Delta G_V = \frac{\Delta S_m}{V_m} (T_m - T) \quad (9)$$

where  $\Delta H_m$  is the molar heat of melting,  $\Delta S_m$  is the molar entropy of melting and  $\alpha$  is an empirical coefficient,  $0.3 < \alpha < 1$  [3]. The combination of Eqs. (4), (8) and (9) yields the following expression for the thermodynamic barrier at  $T_{max} \approx T_g$ :

$$\frac{W^*}{k_B T_g} = C_1 \frac{1}{T_{gr}(1 - T_{gr})}, \quad T_{gr} \equiv \frac{T_g}{T_m} \quad (10)$$

$$C_1 \equiv \alpha^3 \frac{16\pi}{3} \frac{\Delta H_m}{RT_m} = \alpha^3 \frac{16\pi}{3} \frac{\Delta S_m}{R} \quad (11)$$



**Fig. 1.** a) Interfacial energy,  $\sigma$ , versus reduced glass transition temperature,  $T_{gr}$ . These values were calculated at the respective  $T_{gr}$  from the  $\sigma(T)$  expressions obtained by force fitting experimental nucleation rates  $I(T)$  versus temperature curves for 5 stoichiometric glass-forming silicates. The error is of the order of the symbol size and the line is just to guide the eyes. b) Values of  $C_1$  for 5 silicate glass-formers calculated by Eqs. (11), (8) and  $\sigma$  from Fig. 1a. The lower and upper bound lines were calculated from Eq. (12) with  $c_1 = 3.45$  and  $4.85$ , respectively. The data point for BS2 glass lies outside this range due to the incipient nucleation of a metastable phase in this particular composition.

Fig. 5 of reference [1] shows the maximum nucleation rates as a function of reduced glass transition temperature for several silicate glasses. The decreasing  $I_{max}(T_{gr})$  tendency is correctly predicted, but the agreement between the measured data and the calculations of ref. [1] is rather poor for fixed values of  $C_1$ . We will present a new, improved version of that figure later on in this article.

Let us note here that using CNT, the (fitted values of) nucleus/liquid interfacial energy increase with  $T_{gr}$ , as shown in Fig. 1a for 5 silicate glass-formers that undergo internal homogeneous nucleation when properly heated:  $2\text{Na}_2\text{O}\cdot\text{CaO}\cdot\text{3SiO}_2$  (2N1C3S) [9],  $\text{Na}_2\text{O}\cdot\text{2CaO}\cdot\text{3SiO}_2$  (1N2C3S) [10–14],  $\text{Li}_2\text{O}\cdot\text{2SiO}_2$  (L2S) [15],  $44\text{Na}_2\text{O}\cdot\text{56SiO}_2$  (NS) [16],  $\text{BaO}\cdot\text{2SiO}_2$  (B2S) [17]. This increase results in a drop of the maximum nucleation rate for increasing  $T_{gr}$ . Additionally, the temperature dependence of  $C_1$  could also include some correction for the temperature term in Eq. (9), as the temperature evolution of the thermodynamic driving force could deviate from a linear law (to a variable degree) for different glasses.

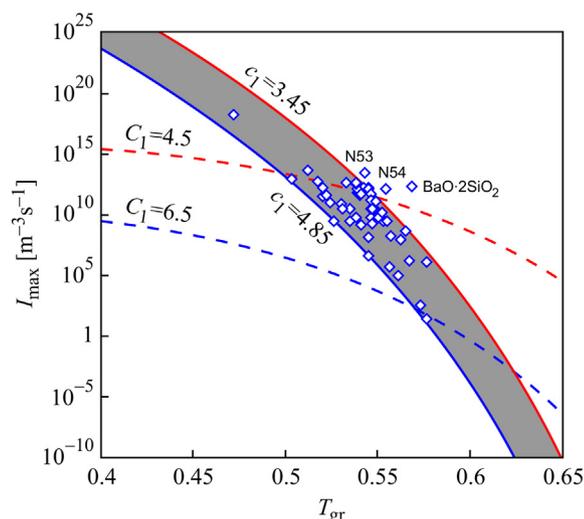
All these tendencies can be taken into account if we let the coefficient  $C_1$  increase with  $T_{gr}$ ; this is the only way to restore agreement between experimental nucleation rates and the predictions of CNT [18] when using the viscosity to replace the diffusion term,  $D(T)$ .

Fig. 1b shows that  $C_1$  depends on the reduced glass transition temperature of each material, hence we use a linear equation to fit to the data

$$C_1 = c_1 + \kappa(T_{gr} - 0.556) \quad (12)$$

For lithium disilicate,  $T_{gr} = 0.556$ , this value is introduced between the brackets of Eq. (12) for the sake of convenience, hence  $c_1 = C_1$  for this glass. Fig. 1b shows the values of  $C_1$  for the same 5 silicate glass-formers used in Fig. 1a, where the lines were calculated from Eqs. (12) and (13) with  $c_1 = 3.45$  and  $4.85$  and  $\kappa = 30.3$ . Note that the values of  $c_1$  and  $\kappa$  were determined from the set of experimental data for 51 silicate glasses (see Fig. 2 below).

Finally, combining Eqs. (7), (10) and (12) yields a simple expression for the maximum nucleation rate as a function of the reduced glass transition temperature:



**Fig. 2.** Maximum steady-state nucleation rate,  $I_{\max}$ , versus reduced glass transition temperature,  $T_{gr}$ . The symbols refer to experimental data of 54 silicate glasses (listed in the supplementary materials). The dashed lines were calculated in ref. [1] using constant values of  $C_1 = 4.5$  (top dashed red line) and  $C_1 = 6.5$  (bottom dashed blue line). The solid lines were calculated in this work for temperature dependent  $C_1$  (see Eqs. (12) and (13)), for  $c_1 = 3.45$  (top solid red line) and  $c_1 = 4.85$  (bottom solid blue line). The experimental errors in  $I_{\max}$  and  $T_{gr}$  are of the order of the symbol size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$I_{\max}(T_{gr}) \approx 10^{24} \exp\left\{-\frac{c_1 + \kappa(T_{gr} - 0.556)}{T_{gr}(1 - T_{gr})}\right\}; [\text{m}^{-3}\text{s}^{-1}] \quad (13)$$

where  $c_1$  and  $\kappa$  are the parameters that best fit the current experimental data. This is the main result of this article.

### 3. Discussion

Fig. 2 shows the maximum homogeneous steady-state nucleation rates,  $I_{\max}$ , versus reduced glass transition temperatures,  $T_{gr}$ , calculated with Eq. (13). The symbols refer to experimental data from several sources, tabulated in the supplementary materials. The dashed lines were calculated in ref. [1] for constant values of  $C_1 = 4.5$  (top dashed red line) and  $C_1 = 6.5$  (bottom dashed blue line); whereas the solid lines were calculated here using temperature dependent  $C_1$  according to Eq. (12), for  $c_1 = 3.45$  (top solid red line) and  $c_1 = 4.85$  (bottom solid blue line) – using the same value of  $\kappa = 30.3$ , for both lines. This variation in  $c_1$  reflects the fact that the melting entropies of most silicate crystals that undergo internal nucleation vary within 4R to 10R (Eqs. (11) and (12)).

Fig. 2 clearly shows that the  $I_{\max}$  strongly decreases with increasing  $T_{gr}$ , and that for  $T_{gr} > 0.6$  the steady-state nucleation rates become so low that it becomes very difficult to measure them in laboratory time/sample-size scales. It is also evident from Fig. 2 that the introduction of a temperature dependent  $C_1$  significantly improves the description and predicting power of the theoretical equations (compare the solid lines calculated in this work with the dashed lines of ref. [1]). Most of the 54 experimental data points are located closely or between the lines for  $c_1 = 3.45$  and  $c_1 = 4.85$ , except for the datum related to the  $\text{BaO}\cdot 2\text{SiO}_2$ , which undergoes nucleation of a metastable phase and has a very low  $\Delta S_m/R = 2.48$  (for comparison,  $\Delta S_m/R = 5.43$ , 5.61 and 6.76 for 2N1C3S, L2S and 1N2C3S, respectively); and also two data points, N53 and N54, referring to crystal nucleation of solid solution crystals in glasses with compositions close to  $\text{Na}_2\text{O}\cdot\text{CaO}\cdot 2\text{SiO}_2$  [19]. Let us note, however, that the lower border in Fig. 2 is well defined, whereas the upper curve is rather diffuse.

In the framework of the current calculations, which reasonably suppose that the temperature of nucleation rate maximum is close to the glass transition temperature, the effect of the  $T_{gr}$  on  $I_{\max}$  has a simple explanation. When  $T_g$  approaches  $T_m$ , that is,  $T_{gr}$  increases, the undercooling and thermodynamic driving force decrease, hence the thermodynamic barrier for nucleation increases at  $T_{\max} \approx T_g$ . Also, as shown in refs. [1, 2], the difference  $T_{\max} - T_g$  decreases with increasing  $T_{gr}$ . Thus, increasing  $T_{gr}$  results not only in an increase of the thermodynamic barrier for nucleation, but also in deceleration of the diffusion process.

The difference  $T_{\max} - T_g$  for most of these 54 glasses varies from  $-15$  to  $+35$  C. It is important to note that for  $\text{BaO}\cdot 2\text{SiO}_2$ ,  $T_{\max} = T_g + 20$  C (which leads to a smaller viscosity and a pre-exponential somewhat higher than the characteristic value calculated at  $T_g$ ). This composition has a relatively small  $\sigma$  (see Fig. 1a) and a very low  $\Delta S_m/R \sim 2.5$  and, finally, a metastable phase nucleates first in this material. This favorable combination of factors leads to an unusually high nucleation rate for the respective  $T_{gr}$  and explains the datum far outside the borders of Fig. 2.

Recently, Gupta et al. [2] have shown that the values of  $T_{\max}$  are located above or at  $T_g$  for  $T_{gr} < 0.6$ , but they are shifted below the respective  $T_g$  as the value of  $T_{gr}$  increases. This result indicates that the nucleation time-lags increase with  $T_{gr}$ , and (as shown here) the values of  $I_{\max}$  decrease with increasing  $T_{gr}$ . This combination of factors explains the well-known fact that only glasses with  $T_{gr} < 0.6$  display internal homogeneous nucleation in laboratory time/sample-size scales. It also explains the extremely low homogeneous nucleation rates, which result in the outstanding glass-forming ability for glasses with  $T_{gr} > 0.75$  – e.g. albite and  $\text{B}_2\text{O}_3$  – as shown recently by Zanotto and Cassar [20].

It should be noted that differences between the  $I_{\max}$  of different glasses for a given value of  $T_{gr}$  can reach 6 orders of magnitude, whereas a change of  $T_{gr}$  from 0.47 to 0.58 (for which experimental data are available) results in a drop of 17 orders of magnitude in  $I_{\max}$ ! This means that, at least in the case of silicate glasses, the effect of  $T_{gr}$  on  $I_{\max}$  is much stronger than that of other parameters, which usually also depend on  $T_{gr}$ . This trend can be most readily appreciated in Fig. S1 in the supplementary materials. Most likely, this result reflects the significant role of the strong bonded silicon-oxygen tetrahedra in the processes of crystallization and vitrification. Only an analysis with a large number of glasses of other families, for which the temperature dependence of the nucleation rate are known, as in the present case, will make it possible to confirm (or not) such trend. Unfortunately, however, such datasets are not yet available for other types of inorganic, metallic and organic glasses. Therefore, for the time being, our findings are restricted to silicate glasses.

### 4. Conclusions

We used the CNT, combined with the theoretical value of the pre-exponential constant and an average (temperature dependent) surface energy for silicate glass-formers, to derive an equation to estimate their maximum nucleation rates,  $I_{\max}$ , as a function of the reduced glass transition temperatures,  $T_{gr}$ . Our calculations describe the experimentally observed trend, in which  $I_{\max}$  strongly decreases with increasing  $T_{gr}$ , quite well. Moreover, in turn, this trend explains the fact that only glasses with  $T_{gr} < 0.6$  display measurable homogeneous nucleation in laboratory time/sample-size scales.

The model predictions are surprisingly good for 51 out of 54 compositions tested. A consequence of our analysis and resulting expression for  $I_{\max}(T_{gr})$  is that it can predict (within a couple of decades) the maximum homogeneous nucleation rate of silicate systems based solely on their  $T_{gr}$ . Therefore, it is now possible to choose glass-forming silicate compositions that show very low or very high homogeneous nucleation rates, as needed. Our model thus provides a very valuable tool for the design of ultra-stable glasses (against crystallization) or glass-

ceramics having high crystal nucleation rates.

## Acknowledgments

The authors would like to thank FAPESP – São Paulo Research Foundation, grant # 2013/007793-6 (Brazil) for the financial support of this work, V. Fokin is also grateful to the University of São Paulo, Brazil, for the Visiting Researcher Fellowship Grant # 2016.1.1376.18.4.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jnoncrysol.2018.08.002>.

## References

- [1] V.M. Fokin, E.D. Zanutto, J.W.P. Schmelzer, Homogeneous nucleation versus glass transition temperature of silicate glasses, *J. Non-Cryst. Solids* 321 (2003) 52–65, [https://doi.org/10.1016/S0022-3093\(03\)00089-9](https://doi.org/10.1016/S0022-3093(03)00089-9).
- [2] P.K. Gupta, D.R. Cassar, E.D. Zanutto, On the variation of the maximum crystal nucleation rate temperature with glass transition temperature, *J. Non-Cryst. Solids* 442 (2016) 34–39 <https://doi.org/10.1016/j.jnoncrysol.2016.03.024>.
- [3] K.F. Kelton, A.L. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology*, Pergamon, Amsterdam, 2010.
- [4] A.S. Abyzov, V.M. Fokin, A.M. Rodrigues, E.D. Zanutto, J.W.P. Schmelzer, Effect of elastic stress on the thermodynamic barrier for crystal nucleation, *J. Non-Cryst. Solids* 432 (2016) 325–333, <https://doi.org/10.1016/j.jnoncrysol.2015.10.029>.
- [5] V.M. Fokin, A.S. Abyzov, E.D. Zanutto, D.R. Cassar, A.M. Rodrigues, J.W.P. Schmelzer, Crystal nucleation in glass-forming liquids: Variation of the size of the “structural units” with temperature, *J. Non-Cryst. Solids* 447 (2016) 35–44 <https://doi.org/10.1016/j.jnoncrysol.2016.05.017>.
- [6] P.K. Gupta, D.R. Cassar, E.D. Zanutto, Role of dynamic heterogeneities in crystal nucleation kinetics in an oxide supercooled liquid, *J. Chem. Phys.* 145 (2016) 211920/1–211920/8 <https://doi.org/10.1063/1.4964674>.
- [7] A.S. Abyzov, V.M. Fokin, N.S. Yuritsyn, A.M. Rodrigues, J.W.P. Schmelzer, The effect of heterogeneous structure of glass-forming liquids on crystal nucleation, *J. Non-Cryst. Solids* 462 (2017) 32–40 <https://doi.org/10.1016/j.jnoncrysol.2017.02.004>.
- [8] I.S. Gutzow, J.W.P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*, Springer, Heidelberg, 2013.
- [9] A.M. Kalinina, V.N. Filipovich, V.M. Fokin, Stationary and non-stationary crystal nucleation rate in a glass of  $2\text{Na}_2\text{O}\cdot\text{CaO}\cdot 3\text{SiO}_2$  stoichiometric composition, *J. Non-Cryst. Solids* 388/39 (1980) 723–728, [https://doi.org/10.1016/0022-3093\(80\)90522-0](https://doi.org/10.1016/0022-3093(80)90522-0).
- [10] O.V. Potapov, V.M. Fokin, V.L. Ugolkov, L.Y. Suslova, V.N. Filipovich, Influence of  $\text{Na}_2\text{O}$  content on the nucleation kinetics in glasses of compositions close to the  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  stoichiometry, *Glass Phys. Chem.* 26 (2000) 27–32 <https://doi.org/10.1007/BF02731940>.
- [11] N.S. Yuritsyn, Nucleation of crystals in sodium-calcium-silicate glasses of the metasilicate section, *Glas. Phys. Chem.* 41 (2015) 112–115, <https://doi.org/10.1134/S1087659615010253>.
- [12] V.M. Fokin, E.D. Zanutto, J.W.P. Schmelzer, Method to estimate crystal/liquid surface energy by dissolution of subcritical nuclei, *J. Non-Cryst. Solids* 278 (2000) 24–34, [https://doi.org/10.1016/S0022-3093\(00\)00335-5](https://doi.org/10.1016/S0022-3093(00)00335-5).
- [13] G.A. Sycheva, Crystal growth and nucleation in glasses in the lithium silicate system, *J. Crystallization Process Technol.* 6 (2016) 29–55, <https://doi.org/10.4236/jcpt.2016.64004>.
- [14] C.J.R. Gonzalez-Oliver, P.F. James, Crystal nucleation and growth in a  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  glass, *J. Non-Cryst. Solids* 388/39 (1980) 699–704, [https://doi.org/10.1016/0022-3093\(80\)90518-9](https://doi.org/10.1016/0022-3093(80)90518-9).
- [15] M.L.F. Nascimento, V.M. Fokin, E.D. Zanutto, A.S. Abyzov, Dynamic processes in a silicate liquid from above melting to below the glass transition, *J. Chem. Phys.* 135 (2011) 194703/1–18, <https://doi.org/10.1063/1.3656696>.
- [16] V.M. Fokin, N.S. Yuritsyn, The nucleation and growth rates of sodium metasilicate crystals in sodium silicate glass  $44\text{N}_2\text{O}\cdot 56\text{SiO}_2$ , *Glass Phys. Chem.* 23 (1997) 236–239.
- [17] A.M. Rodrigues, *Diffusion Processes, Crystallization, and Viscous Flow in Barium Disilicate Glass*, Ph.D. Thesis Federal University of São Carlos, Brazil, 2014.
- [18] V.M. Fokin, E.D. Zanutto, N.S. Yuritsyn, J.W.P. Schmelzer, Homogeneous crystal nucleation in silicate glasses: A 40 years perspective, *J. Non-Cryst. Solids* 352 (2006) 2681–2714, <https://doi.org/10.1016/j.jnoncrysol.2006.02.074>.
- [19] E.N. Soboleva, N.S. Yuritsyn, V.L. Ugolkov, Kinetics of crystal nucleation of  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ -based solid solutions in glasses of the  $\text{Na}_2\text{SiO}_3\text{-CaSiO}_3$  pseudo-binary join, *Glas. Phys. Chem.* 30 (2004) 481–486 <https://doi.org/10.1007/s10720-005-0002-3>.
- [20] E.D. Zanutto, D.R. Cassar, The microscopic origin of the extreme glass-forming ability of albite and  $\text{B}_2\text{O}_3$ , *Sci. Rep.* 7 (2017) 43022, <https://doi.org/10.1038/srep43022>.