



Crystallization in glass-forming liquids: Effects of decoupling of diffusion and viscosity on crystal growth



Jörn W.P. Schmelzer^{a,*}, Alexander S. Abyzov^b, Vladimir M. Fokin^{c,d}, Christoph Schick^a, Edgar D. Zanotto^d

^a Institut für Physik der Universität Rostock, Wismarsche Strasse 43–45, 18057 Rostock, Germany

^b National Science Center, Kharkov Institute of Physics and Technology, 61108 Kharkov, Ukraine

^c Vavilov State Optical Institute, ul. Babushkina 36–1, 193 171 St. Petersburg, Russia

^d Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13565–905, São Carlos-SP, Brazil

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ABSTRACT

The effect of decoupling of viscosity and diffusion, i.e. of the breakdown of the Stokes–Einstein–Eyring equation, on crystal growth processes is analyzed. A criterion is formulated which gives the possibility to establish, based exclusively on experimentally measurable data, whether and at which temperature decoupling occurs in a given system. The results of our analysis are compared with alternative approaches. A theoretical model is advanced allowing one to describe the crystal growth kinetics in the whole temperature range where crystallization may proceed, i.e., between the absolute zero and the melting or liquidus temperature. A relation is derived allowing one to correlate the decoupling temperature with the glass transition temperature, and the fragility of the liquid. The results are confirmed by experimental data.

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1. Introduction

Crystallization is a very important process in glass technology, since the rates of crystal nucleation and growth of glass-forming melts determine whether a given liquid can be easily vitrified or will likely crystallize on cooling. Crystallization is also the controlling step for the study and development of glass-ceramics. By these reasons, an adequate knowledge of the laws describing nucleation and crystal growth is of outstanding importance [1,2,3,4,5].

To describe the processes of phase formation and their evolution, the classical theories of nucleation and growth are widely employed [2,3,6,7]. In theoretical analyses, the Stokes–Einstein–Eyring (SEE) equation is frequently utilized. This relation allows one to replace the effective diffusion coefficients, D , governing nucleation and growth by the Newtonian viscosity, $\eta(T)$, via $D \propto (1/\eta)$. For one-component liquids, D denotes the diffusion coefficient of the ambient phase particles in the liquid, for multi-component systems it can be expressed via the partial

diffusion coefficients of the different components and their molar fractions in the liquid [8]. Further-on, we will omit the term effective in referring to the diffusion coefficient.

It is well-known, however, that at a certain temperature denoted as decoupling temperature, T_d , decoupling of diffusion and viscosity takes place, an intriguing phenomenon leading to the breakdown of the SEE relation [9,10,11,12]. Consequently, to appropriately describe experimental crystallization rate data for any given melt, one has to know the value of T_d and to develop a theory that allows the formulation of crystal nucleation and growth equations that appropriately account for decoupling effects. The present analysis is devoted to this circle of topics concentrating on the effect of decoupling on crystal growth. Since the state of the critical clusters in nucleation may be different from that of the newly evolving crystal phase and depend on the size of the crystallites [3,6], decoupling of viscosity and diffusion in nucleation may take place in a different temperature range (cf. also [13]). Decoupling in nucleation will be studied in more detail in a forthcoming contribution.

The paper is structured as follows: In Section 2, the classical equations for the description of crystal growth are formulated. In Section 3, a criterion is developed that allows one to determine, for a given melt, based exclusively on directly measurable data, whether and at which

* Corresponding author.

E-mail address: juern-w.schmelzer@uni-rostock.de (J.W.P. Schmelzer).

temperature decoupling of diffusion and viscosity occurs in crystal growth. The results of our analysis are compared with alternative approaches, in particular, with the approach developed recently by Ediger et al. [10]. In Section 4, a theoretical model is advanced and tested giving the possibility to describe the crystal growth kinetics in the whole temperature range where crystallization may proceed. In addition, in Section 5 a relation is derived connecting decoupling and glass transition temperatures with liquid fragility. These estimates are verified by comparison with experimental data. A discussion of the results and possible developments (Section 6) completes the analysis.

2. Basic equations

In the present section we summarize the basic equations which serve as the starting point for further analysis (for details see [14,15]). For the macroscopic linear growth rate, u , we use the commonly employed relation [16,17,18]

$$u = f \frac{D}{4d_0} \left[1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right], \quad (1)$$

where f ($0 < f \leq 1$) is a parameter that has different values for different modes of growth, k_B is the Boltzmann constant, T the absolute temperature, d_0 a characteristic size parameter that is determined by the particle number density, $c = (1/d_0^3)$, of the basic units of the ambient phase, D the diffusion coefficient governing the processes of aggregation of ambient phase particles to the crystalline phase. The diffusion coefficient is expressed as [3,12]

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right), \quad (2)$$

where $E_D = E_D(T)$ is the activation energy for diffusion and D_0 a kinetic pre-factor weakly dependent on temperature. For analytical estimates and numerical illustrations, we express the thermodynamic driving force, $\Delta\mu$, for growth in its simplest form as

$$\Delta\mu = q \left(1 - \frac{T}{T_m} \right), \quad q = T_m \Delta s_m, \quad (3)$$

where q ($q > 0$) is the latent heat of crystallization per particle and Δs_m is the melting entropy per particle at the equilibrium melting temperature, T_m . This equation was widely employed by some of the founders of the classical theory of crystal nucleation and growth processes, M. Volmer, Ya. I. Frenkel, and D. Turnbull.

In applications of the classical theory of crystal growth to glass-forming liquids, the diffusion coefficient, D , governing nucleation and growth is usually not known and is thus frequently estimated via the SEE relation [3]:

$$D \cong D_\eta = \gamma \frac{k_B T}{d_0 \eta}. \quad (4)$$

This equation allows one to replace the diffusion coefficient, D , by the inverse of the Newtonian viscosity, η . The parameter γ is a constant. Its value depends on the theoretical approach employed and the approximations made in the derivation [3] and on the specification of the size parameter, d_0 , of the basic moving molecular units of the melt. Provided Eq. (4) holds, D can be replaced by the inverse of the viscosity, which in turn can be described by a relation similar to Eq. (2)

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{k_B T}\right), \quad (5)$$

where $E_\eta(T)$ is the activation energy of viscous flow which frequently depends on temperature. In this limiting case (when Eq. (4) holds), we have

$$E_D(T) = E_\eta(T). \quad (6)$$

For glass-forming liquids, the temperature dependence of the activation energy for viscous flow, $E_\eta(T)$, can be obtained by experiment via measurements of the liquid viscosity as a function of temperature.

3. Decoupling of diffusion and viscosity: experimental test

3.1. Decoupling parameter

As we have already mentioned, the replacement of the diffusion coefficient by viscosity according to Eq. (4) is quite accurate in the description of the crystal growth kinetics at temperatures near to the melting or liquidus temperature ($T_d < T < T_m$) but often fails at high undercoolings [9,10,11] due to a decoupling of diffusion and viscosity. Consequently, in applications of the theory, it is of interest to verify whether a given melt undergoes such decoupling within the range of temperatures considered in the experiment.

As a measure of the deviation of the diffusion coefficient, D , from its approximation, D_η (when the diffusion coefficient is expressed by the inverse of viscosity according to Eq. (4)), we may employ a decoupling parameter, Π_{dec} , here defined by

$$\Pi_{dec} = \frac{D}{D_\eta}. \quad (7)$$

This parameter is unity when Eq. (4) holds and becomes larger than one if diffusion and viscosity (or structural relaxation) are governed by different molecular processes. Advancing proposals formulated in [10, 19] to verify, exclusively based on experimentally measurable data, whether decoupling of diffusion and viscosity occurs in a given melt, we utilize Eqs. (3), (4), and (7) to replace D by the diffusion-controlled crystal growth rate, u , and D_η by the inverse of the Newtonian viscosity via Eq. (4). We thus obtain

$$\Pi_{dec} = \frac{D}{D_\eta} = \frac{4d_0^2}{\gamma f k_B T \left[1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right]} (u\eta). \quad (8)$$

The ratio $(\Delta\mu/k_B T)$ is equal to zero at the melting or liquidus temperature and increases monotonically with decreasing temperature. Consequently, with decreasing temperature, below a certain reference temperature, T_{ref} , the exponential term within the square brackets in Eq. (8) becomes very small compared with one. This reference temperature, T_{ref} , we define by

$$\frac{\Delta\mu(T_{ref})}{k_B T_{ref}} = e, \quad e = 2.718\dots \quad (9)$$

This reference temperature is located near T_m and the SEE relation is a sufficiently accurate approximation at $T \geq T_{ref}$. This result is confirmed by a variety of investigations and, in particular, by the study of the particular melts analyzed in detail in the present paper.

Having defined the reference temperature, we can also introduce the reduced decoupling parameter

$$\Pi_{dec}^{red} = \frac{\Pi_{dec}(T)}{\Pi_{dec}(T_{ref})}, \quad (10)$$

which, in the range of $T \leq T_{ref}$, can be expressed in the form

$$\Pi_{dec}^{red} = \left(\frac{T_{ref} f(T_{ref})}{T f(T)} \right) \left(\frac{u(T)\eta(T)}{u(T_{ref})\eta(T_{ref})} \right) \quad \text{at} \quad T \leq T_{ref}. \quad (11)$$

The description of crystal growth in different glass-forming systems and beyond is, of course, a very complicated problem with many facets [3,17,18]. We consider here mainly the three most important modes of growth for the systems under consideration, continuous or normal growth, dislocation mediated growth, and two-dimensional nucleation mediated growth. A detailed analysis of these different modes of growth in application to the systems under consideration was performed in [3], summarizing existing research on this topic. The general conclusion is that for the growth kinetics of glass-forming melts, mainly normal or dislocation mediated growth is of relevance, growth mediated by two-dimensional nucleation dominates only in exceptional cases when special precautions are undertaken. By this reason, we can restrict here the considerations to normal and dislocational growth modes. In the first case, the parameter f has values near to one. For growth mediated by dislocations, f can be expressed as $f \cong (T_m - T)/(2\pi T_m)$. In both these cases (and also beyond with a variety of modifications of expressions for this parameter f), the temperature dependence of the parameter f is weak as compared with the exponential terms introduced into Eq. (11) via viscosity and diffusion coefficient. By mentioned reasons, we may express Eq. (11) to a good approximation as

$$\Pi_{dec}^{red} \cong \left(\frac{u(T)\eta(T)}{u(T_{ref})\eta(T_{ref})} \right) \quad \text{at} \quad T \leq T_{ref}. \quad (12)$$

Similar to the decoupling parameter Π_{dec} introduced by Eq. (7), the reduced decoupling parameter, Π_{dec}^{red} , is equal to one when the SEE relation holds and deviates from one when decoupling of viscosity and diffusion occurs. The latter relation has, however, one great advantage; it can be computed by employing only directly measurable properties of the sample under consideration, i.e., viscosities and crystal growth rates. And there is no need to specify the mode of growth (cf. also [11]). Note as well that instead of the reference temperature specified by Eq. (9), one could also use any temperature in the range $T_d < T < T_{ref}$ as the reference temperature for the computations. Such modification would not change the results of determination of T_d . This fact underlines once again the statement that the omission of the term $(T_{ref} f(T_{ref})/T f(T))$ in the transition from Eq. (11) to Eq. (12) is of no relevance for the determination of the decoupling temperature and related quantities. Since T_{ref} can be also chosen to have a value near to T_d in the considered interval, this term is then near to T_d nearly equal to one.

The results of such computations of the decoupling parameter for different glass-forming liquids are presented in Fig. 1. In this figure, the

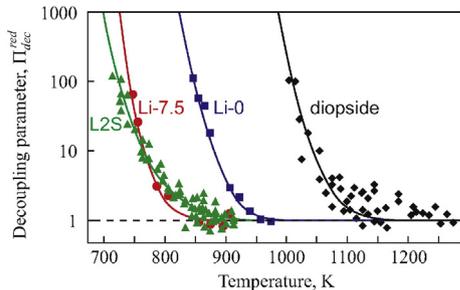


Fig. 1. Reduced decoupling parameter Π_{dec}^{red} versus temperature for glasses of compositions in mol% 16.4Na₂O·33.3CaO·50.3SiO₂ (Li-0), 14.8Na₂O·29.0CaO·48.7SiO₂·7.5Li₂O (Li-7.5), lithium disilicate (L2S), and diopside (CaO·MgO·2SiO₂). The values of crystal growth rates and viscosity were taken from [13,19,20,21,22]. The circles and squares were computed based on experimental data via Eq. (11). The full curves were drawn employing Eqs. (25)–(28).

reduced decoupling parameter Π_{dec}^{red} estimated using Eqs. (9) and (12) is shown as a function of temperature for 16.4Na₂O·33.3CaO·50.3SiO₂ (Li-0), 14.8Na₂O·29.0CaO·48.7SiO₂·7.5Li₂O (Li-7.5), lithium disilicate (L2S), and diopside glasses. The values of the crystal growth rates and viscosity were taken from [13,19,20,21,22].

As evident from Fig. 1, decoupling does not proceed sharply at some given temperature, but takes place in a certain temperature interval. This situation is to some extent similar to the glass transition [23,24] and the question arises how the decoupling temperature has to be determined most appropriately. One possible way of determination of the decoupling temperature is illustrated in Fig. 2 for the case of Li-0. Experimental data are interpolated by a continuous curve corresponding to a model discussed below. This continuous curve can be replaced then by two straight lines, one given by $\Pi_{dec}^{red} = 1$ in the range of $T_d \leq T$, and a second straight line involving a tangent-construction describing the behavior below T_d . Both T_d and the resulting tangent depend on the value of temperature or the value of $\Pi_{dec}^{red}(T)$ at which the tangent to $\Pi_{dec}^{red}(T)$ is determined. Having in mind both the uncertainties in the determination of the curve interpolating experimental data and the choice of the temperature T at which the tangent is determined, we proceed here in a different way. We determine the value of the decoupling temperature via the condition $\Pi_{dec}^{red} = e$. This procedure is illustrated in Fig. 3. The decoupling temperatures, specified by this method, are $T_d^{(Li-0)} \cong 907$ K, $T_d^{(Li-7.5)} \cong 788$ K, $T_d^{(lithium\ disilicate)} \cong 809$ K, and $T_d^{(diopside)} \cong 1072$ K. This criterion is widely equivalent to a fit of the $\Pi_{dec}^{red}(T)$ -data in the range where experimental data are available, involving two straight lines similar as used in the tangent-method but relying exclusively on the existing experimental data.

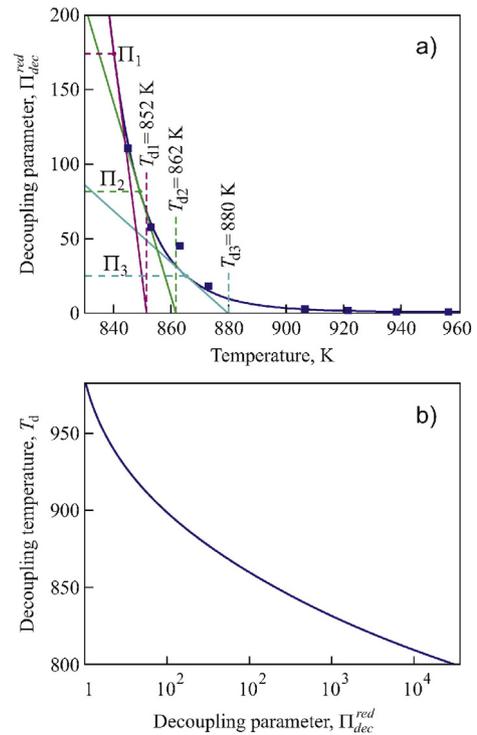


Fig. 2. Illustration of the tangent-method of determination of the decoupling temperature employing data for Li-0: In such approach, the experimental data are interpolated first by a continuous curve. This continuous curve can be replaced then by two straight lines, one given by $\Pi_{dec}^{red} = 1$ in the range $T \leq T_d$, and a second one involving a tangent-construction as illustrated in the figure. The values of the decoupling temperature, T_d , and the resulting tangent depend on the temperature or the value of $\Pi_{dec}^{red}(T)$ at which the tangent to $\Pi_{dec}^{red}(T)$ is determined. The value of the decoupling temperature obtained by such method in dependence on the value of $\Pi_{dec}^{red}(T)$ at which the tangent to $\Pi_{dec}^{red}(T)$ is determined is shown in panel b.

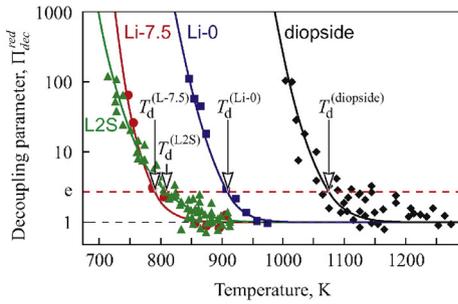


Fig. 3. Illustration of the method of determination of the decoupling temperature utilized in the present paper. The value of T_d is determined by the condition $\Pi_{dec}^{red} = e$. This criterion is equivalent to a fit of the $\Pi_{dec}^{red}(T)$ -data in the range where experimental data are available, involving two straight lines.

3.2. Comparison with alternative approaches

The results shown in Fig. 1 allow one to verify for the aforementioned systems a hypothesis advanced in [10] (cf. also [11] for a first discussion). In their analysis, the authors of [10] separated the kinetic part of the growth rate equation by introducing a quantity u_{kin} :

$$u_{kin} \equiv \frac{u}{[1 - \exp(-\Delta\mu/k_B T)]}. \quad (13)$$

They then presented the growth rate data in $\log(u_{kin})$ versus $\log(\eta)$ coordinates. Accounting for Eqs. (3) and (13), u_{kin} is proportional to the diffusion coefficient, D . Therefore, for temperatures higher than the decoupling temperature, T_d , where the SEE equation holds, one can write in line with above given considerations

$$u_{kin} \sim \eta^{-1}. \quad (14)$$

However, it is stated in [10] that for almost all the organic and inorganic materials investigated by them, the kinetic coefficient for crystal growth scales with the shear viscosity, η , as $\eta^{-\xi}$ (where ξ is a constant) in the entire temperature range analyzed (cf. Fig. 2 and Tables I and II in [10]) and that the value of ξ depends systematically on the fragility of the liquid. Such assumption, following [10], implies that the growth kinetics can be described by a constant (for a given melt) scaling parameter ξ as

$$u_{kin} \sim \eta^{-\xi}. \quad (15)$$

The value of ξ can be estimated then by

$$\xi \approx - \frac{d \log(u_{kin})}{d \log(\eta)}. \quad (16)$$

Accounting for the proportionality of u_{kin} and D , the mentioned authors suggested that the melts analyzed were governed by a mode of growth characterized by $D \propto \eta^{-\xi}$ in the entire temperature range under investigation with a fragility-dependent value of the exponent $\xi \leq 1$ being constant for a given melt. Indeed, according to the caption of Fig. 2 in [10], the “crystal growth rate... plotted against the supercooled liquid viscosity η for (a) organic and (b) inorganic liquids... are well described by a straight line in the log-log format, usually with a slope significantly less than unity”. Therefore, in such a formulation, there is no temperature range where the SEE relation holds. Such conclusion is in conflict with our results, results of other authors, and as it seems also with results reported in [25,26,27].

Generally, the assumption $D \propto \eta^{-\xi}$ implies that, in terms of Eqs. (2) and (5), the relation

$$E_D = \xi E_\eta \quad (17)$$

is supposed to hold. Provided that ξ is treated as a function of temperature, Eq. (17) is merely a redefinition of the activation energy for diffusion. Therefore, the central problem here is whether the exponent ξ can really be considered as a constant.

Provided the scaling relation $D_\eta \propto \eta^{-\xi}$ (in our notation) proposed in [10] is fulfilled, then D_η in Eq. (7) should be expressed by

$$D_\eta \propto 1/\eta_\xi, \quad \eta_\xi = \eta_0 \exp\left(\frac{\xi E_\eta}{k_B T}\right), \quad (18)$$

resulting in a modified decoupling parameter of the form

$$\tilde{\Pi}_{dec}^{red} \equiv \left(\frac{u(T) \left(\frac{\eta(T)}{\eta_0}\right)^\xi}{u(T_d) \left(\frac{\eta(T_d)}{\eta_0}\right)} \right). \quad (19)$$

The criterion of validity of the mentioned hypothesis formulated in [10] consists, in this case, in the fulfillment of the equation $\tilde{\Pi}_{dec}^{red} = 1$, allowing us to verify whether the mentioned scaling hypothesis works.

From this condition, we obtain the following relation for ξ :

$$\xi = \frac{\ln\left(\frac{u(T_d) \eta(T_d)}{u(T) \eta_0}\right)}{\ln\left(\frac{\eta(T)}{\eta_0}\right)} = 1 - \frac{\ln(\Pi_{dec}^{red})}{\ln(\eta(T)/\eta_0)}. \quad (20)$$

Using this method, ξ can be determined directly based on experimental data. Consequently, Eq. (12) allows us to establish whether decoupling occurs for a given melt (i.e. by analyzing in which temperature range below T_{ref} the relation $\Pi_{dec}^{red} = 1$ is fulfilled and at which temperature it ceases to be valid) and, if it occurs, to determine the decoupling temperature (where Π_{dec}^{red} starts to deviate from one). Finally, Eq. (20) allows us to establish the value of ξ and to test whether it is a constant or not.

Some representative results of such analysis are shown in Fig. 3 (cf. also Fig. 1 in [15]). The results demonstrate that decoupling really occurs and that a range of temperatures ($T > T_d$) indeed exists where the SEE relation holds. In Fig. 4, for the systems under consideration, those values of the exponent ξ as a function of temperature are given for which the relation $\tilde{\Pi}_{dec}^{red} \approx 1$ is fulfilled (cf. Eq. (20)). It is evident that assuming a constant value of this parameter ξ is not sufficient for an appropriate description of the growth kinetics. The sample is transferred continuously from the temperature range where viscosity and diffusion are coupled to a range of temperatures where they are decoupled. The transition region and the behavior at lower temperatures are characterized

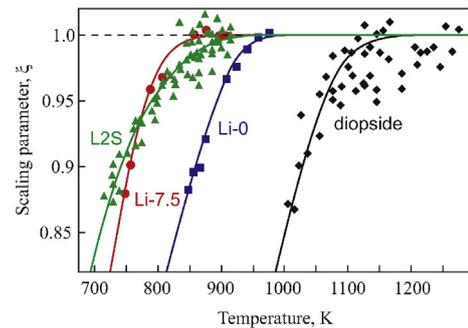


Fig. 4. Temperature dependence of the scaling parameter ξ required to express the diffusion coefficient D via a modified Stokes–Einstein–Eyring relation according to the proposal advanced in [10]. The results are given again for glasses of compositions in mol% 164Na₂O·33.3CaO·50.3SiO₂ (Li-0), 14.8Na₂O·29.0CaO·48.7SiO₂·7.5Li₂O (Li-7.5), lithium disilicate (L2S), and diopside. The values of crystal growth rates and viscosity were taken from [13,19,20,21,22]. The circles and squares were computed based on experimental data via Eq. (20). The dashed lines result from the simple model, Eq. (24). The full curves were drawn employing Eqs. (25)–(28).

by variations of ξ with temperature and cannot be described by a constant value of ξ .

4. Kinetics of decoupling: a theoretical model

For a theoretical explanation of the above described behavior, we consider the following simple model, adapting a suggestion formulated by Rössler [28]. We make use of the known fact that the temperature dependence of viscosity remains unchanged at the decoupling interval and is governed in the entire temperature range of temperatures by the Vogel–Fulcher–Tammann (VFT) equation,

$$\eta = \eta_0 \exp\left(\frac{E_*}{k_B(T - T_0)}\right). \quad (21)$$

The diffusion coefficient is supposed to behave differently above and below a temperature \tilde{T}_d as

$$D = \begin{cases} D_0 \exp\left(-\frac{E_*}{k_B(T - T_0)}\right) & \text{for } T \geq \tilde{T}_d \\ D_0 \exp\left(-\frac{E_*}{k_B T \left(1 - \frac{T_0}{\tilde{T}_d}\right)}\right) & \text{for } T \leq \tilde{T}_d. \end{cases} \quad (22)$$

In such an approach, the mechanism controlling crystal growth changes from a liquid-like mode, correlated with the dynamics of relatively large cooperatively rearranging regions, into a solid-state-like (faster) diffusion mode governed by an Arrhenius-type process. In the latter mode of diffusion, the activation energy for diffusion does not depend on temperature [12,28,29,30]. The temperature \tilde{T}_d is the decoupling temperature introduced in the model with Eq. (22). Its value is correlated with the decoupling temperature, T_d , defined above based on experimental data, but not necessarily identical to it. We employ it here as a fitting parameter allowing one to arrive at the best possible description of diffusion data based on the model advanced.

Provided that the scaling hypothesis $D_\eta \propto \eta^{-\xi}$ (proposed in [10]) is valid, the relations

$$\frac{\xi E_*}{k_B T \left(1 - \frac{T_0}{T}\right)} = \frac{E_*}{k_B T \left(1 - \frac{T_0}{\tilde{T}_d}\right)} \quad (23)$$

or

$$\xi = \frac{\left(1 - \frac{T_0}{T}\right)}{\left(1 - \frac{T_0}{\tilde{T}_d}\right)} \quad (24)$$

hold. It is evident that in this model approach, ξ is also a function of temperature in the entire range $T \leq \tilde{T}_d$.

The above discussed model has the feature that the transition from one mode of diffusion to a different one proceeds at a singular temperature. In reality, this transition can be expected to proceed in a certain temperature interval. To account for this feature, we reformulate the above described model as follows. The diffusion coefficient is supposed to behave differently above and below the temperature \tilde{T}_d . We describe it as the sum of two terms

$$D = D_\eta + D_A \Upsilon(T), \quad (25)$$

where D_η is expressed by a VFT type dependence

$$D_\eta = D_0 \exp\left(-\frac{E_B}{k_B(T - T_0)}\right), \quad (26)$$

which is supplemented for temperatures below \tilde{T}_d by diffusion governed by an Arrhenius-type law,

$$D_A = D_{A0} \exp\left(-\frac{E_A}{k_B T}\right). \quad (27)$$

Here, the function

$$\Upsilon(T) = \frac{1}{2} \left[1 - \tanh\left(\frac{T - \tilde{T}_d}{\Delta T_d}\right) \right] \quad (28)$$

is introduced. The value of this function $\Upsilon(T)$ varies from one to zero with increasing T in a narrow interval ΔT_d (the width of the decoupling region) around $T = \tilde{T}_d$. Eqs. (25)–(28) allows us to model a continuous transition between the two different diffusion modes.

The parameters E_B and T_0 were computed by fitting the parameters of the VFT equation to the systems under consideration. The parameters E_A , D_{A0} , \tilde{T}_d , and ΔT_d were estimated from the best fit to the experimental data. For all the considered sets of experimental data, we obtained $\Delta T_d \approx 0.06 \tilde{T}_d$. The other parameters are listed in Table 1.

The diffusion coefficients for Li-0 (D_η , D_A , and D versus temperature) are shown in Fig. 5. The respective values of Π_{dec}^{red} , ξ , and u_{kin} are given by the full curves in Figs. 1, 3, 4, and 6. In particular, Fig. 6a shows the $\log(u_{kin})$ versus $\log(\eta)$ dependencies for 16.4Na₂O · 33.3CaO · 50.3SiO₂, 14.8Na₂O · 29.0CaO · 48.7SiO₂ · 7.5Li₂O, lithium disilicate, and diopside glasses. These dependencies are well-approximated by straight lines for $T > \tilde{T}_d$ with a slope equal to minus one ($\xi = 1$). Near and below the temperature $T \sim \tilde{T}_d$, the value of ξ progressively decreases with decreasing temperature. This result agrees with the data presented in Fig. 4 providing evidence for decoupling of the mechanisms controlling diffusion and viscous flow. In Fig. 6, for one of the glasses (diopside), experimental data and our interpolation via Eqs. (25)–(28) are shown again by a full curve. The dashed line is drawn assuming the validity of the SEE relation, extrapolating the behavior for temperatures $T > \tilde{T}_d$ to temperatures $T \leq \tilde{T}_d$. The dotted curve is the straight line adapted from Fig. 2 in the paper by Ediger et al. [10], replacing D by $D \propto \eta^{-\xi}$ with a constant value of ξ . The presentation of the data in double logarithmic coordinates and the partly narrow temperature interval likely led the authors of [10] to misleading interpretations of the growth kinetics and, in particular, of the decoupling phenomenon.

5. Decoupling temperature and fragility

The analysis performed in the preceding sections allows us to establish, based exclusively on experimental data, whether a decoupling of diffusion and viscosity takes place (specified by the decoupling

Table 1

Parameters employed for the theoretical description of the diffusion coefficients, Eqs. (25)–(28). The parameters E_B and T_0 were computed from the parameters of the VFT equation for the systems under consideration. The parameters E_A , D_{A0} , \tilde{T}_d , and ΔT_d were estimated for the best fit of the measured data by the above mentioned equations. For all considered sets of experimental data, $\Delta T_d \approx 0.06 \tilde{T}_d$ holds. The other parameters are given in the table.

	E_A , J	E_B , J	D_{A0}/D_0	T_0 , K	\tilde{T}_d , K
Li-0	$5.217 \cdot 10^{-19}$	$1.65 \cdot 10^{-19}$	$1.191 \cdot 10^4$	547	929
Li-7.5	$6.525 \cdot 10^{-19}$	$0.858 \cdot 10^{-19}$	$2.094 \cdot 10^{14}$	565	810
Lithium disilicate	$1.091 \cdot 10^{-19}$	$2.073 \cdot 10^{-19}$	$3.966 \cdot 10^8$	491	850
Diopside	$7.938 \cdot 10^{-19}$	$1.259 \cdot 10^{-19}$	$2.237 \cdot 10^{11}$	751	1100

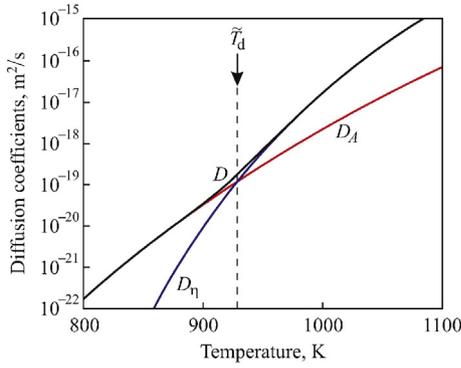


Fig. 5. Values of the diffusion coefficients governing growth of the crystalline phase in Li-0 glass-forming melt above and below the decoupling temperature, \tilde{T}_d . D , D_η , and D_A are described by Eqs. (25)–(28), respectively (see text for more details).

temperature, T_d). Another question is how the decoupling temperature can be estimated theoretically or correlated with other directly measurable parameters of a given melt. In principle, this problem can be analyzed rigorously only based on a microscopic approach tracing for a given melt the mechanisms of diffusion and viscous flow. Here, as a first estimate we would like to address this problem from another viewpoint formulating, based on viscosity data, a hypothesis that is then tested by experimental data. The results of the analysis performed in the present section may serve as a first estimate to the location of the decoupling temperature for a given melt as a starting point for more detailed investigations as discussed in Section 3.

The approach is based on the hypothesis that *decoupling occurs when the logarithm of the ratio of the viscosities at the glass transition*

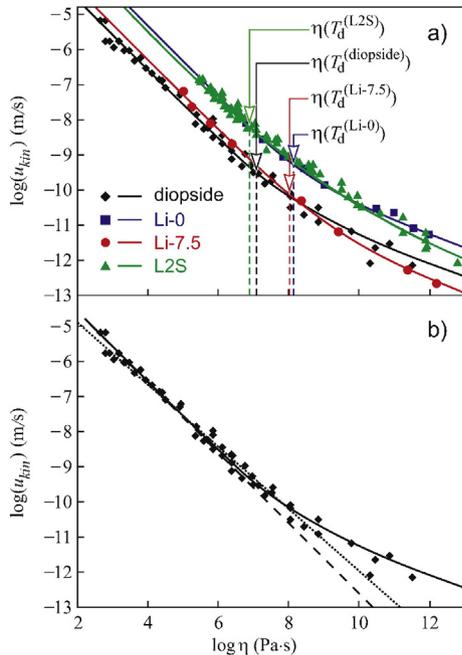


Fig. 6. a) Crystal growth rate versus viscosity of supercooled lithium disilicate (L2S), diopside, Li-0, and Li-7.5 glass-forming melts. The symbols refer to experimental data [13,19,20,21,22], the full curves were drawn utilizing Eqs. (25)–(28). b) Crystal growth rate versus viscosity of supercooled liquid diopside. The symbols and black curve have the same meaning as in Fig. 4a. The dashed line is drawn assuming validity of the Stokes–Einstein–Eyring relation, and the dotted curve according to the proposal of Ediger et al. [10] replacing D by $D \propto \eta^\xi$ with a constant value of ξ ($\xi = 0.88$).

Table 2

Melting (T_m), decoupling (T_d), and glass transition (T_g) temperatures, viscosities at T_d and T_g , and ratios of the viscosities at these temperatures for a set of liquids. The glass transition temperature refers to a good approximation (cf. Fig. 7) to a viscosity $\eta(T_g) \approx 10^{12}$ Pa s, i.e., the glass transition temperature refers widely to the value one obtains according to Tammann's definition of T_g . The following systems are analyzed: PbO·SiO₂ (PS), Li₂O·2B₂O₃ (L2B), Li₂O·3SiO₂ (L3S), Li₂O·2SiO₂ (L2S), Na₂O·2CaO·3SiO₂–Li₂O (Li-7.5), 2Na₂O·1CaO·3SiO₂ (2N1C3S), Na₂O·2CaO·3SiO₂ (Li-0), cordierite, CaO·MgO·2SiO₂ (diopside), BaO·2SiO₂ (B2S), and Ba₂Ti(Si₂O₇)O (fresnoite).

	T_m [K]	T_d [K]	$\eta(T_d)$	T_g [K]	$\eta(T_g)$	$\log(\frac{\eta(T_g)}{\eta(T_d)})$
PS [11]	1037	775	$2.97 \cdot 10^6$	683	$2.7 \cdot 10^{11}$	4.959
L2B [22]	1190	795	$2.20 \cdot 10^8$	768	$2.09 \cdot 10^{11}$	2.979
L3S [11]	1306	953	$5.36 \cdot 10^6$	734	$1.45 \cdot 10^{12}$	5.433
L2S [13]	1307	809	$1.33 \cdot 10^8$	727	$7.33 \cdot 10^{11}$	3.742
Li-7.5 [19]	1435	788	$1.28 \cdot 10^9$	748	$5.69 \cdot 10^{11}$	2.648
N1C3S [32]	1469	830	$4.71 \cdot 10^6$	743	$8.46 \cdot 10^{11}$	5.255
Li-0 [19]	1564	907	$9.40 \cdot 10^8$	838	$2.49 \cdot 10^{12}$	3.422
Cordierite [11]	1643	1192	$2.47 \cdot 10^8$	1083	$3.9 \cdot 10^{12}$	4.198
Diopside [11]	1664	1072	$1.17 \cdot 10^8$	995	$9.2 \cdot 10^{11}$	3.894
B2S [33]	1693	1016	$3.20 \cdot 10^9$	961	$1.68 \cdot 10^{12}$	2.721
Fresnoite [35]	1714	1009	$1.10 \cdot 10^{10}$	983	$8.7 \cdot 10^{11}$	1.896

temperature and at the decoupling temperature approaches a nearly constant value only weakly depending on the melting temperature, i.e.,

$$\log\left(\frac{\eta(T_g)}{\eta(T_d)}\right) = C(T_m), \quad C(T_m) = a + bT_m. \quad (29)$$

With above considerations (Eq. (29)), we have from Eq. (5),

$$\frac{E_\eta(T_g)}{T_g} - \frac{E_\eta(T_d)}{T_d} = k_B \frac{C(T_m)}{\log(e)}. \quad (30)$$

For a foundation of this hypothesis, in Table 2, experimental data for eleven glass-forming melts are collected (cf. in particular the first and last columns in Table 2). The T_g -data were experimentally obtained from DSC/DTA analysis with moderate cooling and heating rates resulting in experimentally observed glass transition temperatures widely in agreement with Tammann's definition of the glass transition [23] identifying $T_g = T_{12}$ (i.e., with the temperature corresponding to a viscosity $\eta(T_{12}) \approx 10^{12}$ Pa s; cf. Fig. 7). Decoupling occurs for these systems for values of $C(T_m)$ in the range of $1.9 \leq \log(\eta(T_g)/\eta(T_d)) \leq 5.4$, i.e., for values of this parameter located in a relatively narrow interval with an average equal to 3.74.

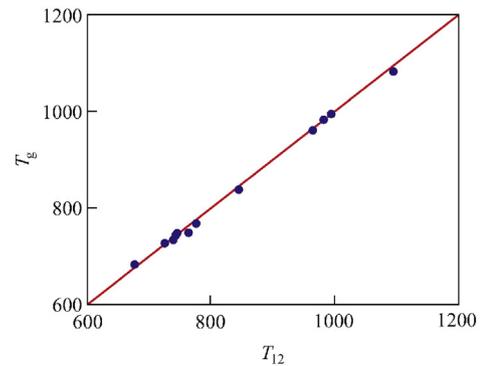


Fig. 7. Correlation between the glass transition temperature, T_g , and the respective value, T_{12} ($\eta(T_{12}) \approx 10^{12}$ Pa s), corresponding to Tammann's [23] definition of the glass transition temperature, is shown. The T_g -data were experimentally obtained from DSC/DTA analysis with moderate cooling and heating rates resulting in experimentally observed glass transition temperatures widely in agreement with Tammann's definition. The data points correspond to the following systems: PbO·SiO₂ (PS) (PS), Li₂O·2B₂O₃ (L2B), Li₂O·3SiO₂ (L3S), Li₂O·2SiO₂ (L2S), Na₂O·2CaO·3SiO₂–Li₂O (Li-7.5), 2Na₂O·1CaO·3SiO₂ (2N1C3S), Na₂O·2CaO·3SiO₂ (Li-0), cordierite, CaO·MgO·2SiO₂ (diopside), BaO·2SiO₂ (B2S), Ba₂Ti(Si₂O₇)O (fresnoite) (see [13,19,22,31,32,33,34,35,36] and Fig. 9 in [37]).

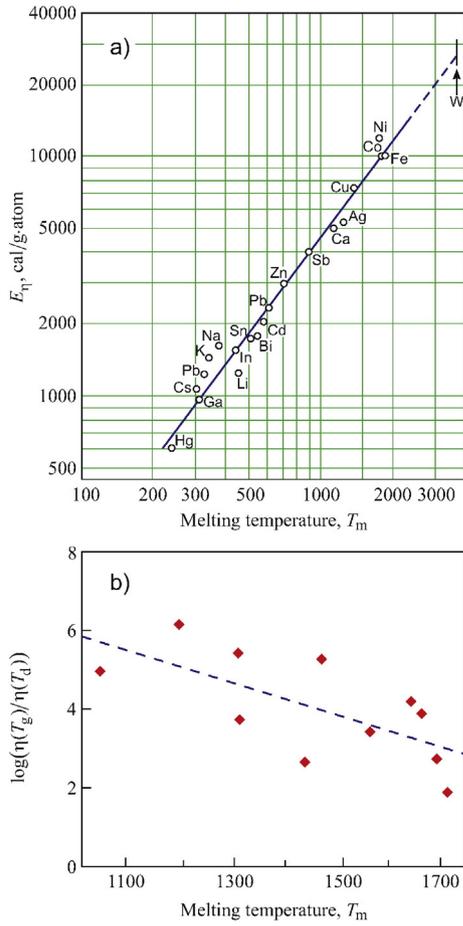


Fig. 8. a) Activation energy of viscous flow, E_η , of metallic melts at the melting temperature, T_m . b) Dependence of the logarithm of the ratio of the viscosities at T_g , respectively, T_d , $\log(\eta(T_g)/\eta(T_d))$, on the melting temperature, T_m , for the set of silicate melts given in Table 2.

A more detailed foundation of Eqs. (29) and (30) can be given based on data on activation energy of the viscosity of metal melts as discussed by Ubbelohde [38]. The results are shown in Fig. 8a. It is evident that for metal melts a quite strong correlation between the activation energy for viscosity at the melting temperature and T_m exists. In the considered here case of the silicate melts we may expect the existence of a similar trend. Following such considerations, in Fig. 8b the dependence of $\log(\eta(T_g)/\eta(T_d))$ on T_m is shown. It is evident that the resulting correlation can be well-described by a linear dependence as proposed in Eq. (29) with $b < 0$.

Let us now search for some consequences of the above formulated hypothesis that could be directly tested experimentally. In particular, we will connect T_d with T_g employing the concept of liquid fragility. The fragility index introduced by Angell [39,40] has been widely discussed in the analysis of the behavior of glass-forming systems, including their glass-forming ability and crystallization kinetics. It was originally defined as

$$m_\eta^{(c.d.)} = \left. \frac{d \log \eta}{d \left(\frac{T_g}{T} \right)} \right|_{T=T_g} \quad (31)$$

In this classical definition, specified here with the superscript (c.d.), (i) the fragility parameter, m , is computed based on the knowledge of the temperature dependence of the viscosity, (ii) temperature is expressed in terms of the ratio (T_g/T) , and (iii) m is then calculated at

the glass transition temperature, $T = T_g$, identifying T_g as the rule with T_{12} . With Eq. (5), we get

$$m_\eta^{(c.d.)} = \frac{\log(e)}{k_B T_g} E_\eta^{(eff)}(T_g), \quad E_\eta^{(eff)}(T) = \left(E_\eta(T) - T \frac{dE_\eta(T)}{dT} \right). \quad (32)$$

By a Taylor expansion of $E_\eta(T_d)$ in the vicinity of T_g , we arrive at

$$E_\eta(T_d) = E_\eta(T_g) + \left(\frac{\partial E_\eta(T)}{\partial T} \right) \Big|_{T=T_g} (T_d - T_g). \quad (33)$$

This relation can be rewritten as

$$E_\eta(T_d) = E_\eta(T_g) - \left(T \frac{\partial E_\eta(T)}{\partial T} \right) \Big|_{T=T_g} \frac{(T_g - T_d)}{T_g} \quad (34)$$

or

$$E_\eta(T_d) = E_\eta(T_g) \left(\frac{T_d}{T_g} \right) + \left(E_\eta - T \frac{\partial E_\eta(T)}{\partial T} \right) \Big|_{T=T_g} \frac{(T_g - T_d)}{T_g}. \quad (35)$$

Employing, in addition, Eq. (30), we obtain

$$\left(E_\eta - T \frac{\partial E_\eta(T)}{\partial T} \right) \Big|_{T=T_g} \frac{(T_d - T_g)}{T_g T_d} = k_B \frac{C(T_m)}{\log(e)}. \quad (36)$$

Finally, with Eq. (32), we get

$$m_\eta^{(c.d.)} \frac{(T_d - T_g)}{T_d} = C(T_m) \quad (37)$$

or

$$\frac{T_d - T_g}{T_d} = \frac{C(T_m)}{m_\eta^{(c.d.)}}, \quad \frac{T_d}{T_g} = \frac{1}{1 - \frac{C(T_m)}{m_\eta^{(c.d.)}}}. \quad (38)$$

It follows that the decoupling temperature is uniquely correlated to glass transition temperature, T_g , and fragility, $m_\eta^{(c.d.)}$.

In Fig. 9, results of a test of Eq. (38) are presented. It is evident that it provides a quite satisfactory description of the experimental data already by setting the parameter C equal to a constant (best fit) value, $C = 3.741$ (Fig. 9a), practically equal to the average computed based on the data given in Table 2. In Fig. 9b, this analysis is further advanced considering $C(T_m)$ as a function of melting or liquidus temperature as suggested by Eq. (29) utilizing the approximation for $C(T_m)$ ($C(T_m) = 7.074 - 0.00229T_m$) as obtained from Fig. 8b. It results in a more accurate description of the experimental data. In Fig. 9c, an alternative best fit of the data is shown choosing $C(T_m) = \tilde{C}(T_m) = 11.44 - 0.00465T_m$. These relations, Eq. (38), can be employed consequently as master curves for the determination of T_d from data on the melting temperature and the viscosity at the glass transition temperature, T_g , respectively, the fragility, $m_\eta^{(c.d.)}$.

6. Summary of results and discussion

The main results of the present analysis can be summarized as follows: (i) a criterion is developed and successfully tested that allows one to establish – based exclusively on experimental data for viscosities and crystal growth rates – whether and at which temperature decoupling of diffusion and viscosity occur for crystal growth in a given melt. (ii) In a further step, this criterion was reformulated allowing us to test whether the hypothesis advanced in [10] concerning the applicability of the relation between diffusion coefficient and viscosity, $D_\xi \propto \eta^{-\xi}$ with a constant value of ξ , which is supposed to be valid

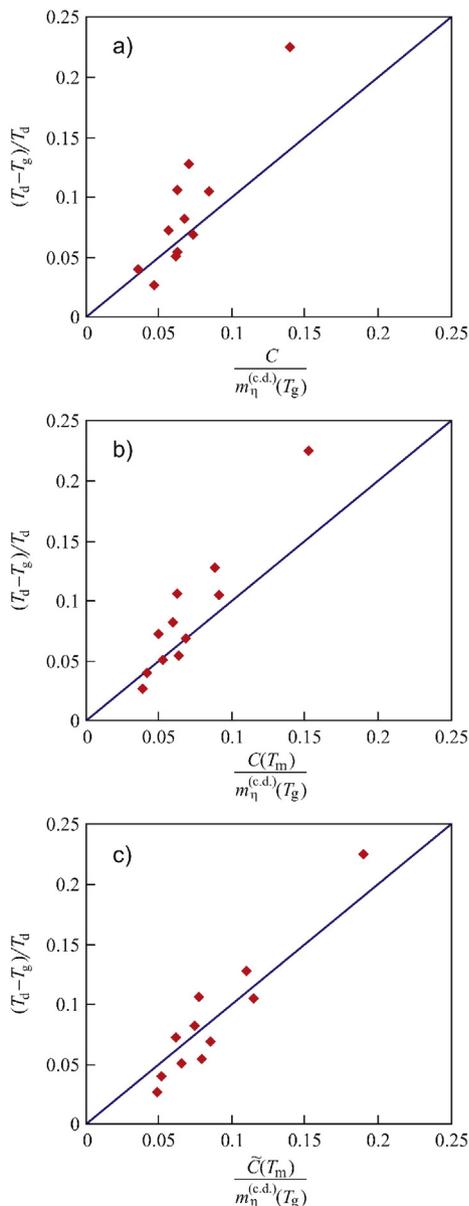


Fig. 9. Illustration the dependence of $(T_d - T_g)/T_d$ on the fragility index in accordance with Eq. (38) (a) with $C = 3.741$, (b) $C(T_m) = 7.074 - 0.0029T_m$, and (c) $C(T_m) = \tilde{C}(T_m) = 11.44 - 0.00465T_m$.

in the whole temperature range of crystal growth, allows one a satisfactory description of the kinetics of crystal growth for the systems analyzed here. It turns out that this hypothesis is not valid. As shown, a relation of the form $D_\xi \propto \eta^{-\xi}$ with a constant value of ξ does not describe the crystal growth kinetics adequately, neither for the systems analyzed in the present paper nor for other systems discussed in the literature. (iii) A theoretical model is advanced allowing one to describe the crystal growth kinetics in the whole temperature range where crystallization may proceed, i.e., both above the decoupling temperature, T_d , i.e. in the range of temperature where the Stokes–Einstein–Eyring relations holds, below T_d where the mechanisms of diffusion and viscosity decouple, and in the transient stage in between both modes of crystal growth. (iv) Finally, a hypothesis is advanced and tested, giving the possibility to estimate the value of the decoupling temperature employing data on the viscosity and its response to variations of temperature both at the glass transition temperature. Based on this concept, theoretical estimates are developed connecting the decoupling temperature with glass transition temperature and fragility. These relationships are

confirmed by available experimental data for systems where the glass transition temperature is widely identical to $T_g = T_{12}$, i.e. to its value according to the definition as proposed by Tammann ($\eta(T_{12}) \approx 10^{12}$ Pa s).

In preceding papers [14,15], general relations for the determination of the maxima of nucleation, growth, and overall crystallization rates have been established and the relevance of fragility index and reduced glass transition temperature for the understanding of crystal nucleation and growth processes was analyzed. The general relations derived in these papers have been illustrated in terms of classical theories of nucleation and growth involving commonly employed relations for the description of the systems under consideration and the properties of the crystals. This analysis has been extended in the present paper to account for the effects of decoupling on crystallization concentrating on crystal growth. In crystal nucleation, the situation is more complex since the properties of the crystal may change with crystal size and surface effects may be also of importance. In a forthcoming paper, we will advance our analysis to the description of peculiarities of nucleation occurring at deep undercoolings [29] and will discuss modifications one has to introduce into classical nucleation theory in order to appropriately describe both crystal formation and growth at such conditions.

7. Conclusions

The effect of decoupling of viscosity and diffusion (i.e. of the breakdown of the Stokes–Einstein–Eyring equation) on crystal growth processes is analyzed. A criterion is formulated which gives the possibility to establish, based exclusively on measurable data, whether and at which temperature decoupling occurs in a given melt. The criterion is applied to several glass-forming systems showing that above a certain decoupling temperature, T_d , the Stokes–Einstein–Eyring equation is fulfilled. Below T_d , the diffusion coefficient is related to viscosity by $D \propto \eta^{-\xi}$, where ξ is a function of temperature. The viscosities at the glass transition temperature, T_g , and at the decoupling temperature, T_d , are shown to be correlated by fragility. The results are confirmed by experimental data.

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