

# Stress development and relaxation during crystal growth in glass-forming liquids

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## Abstract

We analyze the effect of elastic stresses on the thermodynamic driving force and the rate of crystal growth in glass-forming liquids. In line with one of the basic assumptions of the classical theory of nucleation and growth processes it is assumed that the composition of the clusters does not depend significantly on their sizes. Moreover, stresses we assume to be caused by misfit effects due to differences in the specific volume of the liquid and crystalline phases, respectively. Both stress evolution (due to crystallization) and stress relaxation (due to the viscous properties of the glass-forming liquids) are incorporated into the theoretical description. The developed method is generally applicable independently of the particular expressions employed to describe the crystal growth rate and the rate of stress relaxation. We show that for temperatures lower than a certain decoupling temperature,  $T_d$ , elastic stresses may considerably diminish the thermodynamic driving force and the rate of crystal growth. The decoupling temperature,  $T_d$ , corresponds to the lower limit of temperatures above which diffusion and relaxation are governed by the same mechanisms and the Stokes–Einstein (or Eyring) equation is fulfilled. Below  $T_d$ , the magnitude of the effect of elastic stresses on crystal growth increases with decreasing temperature and reaches values that are typical for Hookean elastic bodies (determined by the elastic constants and the density differences of both states of the system) at temperatures near or below the glass-transition temperature,  $T_g$ . By these reasons, the effect of elastic stress must be properly accounted for in a correct theoretical description of crystal nucleation (as some of us have shown in previous papers) and subsequent crystal growth in undercooled liquids. The respective general method is developed in the present paper and applied, as a first example, to crystal growth in lithium disilicate glass-forming melt.

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## 1. Introduction

Elastic stresses are known to play an important role in phase transformations in crystalline solids [1–4]. They may change the course of the transformations both quantitatively and qualitatively. In the vicinity of the glass-transi-

tion temperature,  $T_g$ , glass-forming liquids behave as viscoelastic bodies. Hereby, the elastic properties become increasingly dominant with a decrease of temperature. Near, and especially below  $T_g$ , glasses display properties that are typical for Hookean elastic solids. One thus expects that, in the neighborhood of  $T_g$  and below, elastic stresses may affect significantly the phase transformation processes, in general, and crystallization processes of glass-forming liquids, in particular. Indeed, a variety of experimental results, summarized in Refs. [5,6], demon-

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strates that elastic stresses may have a significant influence on the course of phase transformations in glass-forming liquids. In particular, it has been shown both experimentally and theoretically [7–9] that elastic stresses may qualitatively change the kinetics of growth of single clusters and of Ostwald ripening in glass-forming melts, when the segregating component has a diffusivity much higher than the basic building units of the glass-forming melt. This situation is similar to the results of Stephenson [10] in application to spinodal decomposition.

However, up to now, the effects of stresses developing in the course of crystallization are neglected in most analyses dealing with crystal nucleation and growth in glass-forming liquids. The common argument is that these stresses relax too fast as to affect these phenomena. The above mentioned argumentation is based on several assumptions. First, in line with classical nucleation theory, it is assumed that the state of the crystallites does not depend on their sizes and is widely identical to the state of the newly evolving crystal phase. In such cases, the kinetics of cluster nucleation and growth can be treated similarly to nucleation and growth in one-component systems with appropriately chosen values of the effective diffusion coefficient and thermodynamic driving force [5,6,11,12]. Second, it is assumed that elastic stresses are due to the difference between the specific volumes of liquid and crystalline phase first analyzed by Nabarro [1]. Both these assumptions we will also employ in the present analysis. In addition it is commonly assumed that the Stokes–Einstein/Eyring equation, which connects viscosity (governing relaxation processes) and self-diffusion coefficients (determining the rate of aggregation) holds and retains its validity for temperatures near and below  $T_g$ . However, by different methods of analysis – theoretical, computer simulation and experimental techniques – it has been convincingly demonstrated for a variety of liquids that at some temperature,  $T_d$ , decoupling of diffusion and viscous flow takes place (see Refs. [5,6] for an overview). The value of the decoupling temperature is frequently found at about  $T_d = 1.2T_g$ , but some authors report values of  $T_d \cong T_g$  [13,14]. Above  $T_d$ , the Stokes–Einstein/Eyring equation is typically fulfilled, but below  $T_d$  it is not.

By incorporating these ideas into the theoretical description of crystal nucleation in glass-forming liquids some of us arrived at the conclusion that elastic stresses may have a significant effect on critical nucleus formation in glass-forming liquids [5,6]. These theoretical arguments were then applied for the description of nucleation in lithium disilicate melts and were able to explain a number of effects which have not found a satisfactory explanation before [15,16]. It is thus of significant interest to extend the analysis of the possible effects of stresses on crystal growth.

In the present paper we develop a general formalism that allows us to describe growth processes of a new phase in viscoelastic media taking into account both stress development and relaxation. The stress energy, affecting the growth rate of the crystalline phase in the liquid, results

from an interplay between the rate of stress development (due to the propagation of the crystal-growth front throughout the matrix) and stress dissipation (due to stress relaxation in the viscous matrix). We show that the value of the stress energy, which affects the growth kinetics, depends on the ratio of two characteristic time-scales,  $\tau_G/\tau_R$ , where  $\tau_G$  is the time required to form one monolayer of the newly evolving crystalline phase in steady-state growth, and  $\tau_R$  is a characteristic (Maxwellian) relaxation time of the matrix. If the (short-range) interfacial rearrangements controlling crystal growth are of the same nature as those involved in viscous flow, then stresses relax comparatively fast and have no effect on crystal growth. However, if – as demonstrated to be a typical phenomenon for different classes of glass-forming liquids – *decoupling* of short-range diffusion and viscous flow occurs at some temperature,  $T_d$ , then stresses may have a significant effect on the crystal growth kinetics for temperatures  $T \leq T_d$ . As will be shown in the present paper, the effect of stresses on the driving force of crystallization increases with decreasing temperature reaching values that are typical for Hookean (elastic) solids near or below  $T_g$ .

The paper is organized as follows: in Section 2 a theoretical approach is developed allowing one to determine the effect of stresses on crystal growth. In Section 3 we show that, in the range of temperatures where the Stokes–Einstein (or Eyring) equation holds, elastic stresses do not play any role in crystallization and glass-forming liquids behave, with respect to crystal growth, as Newtonian liquids. However, below  $T_d$ , elastic stresses may have a significant influence on crystal growth. The magnitude of this effect depends on the values of the elastic constants of both phases and on a misfit parameter characterizing the volume changes in crystallization. The theory is applied in Section 4 for the description of crystal growth in lithium disilicate glass. A discussion of the results (Section 5), possible modifications and extensions of the theory (Section 6) and a summary of the conclusions completes the paper.

## 2. Theory: basic assumptions and results

We consider a planar crystallization front with an interfacial area,  $A$ , moving into a direction specified by the  $x$ -axis of an appropriately chosen system of coordinates normal to the considered front. The number of particles in the crystalline phase,  $n$ , can then be written as

$$n = cAx, \quad c \cong \frac{2}{d_0^3}, \quad c = \frac{1}{v_c}, \quad v_c = \frac{1}{2}d_0^3. \quad (1)$$

Here  $c$  is the volume concentration of the ambient phase particles in the crystalline phase,  $v_c$  the volume per particle in the crystalline phases,  $d_0$  is a characteristic size parameter (diameter) of the basic structural units of the system (cf. [17]).

The growth rate,  $U = (dx/dt)$ , can be connected with the change of the characteristic thermodynamic potential,  $\Delta\Phi$ ,

or the difference of the chemical potential per particle in both considered states of the system as [17,18]

$$U = \frac{dx}{dt} = f \frac{D}{4d_0} \left[ 1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right], \quad \Delta\mu = \frac{\partial \Delta\Phi}{\partial n}. \quad (2)$$

Here  $k_B$  is the Boltzmann constant and  $T$  the absolute temperature, and  $f$  is a dimensionless parameter describing the specific properties of the different growth modes. For simplicity of the notation, we will assume here  $f=1$  corresponding to the case of normal growth. But the main results of this analysis are – as will be shown below – independent of this assumption. Instead of the self-diffusion coefficient of the ambient phase particles,  $D$ , we will use the characteristic time of molecular motion,  $\tau$ , in the description employing the relation  $d_0^2 \cong D\tau$ .

In the absence of elastic stresses, the change of the thermodynamic potential, connected with the transfer of  $n$  ambient phase particles into the crystal phase, can be expressed as

$$\Delta\Phi(n) = -n\Delta\mu. \quad (3)$$

Elastic stresses can be incorporated into the above equation by adding a term,  $\Phi^{(e)}$ , i.e. the total energy of elastic deformations connected with the formation of a new phase region with  $n$  particles. In such cases, instead of Eq. (3) we get

$$\Delta\Phi(n) = -n\Delta\mu + \Phi^{(e)}(n). \quad (4)$$

The driving force of crystallization in the absence of elastic stresses,  $\Delta\mu$ , is a function of the temperature difference ( $T_m - T$ ) [17]. In the analysis we will employ either experimentally determined data or, for the derivation of some more general conclusions, the Volmer–Turnbull expression

$$\Delta\mu(T) = \Delta H_m \left( 1 - \frac{T}{T_m} \right), \quad (5)$$

where  $\Delta H_m$  is the enthalpy of melting per particle at the melting temperature,  $T_m$ .

We consider stresses due to misfit effects between the melt and the newly evolving crystalline phase. In this case, we can write generally [1,3,5,6]

$$\Phi^{(e)} = \varepsilon n. \quad (6)$$

A substitution of this expression into Eq. (4) leads to the consequence that elastic stresses effectively result in a decrease of the thermodynamic driving force of crystallization by the quantity  $\varepsilon$ . Indeed, we can write Eq. (4) in the form

$$\Delta\Phi(n) = -n\Delta\mu^{(\text{eff})}, \quad \Delta\mu^{(\text{eff})} = \Delta\mu - \varepsilon. \quad (7)$$

Consequently, for any value of  $\varepsilon$ , from Eqs. (2), (4) and (6) we get

$$\frac{dx}{dt} = \frac{D}{4d_0} \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right]. \quad (8)$$

For purely elastic solids, we have  $\varepsilon = \varepsilon_0$ , where  $\varepsilon_0$  is a parameter that depends on the elastic constants and the

densities of both phases. In general, the stress parameter  $\varepsilon_0$  can be written as [1,19]

$$\varepsilon_0 = \frac{E_c E_m v_c}{3[E_c(\gamma_m + 1) - 2E_m(2\gamma_c - 1)]} \delta^2, \quad \delta = \frac{v_m - v_c}{v_c}, \quad (9)$$

where  $E$  is Young's modulus,  $\gamma$  Poisson's ratio, and  $v$  the volume per particle. The subscripts ( $m$ ) and ( $c$ ) refer to the parameters of melt and crystalline phase, respectively.

Generally, due to viscous relaxation, the inequality  $\varepsilon \leq \varepsilon_0$  holds and the growth rate and the values of the effective elastic stress parameter  $\varepsilon$  must be determined in a self-consistent way as functions of time. In order to do so, we have to develop, in addition, an equation for the time-dependence of  $\varepsilon$ . In general, the solution of the resulting set of equations for the time dependencies of the growth rate and the rate of change of the effective stress parameter  $\varepsilon$  can be found only numerically (as it has been done for the solution of related problems in Refs. [20,21]). However, for steady-state conditions (defined by  $dx/dt = \text{constant}$ ) the effective stress parameter,  $\varepsilon$ , is also a constant. So, the conditions for steady-state growth are

$$\frac{dx}{dt} = \text{const}, \quad \varepsilon = \text{const}. \quad (10)$$

Here we restrict the analysis to such steady-state conditions allowing one to analytically determine the basic factors that affect the crystal growth rate.

In order to proceed with the derivation, let us denote by  $\tau_G$  the time required to form one crystalline monolayer. We assume further that the effective stress parameter,  $\varepsilon$ , is given by the solution of the stress relaxation equation via

$$\varepsilon = \varepsilon_0 \exp\left\{-\frac{\tau_G}{\tau_R}\right\} \quad (11)$$

for Maxwellian relaxation or

$$\varepsilon = \varepsilon_0 \exp\left\{-\left(\frac{\tau_G}{\tau_R}\right)^\beta\right\} \quad (12)$$

for the stretched exponential relaxation mechanism. In Eq. (12),  $\beta$  is a parameter specifying the relaxation behavior of the particular liquid analyzed. In other words, we assume that the time of formation of one monolayer determines the effective time-scale at which stress relaxation may occur.

The time  $\tau_G$  is determined by the growth rate Eq. (8). Then, in order to allow for the formation of one monolayer,  $dx$  has to be set equal to  $dx \cong d_0$  ( $d_0$  is the diameter of an ambient phase unit). Consequently, employing the expression for the growth rate Eq. (8),  $\tau_G$  can be expressed via

$$\frac{d_0}{\tau_G} = \frac{D}{4d_0} \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right]. \quad (13)$$

In this way, in the case of steady-state growth, Eqs. (11) or (12) and Eq. (13) allow us to determine the two unknown quantities  $\varepsilon$  and  $\tau_G$  provided such solution does indeed exist.

In order to prove the existence of such a solution, we rewrite Eq. (13) in the form

$$\frac{4d_0^2}{D} = f(\tau_G) = \tau_G \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon(\tau_G)}{k_B T}\right) \right]. \quad (14)$$

The auxiliary function  $f(\tau_G)$  is equal to zero for  $\tau_G \rightarrow 0$ , it increases monotonically with increasing  $\tau_G$  and tends to infinity for  $\tau_G \rightarrow \infty$ . Consequently, for any set of parameters (in particular, for any value of the ratio  $(4d_0^2/D)$ ), there exists one and only one solution for  $\tau_G$  and, according to Eqs. (11) or (12), one and only one solution for the effective stress parameter,  $\varepsilon$ .

### 3. Decoupling, elastic stresses and crystal growth

In the analysis of the possible effect of elastic stresses on crystal growth in glass-forming liquids, we consider first the case that stress relaxation is governed by Maxwell's equation. Eqs. (11) and (13) yield then

$$\left(\frac{4d_0^2}{D}\right) = -\tau_R \ln\left(\frac{\varepsilon}{\varepsilon_0}\right) \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right]. \quad (15)$$

Employing further the relation [22]

$$\tau_R = \frac{\eta(1 + \gamma_m)}{E_m} \quad (16)$$

between Maxwell's relaxation time,  $\tau_R$ , and viscosity,  $\eta$ , we arrive at

$$4 \left( \frac{E_m d_0^2}{(1 + \gamma_m) k_B T} \right) \left( \frac{k_B T}{D \eta d_0} \right) = -\ln\left(\frac{\varepsilon}{\varepsilon_0}\right) \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right]. \quad (17)$$

Eq. (17) allows one to determine the effective stress parameter  $\varepsilon$  in dependence on temperature and, consequently, the magnitude of the effect of elastic stresses on crystal growth in glass-forming liquids.

As a first general result of the analysis of Eq. (17), we conclude that, as far as the Stokes–Einstein (or Eyring) equation [17],

$$D = \frac{k_B T}{\eta d_0}, \quad (18)$$

is fulfilled, elastic stresses cannot have any effect on crystal growth. The ratio  $(\varepsilon_0/\varepsilon)$  has to be sufficiently large in order that above equation can be fulfilled, i.e.  $\varepsilon$  must be small as compared with  $\varepsilon_0$ .

Indeed, introducing the characteristic time of molecular jumps,  $\tau$ , via the relation [17]

$$\tau = \frac{d_0^2}{D}, \quad (19)$$

we arrive with Eq. (16) at [6]

$$\frac{\tau_R}{\tau} = \left( \frac{k_B T (1 + \gamma_m)}{E_m d_0^3} \right) \left( \frac{D \eta d_0}{k_B T} \right). \quad (20)$$

For liquids of sufficiently low viscosity, the Stokes–Einstein/Eyring equation is fulfilled and the characteristic

times of molecular motion,  $\tau$ , are of the same order of magnitude as Maxwell's relaxation time,  $\tau_R$ . Hence, one can get the following estimate for the Young modulus of the liquid,  $E_m$  (see also [23])

$$\frac{E_m d_0^3}{(1 + \gamma_m)} \cong k_B T. \quad (21)$$

Substitution of Eqs. (18) and (21) into Eq. (17) yields

$$4 \cong -\ln\left(\frac{\varepsilon}{\varepsilon_0}\right) \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right] \quad (22)$$

resulting in

$$-\ln\left(\frac{\varepsilon}{\varepsilon_0}\right) \gg 4 \quad \text{i.e.} \quad \varepsilon \ll \varepsilon_0 e^{-4}. \quad (23)$$

In this way, the effect of elastic stresses can be ignored as far as Eqs. (18) and (21) are fulfilled.

However, when the decoupling temperature,  $T_d$ , is approached in cooling the liquid, molecular motion in the melt (which determines the rate of crystal growth) changes from liquid-like to solid-like. At  $T_d$ , viscous relaxation and molecular motion decouple, the ratio of the characteristic time-scales  $\tau_R/\tau$  increases exponentially with decreasing temperature, the Stokes–Einstein/Eyring equation does not hold any more and, according to Eq. (20), the ratio  $(k_B T/D\eta d_0)$  tends to zero. In order to analyze the dependence of the ratio  $\varepsilon/\varepsilon_0$  in this alternative case, we employ Eq. (20) and rewrite Eq. (17) as

$$4 \left( \frac{\tau}{\tau_R} \right) = -\ln\left(\frac{\varepsilon}{\varepsilon_0}\right) \left[ 1 - \exp\left(-\frac{\Delta\mu - \varepsilon}{k_B T}\right) \right]. \quad (24)$$

Since, below  $T_d$  with a further decrease of temperature, the ratio  $(\tau/\tau_R)$  decreases exponentially, the parameter  $\varepsilon$  tends to  $\varepsilon_0$ . This result is independent on any assumptions concerning the temperature dependence of the stress parameter,  $\varepsilon_0$ , itself, it is exclusively a consequence of the breakdown of the Stokes–Einstein/Eyring equation below  $T_d$ .

A similar analysis, as outlined above in detail for normal growth, can be made for any other modes of growth. The only difference in the resulting equations is that the number '4' in Eqs. (23) and (24) has to be replaced by  $(4/f)$ . Since  $f$  has generally finite positive values less than one, the conclusions remain the same. Note also that a similar analysis with qualitatively equivalent results can be easily performed for the case of stretched exponential relaxation, as given by Eq. (12). Obviously, the only difference is that a replacement  $\ln(\varepsilon_0/\varepsilon) \Rightarrow [\ln(\varepsilon_0/\varepsilon)]^{1/\beta}$  has to be made in Eq. (17). We thus conclude that the results of the present analysis are independent on the specific mechanisms of crystal growth and stress relaxation.

Analogous conclusions have been derived in our previous analyses of stress effects on nucleation. Similarly to crystal growth, elastic stresses do not have any effect on nucleation as far as the Stokes–Einstein/Eyring equation is fulfilled. However, in the temperature range below the decoupling



temperature,  $T_d$ , elastic stress effects may be of considerable importance. It follows that elastic stresses can be of significance both for critical crystallite nucleation – as shown earlier [5,6,15,16] – and for the description of crystal growth, in both cases, in the same range of temperatures,  $T \leq T_d$ . Similarly, as for nucleation, the approach developed here allows one to account for a continuous transition from a behavior of the ambient phase typical for a Newtonian liquid (for temperatures at and above the temperature of decoupling) to a behavior typical for a Hookean solid (for temperatures near and below  $T_g$ ). In order to demonstrate these results, we will analyze in the next section, as an example, stress effects on crystal growth in lithium disilicate glass.

#### 4. Application: crystal growth rates in lithium disilicate glass

According to Eq. (9), for lithium disilicate the effective stress parameter  $\varepsilon$ , determining the effect of elastic stresses on crystal growth, does not exceed, in the vicinity of  $T_g$ , a value of about 4% of the thermodynamic driving force,  $\Delta\mu$ . By this reason, we are aware that the magnitude of the effect of elastic stress on crystal growth will not be strong for this particular system. Despite this disadvantage, the general features of the theory developed above can be clearly demonstrated. The choice of this particular system has the advantages that crystal growth rate data are available over a wide range of temperature and, moreover, we can compare stress effects on crystal growth with the results of the analysis of stress effects on nucleation performed earlier by us for this particular system [15,16]. The availability of such additional information will allow us to derive some additional general conclusions not only concerning the relative magnitudes of the effect of stress on nucleation, on one side, and crystal growth, on the other, but also of more general nature.

Assuming, again, that stress relaxation proceeds in accordance with Maxwell's law (cf. Eq. (11)), Eq. (17) allows us to determine the ratio  $(\varepsilon/\varepsilon_0)$  and, as a next step, the value of  $\varepsilon$  as a function of temperature. The parameters of lithium disilicate glass are taken from the previous analyses of the effect of elastic stresses on crystal nucleation [15,16]. By this reason, we only present here the final results without a detailed discussion on how the respective dependencies were obtained.

The thermodynamic driving force of crystal growth in the absence of stresses,  $\Delta\mu$ , was taken from the experimental investigations performed by Takahashi and Yoshi [29]. The molar mass equals  $M = 150 \text{ g mol}^{-1}$ , the density of the glass and the crystalline phase are  $\rho_{\text{glass}} = 2.35 \text{ g cm}^{-3}$  and  $\rho_{\text{crystal}} = 2.45 \text{ g cm}^{-3}$ , respectively, resulting in a value of the misfit parameter equal to  $\delta = 0.04255$ . The characteristic size of the building units of the crystalline phase equals  $d_0 = 5.88 \times 10^{-10} \text{ m}$ . The melting temperature is  $T_m = 1307 \text{ K}$  and the glass-transition temperature equals  $T_g = 728 \text{ K}$ . For the Poisson ratios of glass-forming melt and crystal, we take  $\gamma_m = \gamma_c = 0.23$ .

To the best of our knowledge, experimental data on the dependence of  $E_m$  on temperature are not available for the system under consideration. By this reason, we have set the Young's modulus of the ambient phase equal to the modulus of the crystal,  $E_c = 76 \text{ GPa}$ . There exists a variety of experimental data and general theoretical arguments indicating the existence of a considerable increase of Young's modulus of glass-forming melts with decreasing temperature near the respective temperature of vitrification,  $T_g$  [6,17,24–28]. The incorporation of such effects (as done, for example, in Ref. [6]) does not affect the results of the present analysis and is, therefore, omitted here.

The temperature dependencies of the viscosity (in Pa s) and the diffusion coefficient (in  $\text{m}^2\text{s}^{-1}$ ) are interpolated via the following equations

$$\log \eta = -2.37 + \frac{3248.6}{T - 500} \quad (25)$$

and

$$\log D \cong -7.57 - \frac{3941}{T - 452}. \quad (26)$$

In both equations, the temperature is given in Kelvin.

For the determination of the effective diffusion coefficient, which determines the rate of crystallization as a function of temperature, we employed measurements of the nucleation time-lag. Such data are available for temperatures in the range  $693 \text{ K} \leq T \leq 763 \text{ K}$  ( $T_g \sim 725 \text{ K}$ ). The results were interpolated in such a way as to fulfill the Stokes–Einstein/Eyring relation for temperatures above  $T_d = 1.2T_g$ . This approach is corroborated by the comparison of diffusion coefficients calculated from viscosity via the Stokes–Einstein/Eyring equation and from growth rates of lithium disilicate crystals in the melt of the same composition [30]. They indicate the possible existence of decoupling of diffusion and relaxation near  $T_d = 1.2T_g$  (see also Fig. 4). The Eyring ratio ( $k_B T / \eta D d_0$ ) versus temperature, shown in Fig. 1, demonstrates significant deviations from the Stokes–Einstein/Eyring behavior for low temperatures.

The ratio  $(\varepsilon/\varepsilon_0)$  and the effective stress parameter  $\varepsilon$  versus temperature, obtained with Eqs. (25) and (26), are shown in Figs. 2 and 3 by full curves. One first sees that, for temperatures in the range  $0.46 \leq T/T_m \leq 0.49$ , the system switches from a liquid-like behavior (where elastic stresses are negligible) to a behavior that is typical for a Hookean solid. However, this transition is found here in a temperature range, where growth rates cannot be experimentally measured in reasonable time-scales (note that the glass-transition temperature for lithium disilicate is  $T_g/T_m \cong 0.557$ ). Therefore, for the considered system, elastic stresses seem to have no sizeable effect on crystal growth rates,  $U$ , in the range of temperatures where  $U$  can be measured.

However, in the present analysis we employed values of the diffusion coefficient calculated from data on the time-lag for nucleation. In this procedure, classical nucleation

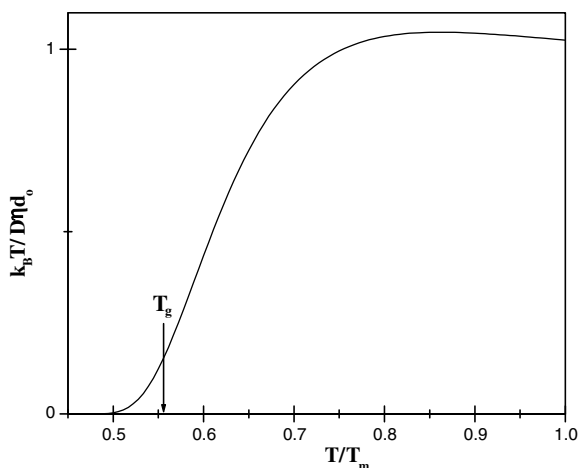


Fig. 1. Eyring ratio,  $(k_B T / \eta D d_0)$ , as a function of temperature. To a good approximation, for  $T > T_d \cong 1.2 T_g$ , the Stokes–Einstein/Eyring equation is fulfilled. For  $T \leq T_d$ , significant deviations are found and the Eyring ratio tends to zero with decreasing temperature.

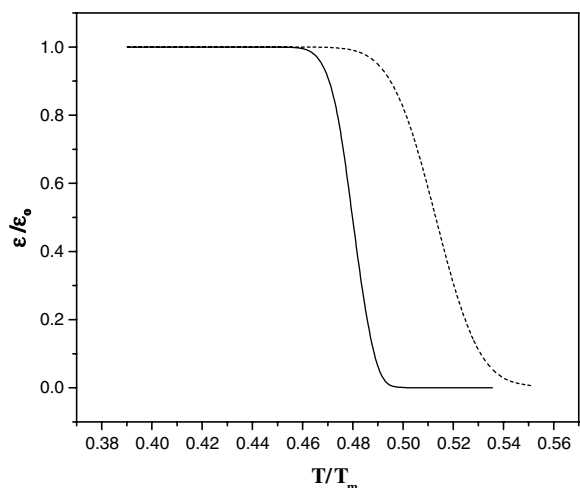


Fig. 2. Ratio  $(\epsilon/\epsilon_0)$  as a function of temperature. The full curve shows the results of the computations if the diffusion coefficient is determined via Eq. (26). The dashed curves correspond to possible corrections of the diffusion coefficient by a factor  $10^2$  (see text). In both cases, the approach of the effective stress parameter to zero is found for temperatures, where Young’s modulus retains values typical for the crystal.

theory has been employed in order to determine the size of the critical clusters as a function of undercooling and normal growth was assumed in describing aggregation processes to clusters of critical sizes. Latter assumption has no effect on the results of the computations of the temperature dependence of effective stress parameter. Indeed, employing time-lag data for the determination of the kinetic coefficients and assuming other modes of growth, actually the product  $Df$  in Eq. (2) is computed and in Eq. (17), we have to replace  $D$  by  $Df$  as well leaving the results of the computations of the stress parameters unchanged. However, taking into account well-known limitations of the classical nucleation theory in application to crystallization [31–33], we have to check whether the estimates of

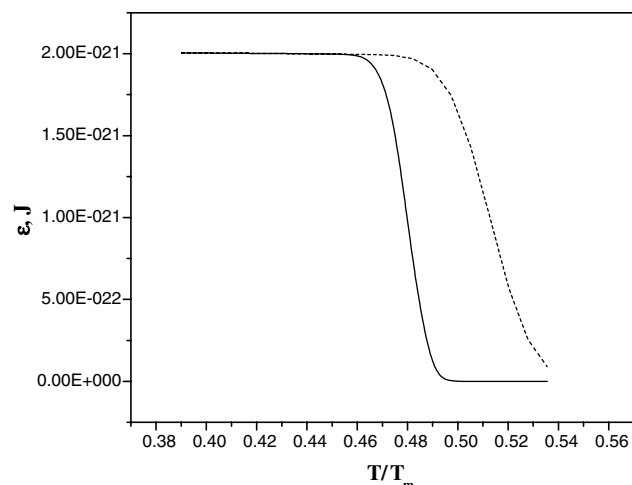


Fig. 3. Effective elastic stress parameter  $\epsilon$  versus temperature. The full curve shows the results of the computations if the diffusion coefficient is determined via Eq. (26). The dashed curves correspond to possible corrections of the diffusion coefficient by a factor  $10^2$  (see text).

the effective diffusion coefficients, obtained in this way, describe crystal growth rates correctly. For these purposes, in Fig. 4 the linear growth rate  $U$ , determined by different methods, is shown as a function of temperature. The dashed curve (1) represents the results if viscosity-data (according to Eq. (25)) are employed for the determination of the diffusion coefficient and growth rates. The full curve gives the respective data obtained with the diffusion coefficient – derived from time-lag measurements (cf. [15]) – without (full curve (2)) and with (circles (3)) an account of elastic stress effects. As we expected and in agreement

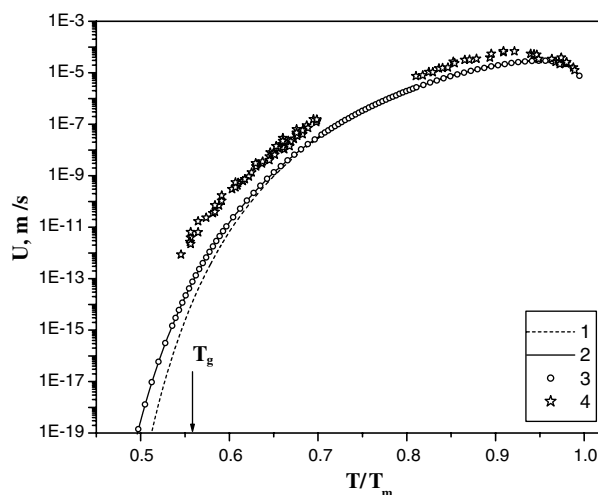


Fig. 4. Crystal growth rate,  $U$ , versus temperature. *Dashed curve*: viscosity (Eq. (25)) and the Stokes–Einstein/Eyring equation (Eq. (18)) are employed for the determination of the diffusion coefficient; *full curve*: data obtained with the diffusion coefficient – derived from time-lag measurements (cf. [15]) – without (full curve) and with (circles) an account of elastic stress effects. In addition, available experimental data are shown [30]. In order to describe adequately the experimental data in the vicinity of  $T_g$ , the diffusion coefficient should increase by a factor of the order  $10^2$ . Available experimental data denoted by stars.

with the results of computations shown in Figs. 2 and 3, elastic stresses do not have any sizeable effect on the growth rate in the considered range of temperatures. In addition, available experimental data on crystal growth rates are shown [30].

Deviations of experimental crystal growth data and predictions in the range of temperatures  $0.8 < T/T_m < 1$ , employing viscosity measurements described by Eq. (25), can be resolved easily: the authors, which performed the analyses in this range, report lower (by a factor 1.5–2) values of viscosity for their systems. Consequently, employing their viscosity data, their growth data are described appropriately by diffusion coefficients determined via the Stokes–Einstein/Eyring equation. Fig. 4 shows also that, in order to describe adequately the experimental growth rate data in the vicinity of  $T_g$ , the diffusion coefficient – obtained from time-lag data via classical theory – has to be increased by a factor  $10^2$  to reproduce the experimental results. The origin of this deviation in the considered range of temperatures can be twofold. First, one can suppose that the classical nucleation theory does not give an appropriate description of the properties and the parameters of the critical clusters. This point of view is supported by the dramatic deviations between the predictions of the classical theory and experimental rates of critical crystallite formation (cf. Refs. [16,31–33]). Such point of view gets additional support also from a generalization of Gibbs' approach as developed in recent years (cf. Refs. [34–36] for an overview). On the other hand, the mentioned theoretical analyses and investigations by other authors, discussed there, show that the kinetic parameters determining nucleation and growth processes may depend on cluster size. In this way, the existing deviation in the estimates of the effective diffusion coefficient can be considered a reflection of existing problems in the description of crystallization kinetics which do not have found a satisfactory general solution so far.

In analyzing the effect of elastic stresses on nucleation in lithium disilicate, in Ref. [16] we determined the driving force of crystallization and the specific interfacial energy from experimental data on time-lag and nucleation rates. In our analysis, both driving force and surface energy were considered as unknown functions of temperature. These results can be employed to determine the diffusion coefficient from time-lag data, again, but in an alternative way as compared with classical nucleation theory. The resulting dependence of diffusion coefficient on temperature is shown in Fig. 5 by a dashed curve. It turns out that it is one order of magnitude larger than the estimates obtained via the classical nucleation theory.

Provided we assume that time-lag data and their interpretation by the classical theory underestimate the diffusion coefficient by the mentioned factor, then we have to repeat the computations, but with higher values of the diffusion coefficients. The results of such computations are shown in Figs. 2 and 3 by dashed curves. Qualitatively, the results of the previous computations, given in Figs. 2

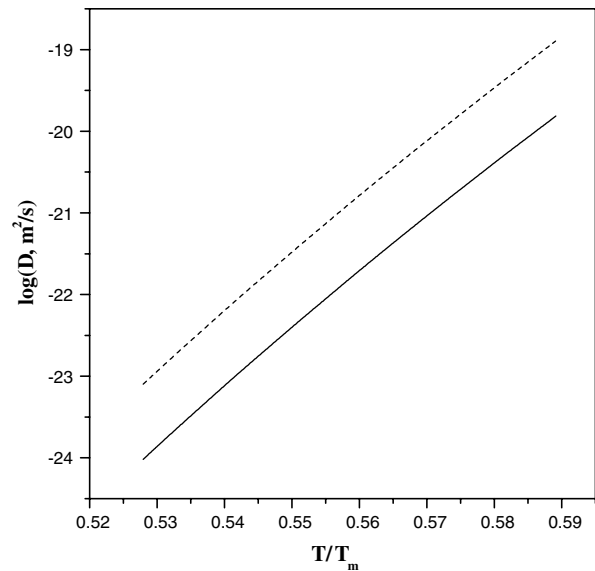


Fig. 5. Effective diffusion coefficient, determining the rate of crystallization, calculated from nucleation time-lag data employing the classical nucleation theory (full curve) and data from a fit of both driving force of crystallization and specific interfacial energy as performed in Ref. [16] (dashed curve).

and 3 by full curves, are not changed, however, the respective curves are moved into a range of considerably higher temperatures (see the dashed curves in Figs. 2 and 3). Such a modification of the values of the diffusion coefficients leads, consequently, to a similar transition of the effect of elastic stresses both on growth and also on nucleation (cf. the analysis in Ref. [15]).

## 5. Discussion

In the present analysis, we developed a general method to treat the effect of elastic stresses on crystal growth taking into account both stress evolution and stress relaxation. We assumed normal growth and Maxwellian relaxation. However, the procedure developed can be similarly performed for any other mechanism of crystal growth and/or relaxation with qualitatively equivalent results.

We have shown that in the range of temperatures where the Stokes–Einstein/Eyring equation is fulfilled, stresses relax too fast to allow for a significant influence on the growth rates. However, as soon as this condition is violated, elastic stresses may be important for the description of crystal growth and have, in general, to be accounted for. In the example analyzed here, elastic stress effects are of importance only in temperature ranges where the growth rate is too low to be experimentally detectable. In this way, the question arises, for which classes of systems elastic effects may be of particular importance?

As mentioned above, as soon as the Stokes–Einstein/Eyring equation is fulfilled, elastic stresses cannot have a significant effect on crystal growth. Consequently, the higher the deviations from the Stokes–Einstein/Eyring

equation immediately below the decoupling temperature, the higher is the possible effect of elastic stresses. With respect to the results shown in Fig. 1, we can reformulate this statements as follows: the effect of elastic stresses increases with increasing rate of approach to zero of the Eyring ratio  $k_B T / (D\eta d_0)$ .

Second, the effect of elastic stresses depends significantly on the ratio of the thermodynamic driving force  $\Delta\mu(T_g)$  and the elastic stress parameter,  $\varepsilon_0$ . An overview of the spectrum of possible values of this ratio for different classes of glass-forming liquids is given in Ref. [37]. As it turns out, the stress parameter  $\varepsilon_0$  can be comparable in magnitude with  $\Delta\mu$ . This is a necessary condition for a significant dependence of the growth rate on stress.

Third, despite the uncertainties connected with the applicability of the classical nucleation theory to crystallization of glass-forming liquids, one can expect that the effect of stresses on nucleation will be, in most cases, much more significant than on growth. Indeed, the steady-state nucleation rate depends exponentially on the driving force squared via

$$I_{st} = I_0 \exp\left(-\frac{\sigma^3 v_c^2}{k_B T (\Delta\mu)^2}\right), \quad (27)$$

where  $\sigma$  is the nucleus/melt surface energy and  $I_0$  a parameter determined mainly by kinetic factors. In contrast, according to Eq. (2), the dependence of the growth rate on the driving force and thus, on the effect of stresses, is rather weak. Elastic stresses can have an effect on growth only as soon as  $\varepsilon_0$  is comparable in magnitude with  $\Delta\mu$ . For the case of lithium disilicate, for example, elastic stresses can reduce the growth rate by less than 2% at 420 °C (this estimate results if one determines  $\varepsilon_0$  via Eq. (9) with  $E_m = E_c$  neglecting stress relaxation). However, as shown in Refs. [15,16], the effect on the nucleation rate can reach several orders of magnitude. Hence, if elastic stresses have a significant effect on growth rates, homogeneous nucleation in the bulk will be totally suppressed, in general. Vice versa, in glasses which crystallize by homogeneous nucleation (i.e. in glasses having a reduced glass-transition temperature  $T_g/T_m \leq 0.6$  (cf. [38])) elastic stresses will not affect significantly the growth rates.

In more detail, the kind of dependence of the growth rates on the thermodynamic driving force is illustrated in Fig. 6. In this figure, the value of the thermodynamic factor,

$$U_{th} = 1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) = 1 - \exp\left[-\left(\frac{\Delta H_m}{k_B T_m}\right) \frac{(1 - T_r)}{T_r}\right], \quad (28)$$

in the expression for the growth rate, Eq. (2), is shown as a function of (a) the reduced thermodynamic driving force,  $\Delta\mu/(k_B T)$ , and (b) the reduced melting entropy,  $\Delta S_{mr} = \Delta H_m/(k_B T_m)$ . In Eq. (28),  $\Delta H_m$  is the melting enthalpy per particle,  $T_r = T/T_m$  and the Volmer–Turnbull equation

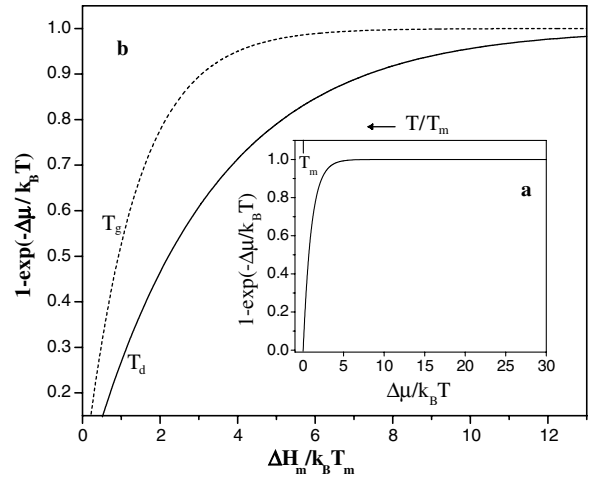


Fig. 6. Value of the thermodynamic factor,  $1 - \exp(-\Delta\mu/(k_B T))$ , in Eq. (2) versus (a) reduced thermodynamic driving force,  $\Delta\mu/(k_B T)$ , and (b) reduced melting enthalpy,  $\Delta H_m/(k_B T_m)$ . In (b) the full curve shows the respective values of this quantity at  $T_d$ , while the dashed curve refers to its value at  $T_g$ . Here  $T_g$  is taken to be equal to  $T_g = (2/3)T_m$  and  $T_d = 1.2T_g$ .

(5) was employed. In Fig. 6(b), the full curve shows the respective values of this quantity at  $T_d$ , while the dashed curve refers to the value of  $U_{th}$  at  $T_g$ . Here we assume  $T_g = (2/3)T_m$  and  $T_d = 1.2T_g$ . The graph presented in Fig. 6(a) is valid for any value of the reduced melting entropy,  $\Delta S_{mr} = \Delta H_m/(k_B T_m)$ . In order to find out the temperature, corresponding to a given point along the curve, one has to know the value of  $\Delta S_{mr}$  (which is a characteristic of the substance under consideration).

As we have shown above, elastic stresses can affect crystal growth rates only at temperatures below the decoupling temperature  $T \leq T_d \cong 1.2T_g$ . It is evident from Fig. 6(a) that, when  $T_d$  corresponds to the right part of the plot where the growth rate weakly depends on  $\Delta\mu$ , elastic stresses can diminish the growth rate only if the values of the stress parameter  $\varepsilon_0$  are close to or exceed the thermodynamic driving force. However, if  $T_d$  corresponds to the left part of the plot, then the growth rate is highly sensitive to slight changes of  $\Delta\mu$  and an effect of elastic stresses can be expected to occur even then if the magnitude of  $\varepsilon_0$  is considerably smaller as compared with  $\Delta\mu$ .

Since the temperature scale in Fig. 6(a) depends on  $\Delta S_{mr}$  we plotted  $U_{th}$  at  $T_d$  and  $T_g$  as a function of  $\Delta S_{mr}$  (Fig. 6(b)). Hereby we estimated  $T_g/T_m$  as 2/3 taking into account the above made conclusion. The interval of the  $\Delta S_{mr}$  variation, employed in Fig. 6(b), is typical for silicate glasses.

According to the solid and dotted lines in Fig. 6(b), the  $U_{th}$  values at  $T_d$  and  $T_g$  and, consequently, the position of  $T_d$  and  $T_g$  on the plot of Fig. 6(a) strongly depend on  $\Delta S_{mr}$ . Since the values of  $U_{th}$  in the range from 0.0 to 0.8 correspond to a strong dependence of the growth rate on the thermodynamic driving force (see Fig. 6(a)), the effect of elastic stresses on growth rates can be expected to be significant in glasses with  $\Delta S_{mr}$  lower than about 5. Therefore,



the probability of having important elastic stress effects increases with decreasing  $\Delta S_{\text{mr}}$ . Taking into account Jackson's [39] criterion for crystal growth mechanisms, we can suppose that normal growth is more affected by elastic stresses than screw dislocation and 2D-surface nucleation mediated growth. By this reason, we performed the respective analyses here explicitly for the case of normal growth.

In the present analysis, we considered the effect of elastic stresses on the growth of crystals of macroscopic sizes. The results can also be employed for the analysis of growth of crystallites of near-critical sizes taking into account, in addition, interfacial contributions to the thermodynamic potential. In this case, we have to add a term  $\sigma A$  into Eq. (4) where  $\sigma$  is the specific interfacial energy and  $A$  the surface area of the growing aggregate. As the result, the effective driving force of crystal growth would contain then an additional term due to interfacial effects proportional to  $-n^{1/3}$ .

## 6. Possible modifications and generalizations

In the present and preceding papers [5,6,15,16], we analyzed the effect of elastic stress evolution and relaxation on nucleation and crystal growth. This analysis was based on two basic assumptions: (i) The state of the newly evolving phase does not depend on the size of the aggregates considered and is widely equivalent to the state of the stable macroscopic phase. (ii) Elastic stresses are due to misfit effects and grow linearly with the size of the newly evolving phase (Nabarro model). The basic result of the analysis is that – as soon as the Stokes–Einstein/Eyring equation is not fulfilled – elastic stresses may have a significant effect both on nucleation and cluster growth. The magnitude of this effect depends, of course, on a variety of additional factors, however, the principal possibility of such effect has always to be taken into account.

Posing the question about possible modifications and generalization of the theory developed, one has to answer the question whether the assumptions of the theory are generally fulfilled or not. A detailed analysis of experimental data on nucleation of glass-forming silicate melts proves that the classical nucleation theory leads to serious problems in treating nucleation data [31–33]. These problems can be resolved in the framework of a newly developed approach to the description of nucleation and growth processes [34–36,40,41]. The basic advantages of this so-called generalized Gibbs' approach consists in its ability to determine theoretically the dependence of the state parameters both of critical, sub- and supercritical clusters on supersaturation and cluster size. Hereby it turns out that the state of the clusters is essentially cluster size and supersaturation dependent. As a consequence, a variety of thermodynamic and kinetic parameters (surface energy, diffusion coefficients, driving force for cluster formation, growth rates) become cluster size dependent as well. Such a size-dependence occurs (due to the variation of the bulk properties

with cluster size) even then if one neglects surface energy terms in the thermodynamic description. In this way, the problem arises to treat theoretically stress evolution and stress relaxation going beyond the classical theory of nucleation and growth and relying on mentioned generalized Gibbs' approach. A first attempt to proceed in this direction can be found in Ref. [16]. The analysis shows that the effect of elastic stresses on nucleation is increased as compared with the case when basic assumptions of classical nucleation theory are employed in the analysis.

Another limitation of the present model is connected with the assumption that stresses are due to misfit effects and can be described by Nabarro-type dependencies. As already mentioned, in the case of segregation in solutions, when the segregating component has a much higher diffusivity than the ambient phase particles, stresses may evolve growing proportional to  $(V - V_0)^2$ . Here  $V$  is the volume of the cluster of the new phase and  $V_0$  some initial volume, where such kind of stresses become dominant. A detailed analysis shows that such model of stress evolution may be effective for sufficiently large clusters when the above mentioned condition is fulfilled. In such situations, several time or length scale parameters (connected with the large differences in the partial diffusion coefficients of the different components of the system) exist and decoupling of relaxation and growth is not connected with the Stokes–Einstein/Eyring equation, but with the differences in the diffusivities. Consequently, in a further generalization of the theory one has to specify more clearly the conditions at which Nabarro-type stresses will be eventually replaced by mechanisms of stress evolution resulting in a more rapid increase of stress with the size of the clusters or regions of the newly evolving phase.

## 7. Conclusions

As far as the Stokes–Einstein/Eyring equation is fulfilled, elastic stresses do not have any effect on crystal growth. However, below the temperature of decoupling of diffusion and viscous flow, when the Stokes–Einstein/Eyring equation breaks down, stresses may have a significant influence on crystal growth. The present results therefore challenge the widespread argument that internal stresses relax too fast to affect crystal growth in glass-forming liquids and could help to explain the often observed lack of agreement between model predictions (which do not take stresses into account) and experimental crystal growth data.

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