The effect of elastic stresses on the thermodynamic barrier for crystal nucleation

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ABSTRACT

For a variety of oxide glass-forming liquids, the thermodynamic barrier for homogeneous crystal nucleation, W_c, exhibits an unusual increase with a decrease in temperature below the maximum nucleation rate. Such behavior differs from the predictions made using the classical nucleation theory. In this article, we seek possible explanations for the increasing W_c by analyzing whether it is caused by internal elastic stresses that arise due to density misfits between the crystal and liquid phases. For this purpose, crystal nucleation rates and induction time data for two glasses that display significantly different density misfits, lithium and barium disilicates, are employed to determine the work of critical cluster formation. To explain the results, quantitative estimates of the effect of the elastic strain energy on the work required to form a critical nucleus are performed for both glasses. The interplay between stress development and relaxation is accounted for. The computations were performed, taking into account not only the possibility of precipitation of the most stable crystal phase but also that different metastable phases may form during the early stages of nucleation. We show that elastic stresses do indeed reduce the thermodynamic driving force for crystallization, and thus increase the barrier to nucleation. However, the sole effect of elastic strain energy cannot explain the aforementioned unusual behavior of the thermodynamic barrier. Hence, a comprehensive explanation to this phenomenon remains an open issue.

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1. Introduction

The experimental determination of crystal nucleation and growth rates in glass-forming liquids at different temperatures and the ability to calculate and predict their kinetics are required for glass preparation (to avoid crystallization) and for the successful development and production of glass-ceramics via controlled crystallization [1–3]. Moreover, due to their high viscosity, glass-forming liquids permit detailed investigations of their crystallization kinetics over wide temperature intervals to verify the predictive power of nucleation and growth theories.

The first estimates of crystal nucleation rates in typical oxide glass-forming melts were performed using a method proposed and used for organic liquids more than a century ago [4]. Since then, numerous attempts to describe experimental nucleation rate data within the framework of the Classical Nucleation Theory (CNT) have been conducted [5–9]. Although CNT provides a good qualitative explanation of nucleation experiments, serious problems arise when it is employed for quantitative descriptions of experimental data. It should be reminded that experimentally observable values of homogeneous

nucleation rates are achieved only at deep undercoolings ($\Delta T = (T_m - T)$, where T_m is the melting temperature), corresponding to critical nuclei of nanometer sizes. Due to the (expected) nano-sizes of the critical nuclei at such deep undercoolings, direct experimental methods for the specification of their properties are not readily available. Therefore, to analyze the experimental nucleation rates in terms of CNT, researchers introduce some appropriate assumptions concerning both the kinetic mechanism of crystalline cluster formation and the (bulk and surface) thermodynamic properties of critical and near-critical clusters.

According to CNT, this procedure is commonly performed in terms of the Gibbs thermodynamic treatment of heterogeneous systems [10]. This classical theory can be generalized [11–13] to describe the critical and near-critical clusters more appropriately. However, such an approach requires more detailed information of the systems under investigation compared to the classical treatment. Using this reasoning, we will follow the classical Gibbs treatment, leaving its generalization and the analysis of its potential to explain the considered effects for a future study [14].

When applying CNT in its original form to analyze or predict nucleation kinetics, the thermodynamic properties of the newly evolving

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crystal phase are considered to be size independent and equivalent to the properties of the evolving macroscopic phases. However, in such an approach, one faces several problems (which are comprehensively reviewed in [5–9] and hence are only briefly summarized in this paper). In the present analysis, we concentrate on the possible means to resolve one of the most serious problems that arise in the treatment of experimental nucleation data using CNT. This is the unexpected behavior of the thermodynamic barrier for nucleation, *i.e.*, the work of critical cluster formation, as a function of temperature, $W_c(T)$, at low temperatures below the nucleation rate maximum. This type of behavior is shown in Fig. 1 for a set of sodium-calcium silicate glasses.

Following the standard assumptions of CNT, the thermodynamic driving force for crystal nucleation, ΔG_V, increases with supercooling, i.e., decreasing temperature, T. In addition, assuming the validity of the capillarity approximation (*i.e.*, a constant liquid-crystal interfacial energy, σ), one expects a monotonic decrease of the work of the critical cluster formation with decreasing temperatures because $W_c(T) \sim \sigma^3/\Delta G_V^2$. However, it is evident from Fig. 1 that the work of critical cluster formation first decreases with decreasing temperatures (as expected from CNT) but then saturates and even increases for any further temperature decrease below the nucleation rate maximum. The search for the origin of such unusual behavior in $W_c(T)$ is the main goal of this and forthcoming papers [14,15], which will test different hypotheses of its explanation.

Such anomalous behavior of $W_c(T)$ and its possible origin and consequences have already been addressed e.g. in [16,17]. The first studies on this effect were performed by some of the authors of this work in [18–20]. At that time, only a few examples of glass-forming liquids exhibiting such behavior were known; hence, they were considered to be anomalous exceptions. With the subsequent development of experimental nucleation research worldwide, it became evident that such behavior is typical for all oxide glass-forming melts studied so far at such deep supercoolings. For this reason, aiming to considerably advance our previous analysis, in the present work, we quantitatively test whether elastic stresses are responsible for the unexpected behavior of $W_c(T)$. Available nucleation rate data are analyzed for two different systems: $Li_2O \cdot 2SiO_2$ (L2S) and $BaO \cdot 2SiO_2$ (B2S). These two systems were selected because they display significantly different density misfits between the liquid and crystal phases. In particular, the choice of the B2S glass was determined by its extremely low density misfit. Because this misfit causes elastic stresses during crystal nucleation, their effect is expected to be quite different for these two systems. Consequently, if the discussed behavior of the work of the critical cluster formation is present also in B2S, then elastic stresses cannot be the main
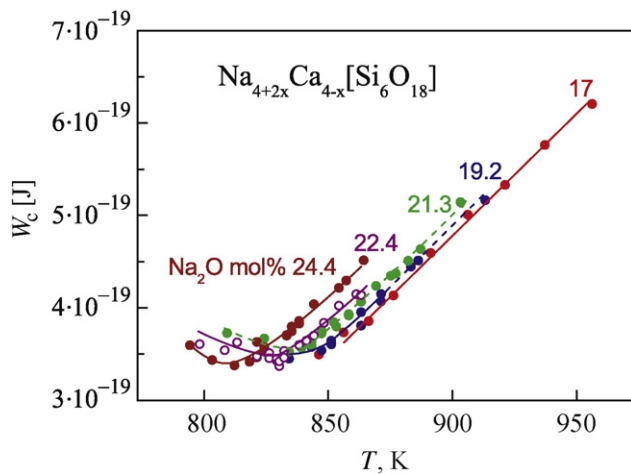
origin of the anomalous behavior. By this reason, to check their possible effect, estimates of the effect of elastic stress energy on the work of critical cluster formation are carried out for both systems and compared then.

The present paper is structured as follows. In Section 2, we outline the basic equations of CNT required to demonstrate how the non-monotonic dependence of the thermodynamic barrier for nucleation (or work of critical cluster formation) is obtained from experimental nucleation rate data. In Section 3, the possible effects of elastic stresses are discussed by computing the reduction of the thermodynamic driving force for crystal nucleation in lithium and barium disilicate glasses (L2S and B2S, respectively) due to stresses accounting also for stress relaxation due to viscous flow. A discussion (Section 4) and summary of the main conclusions (Section 5) complete the paper.

2. CNT and work of critical cluster formation: the problem

The basic equations for the description of the steady-state nucleation rate, I_{st}, and the time-lag for nucleation, τ (which is the time needed for the establishment of a stationary size distribution of crystallites up to the critical size) are:

$$I_{st} = \sqrt{\frac{\sigma}{k_B T}} \frac{D}{d_0^4} \exp\left(-\frac{W_c}{k_B T}\right), \qquad (1)$$

$$\tau = \frac{16}{3} \frac{k_B T \sigma}{\Delta G_V^2 d_0^2 D}, \qquad (2)$$

where W_c is the thermodynamic barrier for nucleation or the work of formation of a nucleus of critical size, which for spherical nuclei is given by the following equation:

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

These relations are used in this study to analyze the nucleation data in the framework of CNT.

In above equations, σ is the specific energy of the critical nucleus/melt interface, k_B is the Boltzmann constant, T is the absolute temperature, D is the effective diffusion coefficient determining the processes of aggregation of ambient phase particles ("structural units") to the crystal-like clusters and d_0 is an effective size parameter of the structural units, which is commonly estimated via the molar volume, V_M, and the Avogadro number, N_A, by:

$$d_0 \approx \left(\frac{V_M}{N_A}\right)^{1/3}. \qquad (4)$$

In the simplest case of a spherical nucleus, the critical radius, R_c, is given by Eq. (5):

$$R_c = \frac{2\sigma}{\Delta G_V}, \qquad (5)$$

where ΔG_V is the thermodynamic driving force for crystallization per unit crystal volume, which is determined by the change of the chemical potential per particle, $\Delta\mu$, in the melt to crystal transformation as:

$$\Delta G_V = \frac{\Delta\mu}{d_0^3}. \qquad (6)$$

To use Eqs. (2), (3), and (5), one needs to specify the thermodynamic driving force for nucleation, ΔG_V. Following Gibbs' [10] description of heterogeneous systems, ΔG_V is the difference of the Gibbs free energies per unit volume of the melt and crystal phases, both of which are measured at the pressure and temperature of the melt, and the

Fig. 1. Thermodynamic barrier for nucleation versus temperature for a series of sodium-calcium silicate glasses. These data have been calculated from measured nucleation rates and induction times, as reported in [21,22]