Crystal nucleation in glass-forming liquids: Variation of the size of the "structural units" with temperature

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ABSTRACT

The description of crystal nucleation rates in supercooled liquids in the framework of the classical nucleation theory (CNT) fails if one uses a fixed size of "structural units". To reconcile the experimental data and CNT, we assumed an increase of the size of the structural units that control nucleation with decreasing temperature for temperatures below the nucleation rate maximum, $T < T_{max}$. This hypothesis was tested for several glass-forming liquids, where crystal formation proceeds by bulk homogeneous nucleation. It can explain the temperature dependence of the nucleation rate in the range $T < T_{max}$, where the description of nucleation rate by CNT drastically fails. The size of the structural units can be related either to the size of the cooperatively rearranging regions (CRR) or to an effective size parameter, accounting for corrections in the theoretical treatment of the kinetics of aggregation in multi-component systems via a quasi-one-dimensional description.

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1. Introduction

Crystal nucleation and growth in supercooled liquids are key phenomena in materials science, especially in glass science and engineering, because they control glass formation and the development and production of glass-ceramics [1]. Therefore, these processes have been intensively studied experimentally and theoretically in recent decades, especially for glass-forming liquids. Fortunately, due to their high viscosity, which results in relatively slow (easily measurable) kinetics, glass-forming liquids have provided a plethora of experimental data on crystallization processes, which can be employed for testing different models and theories, as we will do here.

In the theoretical interpretation of the nucleation kinetics in glass-forming melts, the classical nucleation theory (CNT), originally elaborated for one-component systems, has been predominantly employed because it allows a qualitatively correct description of the crystal nucleation processes. According to CNT, the interplay between the effective diffusion coefficient, D, of the "structural units" that controls the critical nuclei formation and the thermodynamic barrier for nucleation, $W_c(T)$, results in a maximum of the steady-state nucleation rate, $I_{st}(T)$, at a temperature, $T = T_{max}$, where W_c is the work of critical cluster formation. By employing certain assumptions (the main one being that the

nucleus/liquid surface energy is size-dependent which can be related to the decrease of the critical nucleus size (see, e.g., [2,3,4]) with decreasing temperature) and assigning reasonable values to adjustable parameters, one can achieve a quantitative agreement between the calculated and experimental values of $I_{st}(T)$ in the range $T > T_{max}$. However, the theoretical and experimental curves start to diverge at $T \cong T_{max}$, and the discrepancy increases for $T < T_{max}$ [5,6].

To describe the decrease of the experimental nucleation rates occurring at higher temperatures than expected by theoretical estimates employing the standard assumptions of CNT, an anomalous increase of the thermodynamic barrier for nucleation, $W_c(T)$, in the temperature range $T < T_{max}$ has been assumed (Fig. 1).

However, according to the standard method of determination of the work of critical cluster formation employed in the original formulation of CNT (Eq. (4)), the thermodynamic barrier for nucleation must monotonically decrease with decreasing temperature in the range where crystal nucleation is observed [15,16].

The solid lines in Fig. 1 correspond to the reduced thermodynamic barrier estimated according to CNT by Eq. (4) using a size-dependent specific surface energy and thermodynamic driving force data determined experimentally (the difference between free energies of liquid and crystal of the same volume, see details below). At low temperatures,
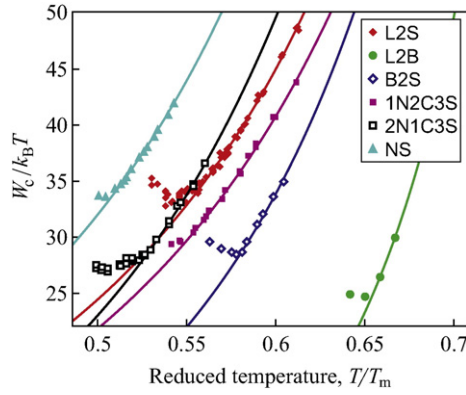
Fig. 1. Reduced thermodynamic barrier for nucleation, $W_c(T)/k_BT$, versus the reduced temperature, T/T_m, for different glasses: $Li_2O \cdot 2SiO_2$ (L2S) [7], $Li_2O \cdot 2B_2O$ (L2B) [8], $BaO \cdot 2SiO_2$ (B2S) [9], $Na_2O \cdot 2CaO \cdot 3SiO_2$ (1N2C3S) [10,11,12], $2Na_2O \cdot 1CaO \cdot 3SiO_2$ (2N1C3S) [13], $44Na_2O \cdot 56SiO_2$ (NS) [14]. T_m is the liquidus temperature.

the values of W_c/k_BT estimated from experimental nucleation rates begin to deviate from the theoretically expected values and reveal for L2S, B2S, and 2N1C3S glasses a well-expressed minimum. Such unusual behavior of $W_c(T)$ cannot be explained in the framework of CNT. Thus, the introduction of additional assumptions or concepts is needed to describe the low temperature part of the temperature dependence of the nucleation rates.

The abovementioned problem was first formulated in connection with the interpretation of nucleation rate data of lithium disilicate glass (see, e.g., [17]), for which crystal nucleation rates were independently measured by two groups as early as 1968 [18,19]. Since then, this glass has served as a model for testing nucleation and growth theories. The development of experimental nucleation research worldwide resulted in the accumulation of a plethora of data and broadened the knowledge concerning these processes. It thus became evident that such unusual behavior of $W_c(T)$, first observed for lithium disilicate glass below T_{max}, is typical for all glass-forming melts at deep undercoolings, not only for silicate glasses (see e.g. [5,20]), but also for metallic glasses (see Fig. 17 in [21]).

One reason for the increase of $W_c(T)$ at $T<T_{max}$ could consist in the reduction of the thermodynamic driving force of crystallization by the elastic stress energy, which might arise during critical nucleus formation due to the density misfit between the melt and the crystal. To check whether elastic stresses could explain this unexpected behavior, a detailed analysis of nucleation based on a model of nucleation in viscoelastic media [22] has been performed for lithium and barium disilicate glasses [20], taking into account both the development and relaxation of stresses. These glasses differ by the values of the density misfits and the relative locations of T_{max} compared with the glass transition temperature, T_g. The analysis was aimed at the separation of the elastic stress effect from other possible effects in the description of the nucleation rates for $T<T_{max}$. For a number of reasons (details in [20]), the calculated values overestimated the elastic stress effect. However, even with such overestimates, we demonstrated that the reduction of the thermodynamic driving force by the elastic stress energy could not explain the (assumed) increase of the calculated thermodynamic barrier for nucleation at $T<T_{max}$, which would be necessary to bring the theory and experimental data into agreement [20].

In alternative attempts to resolve this paradoxical situation, such behavior of $W_c(T)$ was interpreted as a consequence of the increase of the surface energy with decreasing temperature (see e.g., [13]). However, it is hard to provide a reasonable interpretation to such an approach. With a decreasing size of crystals, their melting enthalpy is known to decrease. By this reason, accounting in addition for the Skapski-Turnbull rule, which connects the specific surface energy and the melting enthalpy, a similar behavior is expected for the surface energy. In line with the above considerations, an increase of the specific interfacial

energy with increasing temperature is normally employed in fitting CNT to experimental nucleation rate data for $T>T_{max}$. Consequently, it is theoretically not consistent to assume the opposite behavior for $T<T_{max}$. Thus, the problem of the deviation of the thermodynamic barrier for nucleation for $T<T_{max}$ from that expected from CNT has not been resolved, and other mechanisms should be considered for its resolution.

In the present paper, we continue the analysis of the above problem by employing experimental data for several oxide glasses that reveal homogeneous internal nucleation. To reconcile experimental data and theory, we propose an increase of the size of the "structural units" with decreasing temperature in the range of $T<T_{max}$. This size parameter d can be considered either i) as related to the size of the cooperatively rearranging regions (CRR) that exist in supercooled liquids (see, e.g., [23,24,25,26]) assuming that they could govern crystal nucleation; or ii) as an effective size parameter accounting for corrections of the simple kinetic model employed in CNT when the crystallization kinetics in multi-component systems is treated in terms of a more complex, quasi-one-dimensional, kinetic model. The assumption of an increasing size of the "structural units" with decreasing temperature below T_{max} is tested here for the mentioned glasses and allows one to reconcile theory and experiment. The agreement between experiment and theory was achieved using the standard expression for the work of critical cluster formation, $W_c(T)$, monotonically decreasing, in line with CNT, with decreasing temperature in the whole temperature range, including $T<T_{max}$.

The present paper is structured as follows. In Section 2, we outline the basic equations of CNT required for an analysis of the experimental nucleation rate data. In Sections 3 and 4, the effect of the size of the "structural units" on the nucleation rates is analyzed and interpreted. A discussion (Section 5) and a summary of the main conclusions (Section 6) complete the paper.

2. Basic equations

The main equations of CNT employed in the present work are briefly reviewed in this section. The steady-state nucleation rate, $I_{st}(T)$, is described by (see, e.g. [21,27,28])

$$I_{st} = c\sqrt{\frac{\sigma d_0^2}{k_BT}} \frac{D}{d_0^2} \exp\left(-\frac{W_c}{k_BT}\right), \qquad (1)$$

where T is the absolute temperature and D is the effective diffusion coefficient determining the processes of aggregation of the "structural units" of effective size d_0 to the crystal clusters. For homogeneous nucleation in one-component systems, c is the number density of the "structural units" of the ambient phase,

$$c = 1/d_0^3. \qquad (2)$$

The effective size is commonly estimated via the crystalline molar volume, V_M, and the Avogadro number, N_A, as

$$d_0 \approx \left(\frac{V_M}{N_A}\right)^{1/3}. \qquad (3)$$

W_c in Eq. (1) is the thermodynamic barrier for nucleation, that is, the increase of the free energy of a system due to the formation of a nucleus of critical size. In the simplest case of an isotropic nucleus of spherical shape, we can write.

$$W_c = \frac{16\pi}{3} \frac{\sigma(R_c)^3}{\Delta G_V^2}, \qquad (4)$$