



Lag time to crystal nucleation of supercooled lithium disilicate melts: A test of the classical nucleation theory



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ABSTRACT

A noticeable discrepancy between the observed lag times to crystal nucleation of continuous cooling experiments and the predictions of the classical nucleation theory (CNT) is evident. In particular, in these experiments nucleation at free surfaces and in contact with noble metal is delayed by many orders of magnitude with respect to CNT even if one neglects the heterogeneous character of the phase transition in the kinetic analysis. In this paper it is proposed that delayed nucleation is a consequence of a smaller Gibbs free energy of the evolving critical nucleus as compared to the growing macrocrystal. Considering lag times in scales of the reduced melting temperature T/T_m from 0.5 to 0.92 a difference in the free energy of crystallization of 6.7 kJ mol^{-1} and a melting point depression of 146 K is approximated. The results are in line with the description of heterogeneous systems as introduced by the generalized Gibbs approach but can be also a hint to metastable polymorphs at the nanoscale.

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1. Introduction

Liquid-to-crystal nucleation of supercooled lithium disilicate glass melt has been a subject of extensive experiments [1–5] (see also review in [6]), theory [7,8] and simulations [9–11]. In most of the experimental reports nucleation was studied upon annealing at temperatures above the glass transition of a prior glass melt that was quenched. In particular, double-stage heat-treatments were carried out to allow nucleation during the first hold at the nucleation temperature T_n and to grow these nuclei to observable crystal sizes during the second hold at the development temperature T_d , with $T_d > T_n$. We note that the size of the crystals to be developed at T_d depends on the observation technique used. Frequently, optical microscopy is used, which requires crystals at the micrometer scale. In order to determine the number densities of nuclei from counting crystals of much larger size, negligible small growth rates and nucleation rates are assumed at T_n and T_d , respectively (no overlap of the Tammann rate curves $I_0(T)$ and $U_0(T)$ at T_n and T_d , respectively with $I_0(T)$ = temperature-dependent stationary nucleation rate and $U_0(T)$ = temperature-dependent crystal growth rate). Typical crystal number density curves obtained from the double-stage heat-treatment technique show an initial time period, where no crystals are observed. Then a non-stationary period, where the number density increases non-linearly with time, followed finally by a stationary nucleation behavior (linear increase of the crystal number density with time) [12]. The non-linear period has been related to an experimental induction time t_{ind} as determined by the intercept of the stationary nucleation part with the time axis. Using classical nucleation theory

Collins and Kashchiev [13,14] proposed that the ratio of inherent lag time τ and t_{ind} is constant. The inherent lag time τ equals the time needed for the cluster to diffuse through the near-critical size space of $(G_{n^*} - G_n) \leq kT$, where G_{n^*} and G_n are the cluster energies of the critical and sub/super-critical cluster, respectively, and k is the Boltzmann constant [15]. This process results in the transient character of the crystal number density curve. Later Shneidman [16–18] derived t_{ind} as the sum of the inherent lag time τ to nucleation and the time to grow nuclei to observable sizes. In this approach the lag time is [17]

$$\tau = \frac{N_{t_{ind}}}{I_0 E_1 [\exp(-\gamma)]}, \quad (1)$$

where $N_{t_{ind}}$ is the crystal number density at t_{ind} , E_1 is the first exponential integral and γ is the Euler constant. Additionally, Slezov and Schmelzer [19] introduced τ from a different solution to the transient nucleation problem.

In literature it was reported that the thermal history of glasses affects the induction time of nucleation [20–23]. Since the growth rate U_0 at $T \geq T_n$ in lithium disilicate is positive [24] (= small overlap of Tammann curves) the subsequent heating at a finite rate between T_n and T_d will change the non-stationary crystal number density curve (undercounting). In particular, a survival size of nuclei, which deviates from those at T_d , will alter the deduced temperature dependences of the critical size and of the interfacial energy [25]. On the other hand, in cases of considerable overlap of the Tammann curves, the number density of crystals can be measured directly after single-stage treatments at T_n . Then t_{ind} and the obtained crystal number density curve will be shifted to larger times by the time period, which is needed to grow nuclei at T_n to observable size, since $U_0(T_n) < U_0(T_d)$ [6,26,27].

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In general for any supercooling temperature ΔT ($\Delta T = T_m - T_n$ with $T_m =$ melting temperature (1306 K [28]) and $T_n < T_m$) the classical nucleation theory CNT predicts an inherent lag time τ to nucleation as it is the time to “collect” enough energy via fluctuations to pass the nucleation region (near-critical size space). According to [13,14], the lag time for critical cluster formation (spherical shape) at T_n can be written as

$$\tau = z \frac{kT_n \sigma_{cl}}{\Delta G_v^2 a^2 D_\tau}, \quad (2)$$

where z is a numerical factor ($= 16 / \pi$ [13,14], $= 80 / 3$ [19]), σ_{cl} is the specific free energy of the critical nucleus–liquid interface, a is the mean size of a “structural unit”, ΔG_v is the thermodynamic driving force for crystallization, i.e. the difference between the free energies of the liquid and crystal per unit volume of the crystal and D_τ is the diffusivity of the moving unit through the critical nucleus–liquid interface. Usually the latter process is described by thermally activated diffusion via:

$$D_\tau = \frac{a^2 kT_n}{h} \exp\left(-\frac{\Delta G_{D'}}{kT_n}\right), \quad (3)$$

where h is the Planck constant, $\Delta G_{D'}$ is the activation energy for the transfer of a structural unit from the liquid to a nucleus (kinetic barrier to nucleation).

The Stokes–Einstein (SE) and Eyring (EY) relations are frequently used to correlate diffusion and shear viscosity η in silicate melts [29]. Both the SE relation and the EY relation require the size of a (atom, molecule, cluster or activated complex), which, in principle, involves the problem in selecting the correct size of the moving unit.

In the hydrodynamic SE approach, valid for dilute molecular suspensions, friction (friction factor $f = 6\pi\eta r$ for non slip between the diffusing units) exerts a force on a particle of radius r undergoing Brownian movement through the surrounding medium of viscosity η controlling its mobility. The friction factor itself is related to the self diffusion coefficient D by $f = kT / D$. For a spherical particle much larger than the solvent molecule rearranging gives [30]:

$$D = \frac{kT}{\lambda_{SE}\eta}, \quad (4)$$

where $\lambda_{SE} = 6\pi r$ is the characteristic length in the SE approach. Based on the independent movement of particles in dilute suspensions SE proved to be an effective link between viscosity and diffusivity in monoatomic liquids, but was inadequate for describing ion diffusivity in polymerized liquid silicates [31,32]. The SE relation therefore is a strong test for polymerization in liquids.

Since the SE relation does not hold for small, fast moving ions [33] and the connection of the diffusion of network formers with the viscosity of the melt is suitable [34–36] we used the EY model in our analysis. In the EY model the diffusion of a particle (atom, ion) is based on a hop or a jump, which results when the nearest neighbors of the diffusive particle are pushed aside. EY treats the short-range order in liquids as a quasi-lattice structure in small regions and allows the particle to jump over the potential barrier into its adjacent hole. According to EY reaction rate theory the size of the activated complex λ_{EY} , containing $CN + 1$ particle, is related to the quotient $kT / D\eta$ by [37]:

$$\lambda_{EY} = CN \left(\frac{V_M}{nN_A}\right)^{1/3} = \frac{kT}{D\eta}, \quad (5)$$

where V_M and CN are the molar volume and the coordination number of the moving particles in the cluster, respectively. N_A is Avogadro's number (mol^{-1}) and n is the number of atoms per formula unit.

Experimental crystal number density curves of the deeply supercooled lithium disilicate melts of a narrow temperature range (from approx. 700 to 760 K) close to the glass transition ($T_g = 724$ K

[38]) have been analyzed to gain τ and to test CNT [5,6,26,39,40]. These studies showed that CNT fails to predict the correct (experimentally observed) lag time. In particular, the classical nucleation theory overestimates the work of critical cluster formation and underestimates the value of the steady-state nucleation rate I_0 and, thus, overestimates τ . Accordingly, the kinetic barrier, the size of the moving structural unit and the thermodynamic driving force were adopted, which will be explained in detail below: Nascimento et al. [41,42] investigated the effects of a decoupling at the crossover temperature T_c ($T_c \approx 1.1 T_g$) of the dynamics of crystal nucleation and growth from those of viscous flow, i.e. the validity of the SE and EY relations at $T < T_c$. They concluded from analyzing lag times in a narrow temperature interval ($0.53 \leq T/T_m \leq 0.59$) through Eq. (2) that the effective diffusion coefficient for the transport of structural units through the liquid–crystal boundary D_τ is larger than the SE and EY diffusivity D by a factor of 1.7 for $T > T_g$ but increases exponentially for $T < T_g$ in the temperature range from 693 to 763 K [42]. In their analysis the SE and EY jump length was used as an adjustable parameter with $\lambda = 270$ pm. The temperature-dependent ratio D_τ/D can be approximated by the equation:

$$\frac{D_\tau}{D} = A_1 + A_2 \exp\left(-\frac{T}{A_3}\right), \quad (6)$$

where $A_1 = 1.7$, $A_2 = 1.3 \times 10^{32}$ and $A_3 = 9.7$ K.

Fokin et al. [40] followed a generalized Gibbs approach (GGA) [8] and explained the discrepancy between I_0 , τ and CNT by a thermodynamic driving force for the formation of an evolving nucleus, which is smaller than for the growth of a macroscopic crystal by a constant value of 7.83 kJ mol^{-1} (fit through $I_0 + U_0$ data) and $10.89 \text{ kJ mol}^{-1}$ (fit through $I_0 + \tau$ data). The reduction of ΔG_v corresponds to $a = 588$ pm and results, dependent on the used data set, in the specific interfacial energies of $\sigma_{cl} = 0.122 \text{ Jm}^{-2}$ and $\sigma_{cl} = 0.105 \text{ Jm}^{-2}$. Their analysis was restricted to a narrow temperature interval ($0.53 \leq T/T_m \leq 0.59$).

By contrast to homogeneous volume nucleation, when annealing a lithium disilicate glass above T_g , continuous supercooling from T_m provokes heterogeneous nucleation of the melt in contact with platinum metal (container wall [43–45], thermojunction [46–48] and particles [49]) or at free surfaces of levitated droplets [49]. The inherent lag time of nucleation in those experiments is then

$$\tau = \Delta T \times q^{-1}, \quad (7)$$

where $q =$ cooling rate. These studies showed that the first nucleus grew fast (approximately 7–8 orders of magnitude faster than at the glass transition range [24]), which impedes the formation of a nuclei ensemble (the homogeneous nucleation rate is extremely low at temperatures close to T_m) and allows one to detect the liquid-to-crystal transformation in-situ from the onset of the exotherm using differential scanning calorimetry [43,44,49] or from visual inspection using a high-speed video camera [49]. In any case large parts of the small liquid volume (DSC–pan, levitated droplet) will be consumed by the first crystal during a time interval 1–2 orders of magnitude smaller than τ . Recently, it has been shown that due to the stochastic nature of the nucleation (nucleation is not a deterministic process) τ has to be determined from an ensemble of cooling runs of the same liquid volume [44]. Further, it was shown that repeatedly supercooling of the same volume of liquid results in the same distribution of lag times as isothermal holds at a fixed supercooling temperature. This confirms that the ergodicity of the system (volume average is equal to the time average) at relative low degrees of supercooling is valid [50–53].

Experimental lag times of continuous cooling regimes have not been compared with theoretical predictions. The use of these data will represent a more rigorous approach since the range of supercooling the lithium disilicate melt is extended considerably from a small interval around T_g ($0.53 \leq T/T_m \leq 0.59$) to $0.53 \leq T/T_m \leq 0.92$. Therefore the present study aims to compile τ data of homogeneous and

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