

DR. DANIEL ROBERTO CASSAR (Orcid ID : 0000-0001-6472-2780)

PROF. MARCIO LUIS FERREIRA NASCIMENTO (Orcid ID : 0000-0001-5030-7500)

Article type : Article

The diffusion coefficient controlling crystal growth in a silicate glass-former

Daniel Roberto Cassar¹, Alisson Mendes Rodrigues¹, Marcio Luis Ferreira Nascimento², Edgar Dutra Zanotto¹

¹ *CeRTEV, Department of Materials Engineering, Federal University of São Carlos, São Carlos, São Paulo, Brazil*

² *Vitreous Materials Lab., Department of Chemical Engineering, Polytechnic School, Federal University of Bahia, Rua Aristides Novis 2, Federação, 40210-630, Salvador, Bahia, Brazil*

daniel.r.cassar@gmail.com

1 Abstract

One of the most relevant open issues in glass science refers to our ignorance concerning the nature of the diffusing entities that control crystal nucleation and growth in non-crystalline materials. This information is very relevant because all the existing nucleation and growth equations account for the diffusion coefficient (D_U) of these unknown entities. In this article, we measured the shear viscosity (η) and the crystal growth rates of a supercooled diopside liquid ($\text{CaMgSi}_2\text{O}_6$) in a wide temperature range. The well-known decoupling of viscosity and crystal growth rates at deep supercoolings was detected. We tested and analyzed four different approaches to compute D_U , three existing and one proposed here. As expected, the classical approach ($D_U \sim \eta^{-1}$) and the

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/ijag.12319

This article is protected by copyright. All rights reserved.

fractional viscosity approach ($D_U \sim \eta^{-\epsilon}$) were not able to describe the crystal growth rates near the glass transition temperature. However, our proposed expression to calculate D_U —gradually changing from a viscosity-controlled to an Arrhenian-controlled process—was able to describe the available data in the whole temperature range and yielded the lowest uncertainty for the adjustable parameters. Our results suggest that viscous flow ceases to control the crystal growth process below the so-called decoupling temperature, corroborating some previous studies.

2 Introduction

Understanding and controlling crystal nucleation and growth in glass-forming liquids is a key issue either to avert crystallization¹ to produce a glass or for the development and production of glass-ceramics². Crystallization is such an important feature of glass-forming liquids that it has been the most frequently used keyword in the past 200 years of glass science^{3,4}, and *crystal growth* is a key part of the crystallization process.

However, one faces some adversities when studying the physics of crystal growth. One of the most relevant is our ignorance of what the *diffusing entities* (or *structural entities*)⁵ are that control this phenomenon⁶. The glass research community does not know if crystal growth kinetics is controlled by one chemical element (*e.g.* silicon, the network former) or a set of atoms (*e.g.* one or more silica tetrahedral) in the case of silicate glasses. We also do not know if the controlling entity is temperature-, pressure-, and/or structure-dependent. This information is relevant because the current crystal growth equations take into account the effective diffusion coefficient (D_U) of these unknown units.

What seems to be a consensus⁷⁻¹⁴ is that viscous flow is an adequate property to estimate D_U in a limited temperature range, which spans from the melting point down to the so-called decoupling temperature (T_d). This temperature has been reported for different substances^{11,12} to exceed the laboratory glass transition temperature by a factor of about 1.10 to 1.25.

In this article, we tested four different approaches to estimate D_U , one of them is proposed here for the first time. The test was carried out for a glass with diopside composition ($\text{CaMgSi}_2\text{O}_6$), for which we report a new dataset of viscosity and crystal growth rates. This particular composition was chosen because it has a plethora of available kinetic and thermodynamic data that were necessary to carry out the present analysis, and thus can be considered a “model” glass-former, similarly to what has been proposed for lithium disilicate¹³.

3 Literature review and governing equations

3.1 Crystal growth kinetics

Crystal growth rates in oxide glass-forming systems are usually analyzed by one of the three classical models: *normal growth*, *screw dislocation growth* or *2D secondary nucleation growth*¹⁵. Here, we focus on the *screw dislocation growth* model because it satisfactorily describes the experimental crystal growth data in supercooled diopside liquid in a wide temperature range¹⁴. Readers are invited to study Gutzow & Schmelzer’s book¹ for more detailed information on the different crystal growth mechanisms, and Cassar’s thesis¹⁶ for an in-depth analysis of the *normal* and *2D secondary nucleation growth* for diopside (briefly, these equations did not perform as well as the *screw dislocation growth* for this material).

The *normal* and *screw dislocation growth* modes are described by the same expression, Eq. (1). The difference between these two growth mechanisms is the fraction of sites (f) on the crystal interface available for atomic attachment. *Normal growth* prevails if this parameter is temperature independent and approximately unity (as proposed by Wilson¹⁷ in 1900). Otherwise, if $0 < f < 1$ and f is temperature dependent, the *screw dislocation* mechanism governs growth. This parameter can be estimated by Eq. (2) if one considers screw dislocations that form Archimedean spirals¹⁸ at the liquid–crystal interface.

$$U = f \frac{D_U}{d_0} \left[1 - \exp\left(-\frac{\Delta\mu}{RT}\right) \right] \quad (1)$$

$$f = \frac{d_0 \Delta\mu}{4\pi\sigma V_m} \quad (2)$$

In the above equations, U is the crystal growth rate, D_U is the effective diffusion coefficient controlling crystal growth, d_0 is the jump distance that some (unknown) *diffusing entities* or “structural units” must travel through the liquid to attach onto a growing crystal, σ is the crystal–liquid interfacial energy, R is the universal gas constant and V_m is the molar volume. The driving force for crystallization, $\Delta\mu$, for a closed system in an isobaric condition can be calculated^{19,20} using heat capacity data:

$$\Delta\mu(T) = \Delta H_m \left(1 - \frac{T}{T_m} \right) - \int_T^{T_m} (C_{p,l}(T) - C_{p,c}(T)) dT + T \int_T^{T_m} \frac{C_{p,l}(T) - C_{p,c}(T)}{T} dT, \quad (3)$$

where ΔH_m is the enthalpy of melting, $C_{p,l}$ is the heat capacity of the supercooled liquid, $C_{p,c}$ is the heat capacity of the crystal and T is the absolute temperature.

Finally, the latent heat released at the liquid–crystal interface during crystal growth can significantly increase the interface temperature if it is not dissipated fast enough (oxide liquids are poor heat conductors). Fortunately, Herron & Bergeron²¹ measured the temperature increase at the liquid–crystal interface during the crystal growth process in several oxide glass-formers. Cassar¹⁶ reanalyzed their data and obtained the following empirical expression:

$$\Delta T_i(T) = 10^{0.64} (U(T) \Delta H_m)^{0.58} \quad (4)$$

where ΔT_i is the liquid–crystal interface temperature increase at temperature T . In this expression, U is given in m/s and ΔH_m in J/mol. In this article, we corrected all the analyzed data for this increased interface temperature using Eq. (4).

3.2 The diffusion coefficient for crystal growth

As already stated, the mobility of the diffusing entities that control crystal growth is of major importance for crystal growth. The effective diffusion coefficient D_U represents the magnitude of this mobility, but the nature of the moving units in oxide glasses is not known. Authors^{9–14,22–24} have approached this problem differently, but our analysis indicates that they all use the following general phenomenological equation for D_U :

$$D_U = [x]^n \left[C \frac{T}{\eta^\xi} \right] + [1 - x]^q \left[D_0 \exp \left(-\frac{E_a}{RT} \right) \right]. \quad (5)$$

In the above equation, x is usually set to one (which makes the rightmost term of Eq. 5 equal to zero) or set to be temperature dependent (see Subsection 3.2.3 below), η is the viscosity and C , D_0 , E_a , ξ , n and q are constants. Please note that $C=C_E$ when Eyring's diffusion equation²⁵ is considered.

$$C_E = \frac{k_B}{d} \quad (6)$$

In the above equation, k_B is the Boltzmann constant and d is the diameter of the moving entity that controls viscous flow, usually assumed to be equal to d_0 .

This complex form of D_U (Eq. 5, proposed in this article) results from many attempts to describe D_U in the literature. These attempts will be described below, case by case. In this article, we test four possible expressions of D_U : three published approaches (Cases 1–3) and a new method (Case 4) suggested here. These D_U expressions will be used to fit Eq. (1) to experimental crystal growth rate data measured for a supercooled liquid with diopside composition ($\text{CaMgSi}_2\text{O}_6$), the four D_U expressions can be derived from the general equation (5).

3.2.1 Case 1: Classical D_U approach

In what we term the “classical” approach^{9–11,13,14,22,23}, the mobility of the diffusional units controlling crystal growth is linked to the equilibrium viscosity at all temperatures from the melting temperature (T_m) down to the laboratory glass transition temperature (T_g) and below. This is the simplest assumption from all the cases studied here, and it effectively considers that $n=\xi=x=q=1$, and

$\eta = \eta_{\text{eq}}$ in Eq. (5) (where η_{eq} is the equilibrium viscosity). The final expression for D_U in this case reads:

$$D_U = C \frac{T}{\eta_{\text{eq}}}. \quad (7)$$

Turnbull and Cohen²² were some the first to propose and use this method. More recently, however, several reports^{11,13} indicated that the viscosity is indeed a good parameter to calculate D_U for temperatures near T_m , but does not correctly describe the transport part of crystal growth rates at deep supercoolings, *i.e.*, temperatures near T_g . This observation is the basis of the so-called “decoupling” or “breakdown” of the Stokes–Einstein/Eyring equation that has been extensively discussed elsewhere^{11,13,14,23}.

Various equations describe the temperature dependence of the equilibrium viscosity of oxide glass-formers between T_m and T_g well. Here we use the MYEGA²⁶ expression:

$$\log_{10}(\eta_{\text{eq}}(T)) = \log_{10}(\eta_{\infty}) + \frac{T_g}{T} [12 - \log_{10}(\eta_{\infty})] \exp \left[\left(\frac{m}{12 - \log_{10}(\eta_{\infty})} - 1 \right) \left(\frac{T_g}{T} - 1 \right) \right], \quad (8)$$

where η_{∞} , T_g , and m are taken as adjustable parameters with the following definitions:

$$\eta_{\infty} = \lim_{T \rightarrow \infty} \eta_{\text{eq}}(T), \quad (9)$$

$$\eta_{\text{eq}}(T_g) = 10^{12} \text{ Pa.s}, \quad (10)$$

$$m = \left. \frac{d(\log_{10}(\eta_{\text{eq}}(T)))}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g}, \quad (11)$$

where m is known as the liquid fragility²⁷.

3.2.2 Case 2: D_U with fractional viscosity

In the fractional viscosity approach, Ediger *et al.*²⁴ considered a parameter ξ in the D_U expression that leads to a different temperature dependence of D_U on viscosity (Eq. 12). Their aim was to restore the agreement between crystal growth kinetics and viscous flow in the whole temperature range from T_m down to T_g . According to their approach, there is no decoupling of the Stokes–Einstein/Eyring equation, as observed in the classical approach (Case 1). They found that the higher the fragility of the liquid, the higher the deviation of ξ from unity is. This approach was recently re-

tested for some oxide liquids and challenged by Schmelzer *et al.*¹².

Based on the assumptions of this approach²⁴, we have that $n=x=q=1$, $\eta=\eta_{eq}$, and ξ becomes an adjustable parameter in Eq. (5). The final expression for D_U reads:

$$D_U = C \frac{T}{\eta_{eq} \xi}. \quad (12)$$

3.2.3 Case 3: D_U with viscosity plus an Arrhenian contribution

Schmelzer *et al.*¹² proposed another approach to calculate D_U by adding an additional Arrhenian diffusion term ($D_0 \exp\left(-\frac{E_a}{RT}\right)$) in the “classical” D_U equation. This is equivalent to setting $n=0$, $\xi=q=1$, and $\eta=\eta_{eq}$ in Eq. (5). With these approximations, the final expression for D_U is:

$$D_U = \left[C \frac{T}{\eta_{eq}} \right] + [1 - x] \left[D_0 \exp\left(-\frac{E_a}{RT}\right) \right]. \quad (13)$$

In their manuscript, Schmelzer *et al.*¹² used a hyperbolic tangent function for x :

$$x = \frac{1 + \tanh(\alpha)}{2}, \quad (14)$$

with

$$\alpha = \frac{T - T_d}{\phi T_d}. \quad (15)$$

In Eq. (15), ϕ is a dimensionless parameter that controls the smoothness of x and T_d is the decoupling temperature. The authors¹² considered ϕ as a fixed value equal to 0.06.

Due to the $[1-x]$ term on the right-hand side of Eq. (13), the Arrhenian diffusion term only becomes *significant* for temperatures near and below T_d . For temperatures sufficiently above T_d , Eq. (13) yields similar values to Eq. (7) (the classical approach).

A relevant property of Eq. (13) is that the equilibrium viscosity is used to evaluate D_U at *all temperatures*. That is, no matter how deep a material is cooled below its T_d , the equilibrium viscosity will still be an important parameter to calculate D_U . It will be clearer later on that this is the main difference between this approach and the one that we propose in this manuscript.

4 Materials and methods

4.1 Experimental

The diopside glass used in this research was obtained by the melt-quenching route. Melting was carried out in a bottom-loaded superkanthal electric furnace, model CM Bloomfield. The diopside batch used in this study is the same used by Reis^{28,29}. The chemical reagents used were CaCO₃ (J. T. Baker 99.9%, lot E06348), MgO (J. T. Baker 99.9%, lot E25597) and colloidal silica (Aldrich 99.8%, lot MKAA0249). The powders were heated at 673 K (CaCO₃ and MgO) and at 1173 K (SiO₂) for twelve hours for drying before weighing, and the mixture was homogenized in a Fritsch Pulverisette 6 low rotation mill with eight agate balls. The homogeneous mixture was heated at 1473 K for 48 h prior to melting to produce the diopside crystal phase via solid state reaction, and the diopside crystal was indeed confirmed by XRD²⁸ (JCPDS card 75-1577). Four hundred grams of this polycrystalline mass were melted in a platinum crucible at 1823 K for 15 min, cast into a metallic mold and annealed at 998 K ($\sim T_g$) for 240 min. The analyzed composition of the glass^{28,29} was 25.8 CaO, 18.6 MgO, and 55.4 wt% SiO₂ (with 0.2 wt% impurities). This result is very close to the nominal composition of stoichiometric diopside.

The viscosity and the crystal growth rates were measured isothermally at various temperatures using glass samples of the same batch. The viscosity of our glass near the glass transition temperature was measured at the Institute of Silicate Chemistry, Russian Federation, using a penetration viscometer, which is described elsewhere³⁰. We measured the viscosity using samples of the same batch near the melting point using a Brookfield Model DV-III rotational rheometer.

We measured the advancement rates of the surface crystallized layer using cubic samples of polished faces having an edge size of approximately 2 mm. We used three cubes for each studied temperature and all of them revealed a linear increment of the crystal layer depth l as a function of heat treatment time¹⁶ (this particular glass only shows surface nucleation in laboratory time/size scales). The slopes of $l \times$ time yielded the crystal growth rates, and for each temperature, we took the

average values measured for the three cubes. For the isothermal heat treatments, the samples were dropped inside a vertical furnace already stabilized at the desired temperature. This results in the fastest possible heating rate between room temperature and the treatment temperature.

We confirmed that a wollastonite-like phase (WL) appeared after a certain crystallized layer depth of diopside was reached, as shown and discussed by Fokin *et al.*^{31,32}. Therefore, in this study, we only measured the growth of the diopside crystal layer before this WL phase appeared. The wollastonite-like phase nucleates in the sample interior, just underneath the diopside crystal–liquid interface when a certain level of elastic stress is reached due to the different densities between the crystalline and liquid phases^{31,32}.

4.2 Calculations and data analysis

We analyzed our crystal growth data near and above T_g alongside data measured by Reis *et al.*²⁹ (using samples from this same diopside glass batch) and by Kirkpatrick *et al.*³³. Fortunately, the data from Kirkpatrick *et al.* are well above the temperature where the wollastonite-like phase transforms to diopside.

We calculated the thermodynamic driving force via Eq. (3), for which we used 334.57 J/K·mol for $C_{p,l}$ ³⁴, 137.7 kJ/mol for ΔH_m ³⁴, 1670 K for T_m ³⁴ and Eq. (16) for $C_{p,c}$ ³⁵ (with $C_{p,c}$ in J/K·mol and T in Kelvin):

$$C_{p,c} = 470 - 0.1T + \frac{2.45}{T^2} - 4820\sqrt{T} + 2.81 \times 10^{-5}T^2. \quad (16)$$

We adopted the expression used by Reinsch *et al.*²³, Eq. (17) for the calculation of the jumping distance d_0 from the liquid to the growing crystal interface. We obtained an equation for the molar volume of the liquid phase (Eq. 18, with V_m in m^3/mol and T in Kelvin) by a linear regression of the data reported by Lange³⁶ and Gottsmann & Dingwell³⁷. We assume that $d=d_0$ and $C=C_E$ throughout this manuscript, in agreement with similarly published research^{11–13,23}.

$$d_0 = \left(\frac{V_m}{N_A}\right)^{\frac{1}{3}} \quad (17)$$

$$V_m(T) = 7.01 \times 10^{-5} + 7.21 \times 10^{-9}T \quad (18)$$

We carried out all numerical analyses using the Python programming language with the Jupyter Notebook³⁸ interactive computational environment equipped with the free and open-source NumPy and SciPy modules³⁹. All nonlinear regressions were performed using the module LMFIT⁴⁰ using the Levenberg–Marquardt^{41,42} method. The plots were also generated using Python with the aid of the free and open-source matplotlib module⁴³. All the uncertainties reported in this manuscript are one standard deviation.

4.3 New approach to calculate D_U (Case 4)

Here we propose a new method to compute the effective diffusion coefficient, considering that D_U gradually changes from viscosity-controlled to Arrhenian-controlled.

As already mentioned, one important consideration of the approach of ref. [12] (Case 3) is that the equilibrium viscosity (or whatever mass transport mechanism that controls viscous flow) *always* takes some part in the diffusion process controlling crystal growth, even below T_d . Here we propose and test another possibility: that the equilibrium viscosity *gradually ceases* to control the crystal growth kinetics near and below T_d , *effectively* resulting in a “pure” Arrhenian behavior for temperatures sufficiently below T_d . To account for this behavior, we have set $n=\xi=q=1$ and $\eta=\eta_{eq}$ in Eq. (5). The final expression for D_U in this context is:

$$D_U = [x] \left[C \frac{T}{\eta_{eq}} \right] + [1 - x] \left[D_0 \exp\left(-\frac{E_a}{RT}\right) \right]. \quad (19)$$

We decided to use the same sigmoid function for x as employed in ref. [12]. However, after various tests, we settled with a lower value for ϕ for this case: 0.02. As already mentioned, ϕ controls the smoothness of the sigmoid function used for x . Using a lower value of ϕ results in a curve that has a sharper transition between viscosity-controlled to Arrhenian-controlled D_U . To be

clear, we used a value of $\phi = 0.06$ for the Case 3 calculations for two reasons: the authors¹² tested other values of ϕ and reported this one to be the one that best fitted their data; and to be able to compare our results with those published in ref. [12].

5 Results and Discussion

5.1 Experimental

Figure 1 shows the experimental viscosity data measured for the diopside liquid studied here. The continuous line is the regression of Eq. (8), from which we obtained the following values: $T_g = 1000.1(3)$ K, $m = 64.5(3)$, and $\log_{10}(\eta_\infty) = -1.80(4)$ (η_∞ in Pa.s).

Similarly, Figure 2 shows the experimental crystal growth rates obtained in this study together with data from Reis²⁸ (who used samples from the same batch used in this study) and Kirkpatrick³³.

All the experimental data obtained from this research are reported in Tables S.1 and S.2 as Supplementary Material.

5.2 Crystal growth analysis

5.2.1 Case 1

Figure 3 shows the regression of crystal growth rate data when D_U is given by the considerations in Case 1 (see Subsection 3.2.1). In this approach, we were not expecting a good fit for the data near T_g and this was precisely what we obtained. The regression gives a smaller residual near T_m when only data points to which $T \geq 1.1T_g$ are considered, see Figure 3b in comparison with Figure 3a. The rationale to eliminate the data points below the suspected T_d results from the fact that due to the suspected decoupling, the equilibrium viscosity would no longer describe the growth rates at such deep supercoolings.

Only one adjustable parameter is needed in this approach, the surface energy, σ . From the regressions, we obtained $\sigma = 0.16(2) \text{ J/m}^2$ and $\text{RMS}=0.42$ when all data points were considered (Figure 3a) and $\sigma = 0.22(1) \text{ J/m}^2$ and $\text{RMS}=0.44$ when only data points for which $T \geq 1.1T_g$ were considered (Figure 3b). These are reasonable values of surface energy (comparable to values reported from crystal nucleation studies of silicate glasses that undergo homogeneous nucleation^{44,45}).

5.2.2 Case 2

Figure 4 shows the regression curve of crystal growth rate data when D_U is calculated by the considerations of Case 2 (Subsection 3.2.2). Even though the data near T_m are reasonably well described in this approach, all the available data below 1300 K systematically deviate from the regression curve. Our observation is in agreement with recent critiques of this approach. Two adjustable parameters are needed for this approach: σ and ξ . Our regression yielded $\sigma = 0.20(3) \text{ J/m}^2$ and $\xi = 0.95(1)$, with $\text{RMS}=0.31$.

5.2.3 Case 3

Figure 5 shows the regression curve fitted to crystal growth rate data when D_U is calculated by the considerations in Case 3 (Subsection 3.2.3). It can be readily seen that all crystal growth data are well described by the fit, including the data near T_g . Four adjustable parameters are needed for this approach: σ , E_a , D_0 , and T_d . Our regression yielded $\sigma = 0.26(4) \text{ J/m}^2$, $E_a = 640(60) \text{ kJ/mol}$, $\ln(D_0) = 31(7)$, and $T_d = 1040(140) \text{ K}$, with $\text{RMS}=0.11$ (D_0 in m^2/s).

5.2.4 Case 4

Figure 6 shows the overall results of the new approach suggested here, *i.e.* the regression of crystal growth rate data when D_U is calculated following the considerations of Case 4 (Subsection 4.3). Similarly, as in the previous case, all available data are well described by the regression. The same four adjustable parameters are needed for this approach: σ , E_a , D_0 , and T_d . Our regression

yielded $\sigma = 0.223(9) \text{ J/m}^2$, $E_a = 650(50) \text{ kJ/mol}$, $\ln(D_0) = 31(6)$, and $T_d = 1100(30) \text{ K}$, with $\text{RMS}=0.11$ (D_0 in m^2/s).

5.3 Comparison of D_U expressions

From the four different expressions for D_U studied here, two were unable to describe crystal growth data near the glass transition temperature: the *classical* approach (Case 1) and the *fractional viscosity* approach (Case 2). These are expected results due to the breakdown of the Stokes–Einstein/Eyring equation at T_d , in agreement with former publications in the field^{11,13}. Both cases had a similar performance for fitting data near the melting temperature, but Case 1 has fewer adjustable parameters. Our results for Case 1 show that viscosity can indeed describe the kinetic part of crystal growth at relatively low supercoolings for $T > T_d$ and it may be used when the available or studied data is above the decoupling temperature.

We repeated the analysis for the approach of Schmelzer et al.¹², i.e., D_U expression *with viscosity plus an Arrhenian contribution* (Case 3). As far as we know, this is the first independent study to use this expression after its publication, making this a consistency test. Within this framework, we obtained a T_d value of 1,040(140) K which is statistically equal to the value (1,100 K) reported in their manuscript (they the notation \tilde{T}_d for this parameter). However, we obtained a value of 640(60) kJ/mol for E_a , which is higher than the reported¹² value of 480 kJ/mol. Unfortunately, they did not report the uncertainty for these two parameters. It is possible that both E_a values are statistically equal within the uncertainty, but we cannot be sure. D_0 and σ were not reported.

We also proposed and tested a new approach to this same problem: D_U *undergoing a gradual change from viscosity-controlled to Arrhenian-controlled* (Case 4). This approach fitted well all the available data, with very similar residuals and RMS as in Case 3. This approach also has the same four adjustable parameters as Case 3: σ , D_0 , T_d , and E_a . However, we observed that Case 4 has a clear advantage over Case 3: the uncertainty in T_d is more than five times lower. This is important because

some recent analysis¹² rely on computations that depend on the value of T_d (e.g., to obtain the viscosity at the decoupling temperature) and high uncertainty in T_d can jeopardize this type of analysis. We thus defend that the D_U given by Case 4 has the clear advantage of yielding a lower uncertainty in T_d than the value obtained in Case 3.

The main difference between these two cases is that Case 3 assumes that *equilibrium viscosity* should be accounted to compute D_U , even for temperatures below T_d , whereas Case 4 assumes that viscosity ceases to be a controlling factor in this process below T_d . At this stage, we cannot conclude which one (Case 3 or Case 4) is the best for the physical description of the decoupling phenomenon. In this context, Gillot et al.⁵ studied a diopside glass made via sol-gel and strongly defended that crystallization is *not* controlled by a bulk transport mechanism at deep supercooling (close to the glass transition temperature).

Mathematically, the difference between cases 3 and 4 lies in the value of n (see Eq. 5), which is 0 for the first and 1 for the second. It is possible, however, to set the value of n to any real number between 0 and 1. This changes the shape of the function x^n as can be seen in Figure S.1 of the Supplementary Material. From Eq. (5) we have that when $x^n=1$ viscous flow is controlling D_U and when $x^n=0$ viscous flow no longer controls it. If the shape of x^n changes, then the temperature range at which viscous flow ceases to control D_U also changes. We stress, however, that this “fine-tuning” of the parameter n is currently not possible or supported by the available data.

An open and relevant question is to find out exactly what type of diffusing entities control viscous flow and crystal growth below T_d . For this task, computer simulations, *in-situ* high temperature structural studies between T_g and T_m (e.g., by Raman spectroscopy or NMR), and precise measurements of the diffusion coefficients of the slowest species (Si and O in silicate glasses) are greatly needed to shed light on this very important, intriguing phenomenon.

6 Summary and Conclusions

We carefully measured the viscosity and crystal growth rates in a wide temperature range (extending the available data and knowledge in this field) using samples from the *same batch* of a stoichiometric diopside glass. This approach is much cleaner and rigorous than using samples from distinct batches, as is commonly done when literature data is used for analyses of kinetic processes. Also, we avoided measuring the crystallization rates of the (spurious) wollastonite-like phase.

The well-known decoupling between viscosity and crystal growth rates at deep supercoolings was detected. We tested and thoroughly analyzed four different approaches to compute the effective diffusion coefficient controlling crystal growth, a key parameter controlling the crystallization kinetics that cannot be measured experimentally. As expected, the classical approach and the fractional viscosity approach were not able to describe the crystal growth rates at deep supercoolings near the glass transition temperature. Overall, the approach proposed here (Case 4)—which assumes that D_U gradually changes from a viscosity-controlled to an Arrhenian-controlled process—was able to describe the available crystal growth rate data in the whole temperature range and yielded the lowest uncertainty among the 4 cases. This result supports the concept that viscous flow ceases to control the crystal growth process below the decoupling temperature.

Acknowledgements

We would like to thank Drs. A. J. Barbosa and R. C. M. V. Reis for making the diopside glass used in this study and Dr. Vladimir M. Fokin for his critical and constructive insights. We are grateful to the São Paulo Research Foundation, FAPESP, grant numbers 2011/18941-0 and 2013/07793-6 (CEPID) and The Brazilian National Research Council, CNPq grant no. 150490/2015-1, and no. 201983/2015-0 for fellowships to DRC and AMR.

References

- (1) Zanotto, E. D.; Cassar, D. R. The Microscopic Origin of the Extreme Glass-Forming Ability of Albite and B₂O₃. *Scientific Reports* **2017**, *7*, 43022.
- (2) Zanotto, E. D. A Bright Future for Glass-Ceramics. *American Ceramic Society Bulletin* **2010**, *89*, 19–27.
- (3) Mauro, J. C.; Zanotto, E. D. Two Centuries of Glass Research: Historical Trends, Current Status, and Grand Challenges for the Future. *International Journal of Applied Glass Science* **2014**, *5*, 313–327.
- (4) Nascimento, M. L. F.; Zanotto, E. D. On the First Patents, Key Inventions and Research Manuscripts about Glass Science & Technology. *World Patent Information* **2016**, *47*, 54–66.
- (5) Gillot, J.; Roskosz, M.; Leroux, H.; Capet, F.; Roussel, P. Crystallization of Amorphous Silicates far from Equilibrium Part II: Experimental Insight into the Key Role of Decoupled Cation Mobilities. *Journal of Non-Crystalline Solids* **2011**, *357*, 3467–3473.
- (6) Cassar, D. R.; Lancelotti, R. F.; Nuernberg, R.; Nascimento, M. L. F.; Rodrigues, A. M.; Diz, L. T.; Zanotto, E. D. Elemental and Cooperative Diffusion in a Liquid, Supercooled Liquid and Glass Resolved. *The Journal of Chemical Physics* **2017**, *147*, 014501.
- (7) Schmelzer, J. W. P.; Potapov, O. V.; Fokin, V. M.; Müller, R.; Reinsch, S. The Effect of Elastic Stress and Relaxation on Crystal Nucleation in Lithium Disilicate Glass. *Journal of Non-Crystalline Solids* **2004**, *333*, 150–160.
- (8) Mapes, M. K.; Swallen, S. F.; Ediger, M. D. Self-Diffusion of Supercooled O-Terphenyl near the Glass Transition Temperature. *The Journal of Physical Chemistry B* **2006**, *110*, 507–11.
- (9) Nascimento, M. L. F.; Zanotto, E. D. Mechanisms and Dynamics of Crystal Growth, Viscous Flow, and Self-Diffusion in Silica Glass. *Physical Review B* **2006**, *73*, 024209.
- (10) Nascimento, M. L. F.; Zanotto, E. D. Diffusion Processes in Vitreous Silica Revisited. *Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B* **2007**, *48*, 201–217.
- (11) Nascimento, M. L. F.; Zanotto, E. D. Does Viscosity Describe the Kinetic Barrier for Crystal Growth from the Liquidus to the Glass Transition? *The Journal of Chemical Physics* **2010**, *133*, 174701.
- (12) Schmelzer, J. W. P.; Abyzov, A. S.; Fokin, V. M.; Schick, C.; Zanotto, E. D. Crystallization in Glass-Forming Liquids: Effects of Decoupling of Diffusion and Viscosity on Crystal Growth. *Journal of Non-Crystalline Solids* **2015**, *429*, 45–53.
- (13) Nascimento, M. L. F.; Fokin, V. M.; Zanotto, E. D.; Abyzov, A. S. Dynamic Processes in a Silicate Liquid from above Melting to below the Glass Transition. *The Journal of chemical physics* **2011**, *135*, 194703–194703–194717.

- (14) Nascimento, M. L. F.; Ferreira, E. B.; Zanotto, E. D. Kinetics and Mechanisms of Crystal Growth and Diffusion in a Glass-Forming Liquid. *The Journal of chemical physics* **2004**, *121*, 8924–8928.
- (15) Gutzow, I. S.; Schmelzer, J. W. P. *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*; Springer: London, 2013.
- (16) Cassar, D. R. Crystal nucleation, growth, relaxation and viscous flow in diopside and lithium diborate glasses. Ph.D. thesis, Universidade Federal de São Carlos: São Carlos, 2014.
- (17) Wilson, H. A. XX. On the Velocity of Solidification and Viscosity of Super-Cooled Liquids. *Philosophical Magazine Series 5* **1900**, *50*, 238–250.
- (18) Burton, W.-K.; Cabrera, N.; Frank, F. C. The Growth of Crystals and the Equilibrium Structure of Their Surfaces. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences* **1951**, *243*, 299–358.
- (19) Kelton, K. F. Crystal Nucleation in Liquids and Glasses. In *Solid State Physics*; Ehrenreich, H.; Turnbull, D., Eds.; Academic Press: Berlin, 1991; Vol. Volume 45, pp. 75–177.
- (20) Cassar, D. R. Crystallization Driving Force of Supercooled Oxide Liquids. *International Journal of Applied Glass Science* **2016**, *7*, 262–269.
- (21) Herron, L. W.; Bergeron, C. G. Measurement of Melt-Crystal Interface Temperature during Crystallization in Melts of Binary Borate Glasses. *Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B* **1978**, *19*, 89–94.
- (22) Turnbull, D.; Cohen, M. H. Crystallization Kinetics and Glass Formation. In *Modern aspects of the vitreous state*; MacKenzie, S. D., Ed.; 1960; Vol. 1, pp. 38–62.
- (23) Reinsch, S.; Nascimento, M. L. F.; Müller, R.; Zanotto, E. D. Crystal Growth Kinetics in Cordierite and Diopside Glasses in Wide Temperature Ranges. *Journal of Non-Crystalline Solids* **2008**, *354*, 5386–5394.
- (24) Ediger, M. D.; Harrowell, P.; Yu, L. Crystal Growth Kinetics Exhibit a Fragility-Dependent Decoupling from Viscosity. *The Journal of chemical physics* **2008**, *128*, 034709.
- (25) Eyring, H. Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates. *The Journal of Chemical Physics* **1936**, *4*, 283–291.
- (26) Mauro, J. C.; Yue, Y.; Ellison, A. J.; Gupta, P. K.; Allan, D. C. Viscosity of Glass-Forming Liquids. *Proceedings of the National Academy of Sciences of the United States of America* **2009**, *106*, 19780–19784.
- (27) Angell, C. A. Strong and Fragile Liquids. In *Relaxation in complex systems*; Ngai, K. L.; Wright, G. B., Eds.; Naval Research Laboratory: Springfield, 1985; pp. 3–12.
- (28) Reis, R. M. C. V. Assessments of viscous sintering models and determination of crystal growth rate and crystallized fraction in glasses. Ph.D. thesis, Universidade Federal de São Carlos: São Carlos, 2012.

- Accepted Article
- (29) Reis, R. M. C. V.; Fokin, V. M.; Zanotto, E. D. Determination of Crystal Growth Rates in Glasses Over a Temperature Range Using a Single DSC Run. *Journal of the American Ceramic Society* **2016**, *99*, 2001–2008.
- (30) Klyuev, V. P. Indenter-Penetration Viscometry of Glasses for Small-Sized Samples under Conditions of Continuous Heating. *Glass Physics and Chemistry* **2000**, *26*, 559–565.
- (31) Fokin, V. M.; Abyzov, A. S.; Schmelzer, J. W. P.; Zanotto, E. D. Stress Induced Pore Formation and Phase Selection in a Crystallizing Stretched Glass. *Journal of Non-Crystalline Solids* **2010**, *356*, 1679–1688.
- (32) Abyzov, A. S.; Schmelzer, J. W. P.; Fokin, V. M. Theory of Pore Formation in Glass under Tensile Stress: Generalized Gibbs Approach. *Journal of Non-Crystalline Solids* **2011**, *357*, 3474–3479.
- (33) Kirkpatrick, R. J.; Robinson, G. R.; Hays, J. F. Kinetics of Crystal Growth From Silicate Melts: Anorthite and Diopside. *Journal of Geophysical Research* **1976**, *81*, 5715–5720.
- (34) Richet, P.; Bottinga, Y. Anorthite, Andesine, Wollastonite, Diopside, Cordierite and Pyrope: Thermodynamics of Melting, Glass Transitions, and Properties of the Amorphous Phases. *Earth and Planetary Science Letters* **1984**, *67*, 415–432.
- (35) Krupka, K. M.; Hemingway, B. S.; Robie, R. A.; Kerrick, D. M. High-Temperature Heat Capacities and Derived Thermodynamic Properties of Anthophyllite, Diopside, Dolomite, Enstatite, Bronzite, Talc, Tremolite, and Wollastonite. *American Mineralogist* **1985**, *70*, 261–271.
- (36) Lange, R. A. A Revised Model for the Density and Thermal Expansivity of K₂O-Na₂O-CaO-MgO-Al₂O₃-SiO₂ Liquids from 700 to 1900 K: Extension to Crustal Magmatic Temperatures. *Contrib Mineral Petrol* **1997**, *130*, 1–11.
- (37) Gottsmann, J.; Dingwell, D. B. Supercooled Diopside Melt: Confirmation of Temperature-Dependent Expansivity Using Container-Based Dilatometry. *Contrib Mineral Petrol* **2000**, *139*, 127–135.
- (38) Pérez, F.; Granger, B. E. IPython: A System for Interactive Scientific Computing. *Computing in Science & Engineering* **2007**, *9*, 21–29.
- (39) Oliphant, T. E. Python for Scientific Computing. *Computing in Science & Engineering* **2007**, *9*, 10–20.
- (40) Newville, Matthew; Stensitzki, Till; Allen, Daniel B.; Ingargiola, Antonino. LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python. **2014**.
- (41) Levenberg, K. A Method for the Solution of Certain Non-Linear Problems in Least Squares. *Quart. App. Math.* **1944**, *2*, 164–168.
- (42) Marquardt, D. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *Journal of the Society for Industrial and Applied Mathematics* **1963**, *11*, 431–441.

- (43) Hunter, J. D. Matplotlib: A 2D Graphics Environment. *Computing in Science & Engineering* **2007**, *9*, 90–95.
- (44) Zanutto, E. D.; Fokin, V. M. Recent Studies of Internal and Surface Nucleation in Silicate Glasses. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **2003**, *361*, 591–613.
- (45) Fokin, V. M.; Zanutto, E. D.; Schmelzer, J. W. P. Homogeneous Nucleation versus Glass Transition Temperature of Silicate Glasses. *Journal of Non-Crystalline Solids* **2003**, *321*, 52–65.

Figure caption list

Figure 1 Viscosity data and regression curve with Eq. (8), which covers very wide ranges of viscosity and temperatures. Data obtained for the same batch of diopside glass used for crystal growth.

Figure 2 Experimental crystal growth rates (U) obtained from this study together with data from Reis²⁸ (sample H from their study, using specimens of the same glass batch used here) and from Kirkpatrick³³.

Figure 3 Regression curve of crystal growth rate data with D_U considering Case 1 taking into account (a) all data points and (b) only data for $T \geq 1.1T_g$.

Figure 4 Regression curve of crystal growth rate data with D_U considering Case 2.

Figure 5 Regression curve of crystal growth rate data with D_U considering Case 3.

Figure 6 Regression curve of crystal growth rate data with D_U considering Case 4.













