



The effect of heterogeneous structure of glass-forming liquids on crystal nucleation☆☆☆



Alexander S. Abyzov^{a,*}, Vladimir M. Fokin^{b,c}, Nikolay S. Yuritsyn^d,
Alisson Mendes Rodrigues^c, Jörn W.P. Schmelzer^e

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

^b Vavilov State Optical Institute, ul. Babushkina 36-1, 193171 St. Petersburg, Russia

^c Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13.565-905 São Carlos, SP, Brazil

^d Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Makarova 2, 199034 St. Petersburg, Russia

^e Institut für Physik der Universität Rostock, Albert-Einstein-Strasse 23-25, 18059 Rostock, Germany

ARTICLE INFO

Article history:

Received 14 October 2016

Received in revised form 30 January 2017

Accepted 7 February 2017

Available online xxx

Keywords:

Glass

Crystal nucleation

Thermodynamics

ABSTRACT

A model for the description of crystal nucleation is proposed incorporating into classical nucleation theory concepts of spatial heterogeneity of glass-forming liquids. It is assumed that nucleation processes may proceed with detectable rates only in liquid-like (soft) regions and are suppressed in solid-like (rigid) parts. Determining appropriately the fraction of liquid-like solid-like regions in dependence on temperature this approach allows one to achieve a satisfactory agreement between classical nucleation theory and experiment not only at relatively high temperatures but also at temperatures lower than that of the nucleation rate maximum. The model was tested successfully on several silicate glasses revealing homogeneous volume nucleation. Some other phenomena in the interplay of crystallization and glass transition are also discussed giving an independent verification of the validity of our basic assumption.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

A deep understanding of the crystallization kinetics of glass-forming liquids is essential in different aspects. For example, first, the knowledge of the crystal nucleation and growth rates is required either to avoid crystallization during glass preparation or to control crystallization in glass-ceramics development and production. Second, the high viscosity of glass-forming liquids makes them almost ideal systems for detailed experimental studies of nucleation and growth kinetics. These experimental data can be used then to test the validity and predictive power of phase transition theories also beyond the particular application.

The first measurements of nucleation rates in oxide glass-forming liquids were performed about fifty years ago by Ito et al. [1] and Filipovich & Kalinina [2]. In the following decades, a plethora of experimental data on crystal nucleation kinetics has been accumulated and a deep understanding of this process has been reached. For the description of crystal nucleation, the classical nucleation theory (CNT) has been predominantly employed. According to CNT, the interplay

between the effective diffusion coefficient, $D(T)$, of the “structural units” controlling the kinetics of formation of critical nuclei and the work of critical cluster formation, $W_c(T)$, representing the thermodynamic barrier for nucleation, results in a maximum of the steady-state nucleation rate, $I_{st}(T)$, at a temperature $T = T_{max}$. The experimentally determined temperature dependence of the nucleation rate, $I_{st}(T)$, is qualitatively conform to that predicted by CNT. However, serious problems arise when one tries to quantitatively describe experimental data.

In CNT, the work of critical cluster formation is expressed as being proportional to $W_c(T) \approx \sigma^3 / (\Delta G_v)^2$. The thermodynamic driving force of crystallization, ΔG_v , is determined in CNT approximately as the difference between the Gibbs free energies per unit volume of liquid and crystal of the respective macroscopic phases. When, in addition, the specific interfacial energy, σ , is considered as a constant, then discrepancies between theory and experiment occur which may reach many orders of magnitude. Taking into account the increase of the curvature of critical nuclei with decreasing temperature (due to the increase of the thermodynamic driving force) resulting in the decrease of the critical nucleus/liquid surface energy, σ , one can arrive at an agreement between theory and experiment at $T > T_{max}$. However, a variation only of the specific surface energy of critical nuclei cannot quantitatively explain the sharp decrease of $I_{st}(T)$ at $T < T_{max}$ (see details in [3]). In this temperature range, with decreasing temperature the experimental nucleation rates begin to deviate much stronger from the theoretical dependence even if the temperature (or, equivalently, size) dependence of σ is accounted for. In

☆ PACS numbers: 64.60.Bd General theory of phase transitions; 64.60.Q Nucleation; 82.60.Nh Thermodynamics of nucleation in physical chemistry and chemical physics; 64.70.kj Glasses.

☆☆ Classifications: Liquids, glasses, and crystals.

* Corresponding author.

E-mail address: alexander.abyzov@gmail.com (A.S. Abyzov).

particular, the work of critical cluster formation, $W_c(T)$, estimated via the substitution of experimental nucleation rate and time-lag data into the respective equations of CNT, ceases to decrease but increases with decreasing temperature, again, as illustrated by Fig. 1.

Utilizing the classical Gibbs theory [6], it was shown in [7] and [8] that, employing the standard in CNT approximations, the thermodynamic driving force of crystallization has a maximum at the Kauzmann temperature, T_K . With a weak monotonous decrease of the specific interfacial energy, it results in a minimum of the work of critical cluster formation near T_K . However, for most of the glass-forming systems and in particular for systems considered in the present paper, T_K is much lower than the temperatures at which detectable nucleation rates are observed. Thus, the minimum of the work of critical cluster formation illustrated by Fig. 1 cannot be correlated with the minimum of the thermodynamic barrier for nucleation. Its existence in the range where crystal nucleation was measured in the systems considered by us [3,9] strongly conflicts with CNT. Hence, the introduction of additional concepts into CNT is needed to describe the low temperature part of the $I_{st}(T)$ dependence.

In order to overcome these problems (sharp decrease of $I_{st}(T)$ at $T < T_{max}$, existence of a minimum and subsequent increase of $W_c(T)$ with decreasing temperature), in a preceding paper [9], we assumed an increase of the average size d_0 of the “structural units” (identifying them with the cooperatively rearranging regions (CRR) in the liquids or considering its increase as a consequence of a more complex kinetics as compared to a quasi-one-component description of the liquid commonly employed in CNT for the interpretation of experimental data) with decreasing temperature in the range $T < T_{max}$ resulting in the decrease of both the mobility of the basic structural units of the melt and the number of potential places available for homogeneous nucleation. Both effects decrease the nucleation rate, restoring the agreement between theory and experiment, as shown for several glasses revealing homogeneous bulk nucleation. In line with common expectations, in such approach the value of W_c , which is computed by us via the basic theoretical equations commonly employed in CNT, decreases with decreasing temperature including the range $T < T_{max}$. Attempts to resolve above formulated problem accounting for an increase of the size of the CRR with decreasing temperature are made also in [10].

In the present paper, we search for an alternative possible solution of above mentioned problem. In contrast to the assumption employed in [9], we now remain here within the spectrum of basic assumptions of CNT (in particular, we assign a constant value to the size parameter) but advance a description of crystal nucleation incorporating into classical nucleation theory concepts of spatial heterogeneity of glass-forming liquids. A brief overview on different models of spatial heterogeneity of liquids, widely discussed in the literature, is given here in Discussion section. We assume that nucleation processes may proceed with

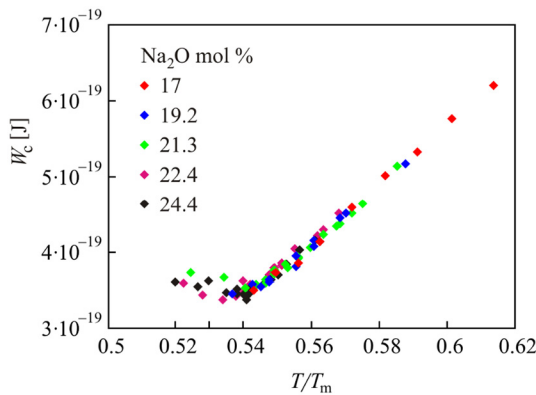


Fig. 1. Thermodynamic barrier for nucleation versus reduced temperature, T/T_m , for a series of sodium-calcium silicate glasses $x\text{Na}_2\text{O} \cdot (0.5-x)\text{CaO} \cdot 0.5\text{SiO}_2$ [3–5]. Here T_m is the melting or liquidus temperature.

detectable rates only in liquid-like (soft) regions and are suppressed in solid-like (rigid) parts employing notations as put forward by Thorpe and coworkers [11–13]. Determining appropriately the fraction of liquid-like and solid-like regions in dependence on temperature this approach allows us to achieve a comprehensive agreement between classical nucleation theory and experiment not only at relatively high temperatures but also at temperatures lower than that of the nucleation rate maximum. Several related phenomena are discussed as well giving additional support to our approach.

Thorpe's concept of rigid and floppy modes was utilized in [14] in the analysis of the degree of undercooling of fresnoite glasses estimated from DSC cooling curves. To the best of our knowledge, the interpretation of experimental data on crystal nucleation rates in dependence on temperature based on the concept of heterogeneous glass structure is performed here for the first time. Note that in the present paper we do not associate the obtained results with any particular model of spatial heterogeneity. The results obtained by us may serve as a criterion of validity of any given model, however, this topic is beyond the scope of the present analysis.

The present paper is structured as follows. In Section 2, we outline the basic equations of CNT required for the analysis of the experimental nucleation rate and time-lag data. In Section 3, a description of the effect of the structural heterogeneity of the glass-forming systems on the nucleation rate is introduced and analyzed. In Section 4, we consider in detail some consequences of melt structure transition from a homogeneous to a heterogeneous one correlating it with the decoupling of diffusion and viscosity, the temperature dependence of the activation energy of viscous flow, and glass transition. A discussion of the results (Section 5) and a summary of the 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 is described in the conventional form by

$$I_{st} = C \sqrt{\frac{\sigma d_0^2 D}{k_B T}} \frac{D}{d_0^2} \exp\left(-\frac{W_c}{k_B T}\right), \quad (1)$$

where T is the absolute temperature, k_B is the Boltzmann constant, D is the effective diffusion coefficient determining the aggregation of the “structural units” of effective size, d_0 , to the crystal clusters, C is the number of sites where nucleation may be initiated. For homogeneous bulk nucleation in one-component systems, $C = c$ holds, where c is the number density of the “structural units” of the ambient phase which can be expressed as $c = d_0^{-3}$. The effective size of the structural units is commonly estimated via the molar volume, V_M , of the crystal and the Avogadro number, N_A , as $d_0 \approx (V_M/N_A)^{1/3}$. W_c in Eq. (1) is the work of formation of a nucleus of critical size. It is equal to the thermodynamic barrier a crystalline embryo must overcome to grow to macroscopic sizes. In the case of an isotropic crystal nucleus of spherical shape, one can write independent on any assumptions about driving force and specific interfacial energy [6,12]

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

Here, R_c is the critical nucleus radius. For the specification of the thermodynamic driving force, ΔG_V , we will employ here the approximation advanced first by Tammann, Meissner, and Rie (see details in [7,8])

$$\Delta G_V = \frac{q}{d_0^3} \left(1 - \frac{T}{T_m}\right), \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/5441288>

Download Persian Version:

<https://daneshyari.com/article/5441288>

[Daneshyari.com](https://daneshyari.com)