



# A generalized domain approach for describing the stress relaxation in a phase separated borosilicate glass



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## ABSTRACT

In this work we propose a generalized domain approach for modeling the stress relaxation behavior of phase separated borosilicate glasses. The generalization of the domain approach is done by taking two fundamental steps. First, we assume the boron groups to be the soft boundaries in the borosilicate glasses. Second, we introduce the time-dependent power law into the Kohlrausch function. Using the generalized domain approach, we explained why the value of the stretched exponent of the stress relaxation in borosilicate glasses anomalously deviates from the converged exponent value of 3/5. In addition, we introduce a pre-time, i.e., the time for glass to reach the structural equilibrium, into the generalized domain approach in order to compensate the variation of viscosity caused by phase separation. It is found that the pre-time is closely correlated with the time for borosilicate glasses to reach structural equilibrium before stress relaxation experiment.

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## 1. Introduction

The study of glass relaxation is crucial for understanding the nature of glass and glass transition [1,2]. As a decay function, the Kohlrausch–Williams–Watts (KWW) equation [3] is generally accepted to describe the glass relaxation behavior due to its simplicity. In addition, the Phillips diffusion-trap model has been attracting attention due to bifurcation of the stretching exponent of the KWW equation into two “magic” values: 3/5 for short-range pathways and 3/7 for long-range pathways respectively. These two “magic” values were found to correspond to the stretching exponents in both stress and structural relaxation functions on a series of industrial glasses with ideal microscopic homogeneity [2]. Moreover, with the improvement of glass homogenization technology, the measured stretching exponents are gradually approaching the magic values [4], even for aluminosilicate glasses at room temperature [5].

Again, the magic values derived from the Phillips model can be only obtained if we measure the relaxation processes of microscopically homogeneous glasses. However, the homogeneity in glasses is hardly attained due to dynamical and structural heterogeneities, as well as macroscopic defects such as phase separation, partial crystallization and poor mixing of the melt [6]. The hyperquenched glasses exhibit heterogeneous structures, which are indicated by a broad enthalpy relaxation peak in the calorimetric curve below the glass transition temperature ( $T_g$ ) [7]. The hyperquenched glasses have been widely studied in terms of their complicated enthalpy

relaxation behavior [8,9]. Great effort has been made in describing the glass relaxation, e.g., by establishing phenomenological models such as the Tool–Narayanaswamy–Moynihan (TNM) model [10,11], the thermorheological complexity (TC) model [12], heterogeneous TNM model [13], the composite relaxation function (CRF) [14], the modified stretched exponential (MSE) equation [15] and the model combining CRF and MSE [16].

For the phase separated glasses, the TC behavior is considered to be relevant to the changing topological profile [17] during phase separation. But to our best knowledge, this aspect of phase separated glasses is not well understood compared to that of hyperquenched glasses, particularly concerning the stress relaxation behavior. Therefore, in this work we will closely look into this aspect by taking the well-known Pyrex glass as an example, which has a tendency to spinodal phase separation. Simmons et al. measured shear viscosity of two borosilicate glasses by fiber-elongation technique and determined an independent region with a radius of 58 Å [18]. Rekhson experimentally derived the stress relaxation functions of the Pyrex glass in the KWW fashion in the glass transition region [19]. It was found that the stretching exponent was more temperature-dependent in Pyrex glass than that in other commercial glasses. However, it should be noted that the specific mathematic description on the TC behavior is absent in the stress relaxation function. Although the existing models are incapable of capturing the detailed features of the stress relaxation in phase separated glasses, a systematic work about the viscoelastic phase separation (VEPS) problem has already been carried out in polymers in order to solve the dynamic asymmetry of different phases. Tanaka divided VEPS into type A and type B. In type A only the slow component can support elastic stress while in type B both slow and fast components can support

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stress [20]. Considering that the stretched exponential behavior in heterogeneous cross-linked polymers may be caused by a broad size distribution of noninteracting network domains, Gurtovenko et al. derive a model for type A [21]. Recently, Baeurle and Hotta extended this approach to study the stress decay of thermoplastic elastomers subjected to an extensional strain [22].

In this work, we generalize Gurtovenko's approach, i.e., the domain approach, by adding new theoretical considerations regarding the stress relaxation in borosilicate glass network. As an assumption of the generalized approach we regard the silica-rich phase as the only component that can support the applied stress. We introduce a multiplicative time-dependent power-law representing the changing size distribution of the domains into the KWW function. The temperature-dependent stretching exponent  $\beta$  obtained by Rekhson [19] appears to be attributed to the power law term rather than the pure KWW term. The change of the power law term with temperature and time is reflected by the variation of viscosity during phase separation incorporating with the relaxation time dispersion [23]. In addition, a temporal parameter is involved in this generalized domain approach in order to compensate the pre-time for the system to attain equilibrium before stress relaxation measurement.

## 2. Theoretical model

The domain approach is firstly proposed by Gurtovenko et al. in order to describe the relaxation dynamics of inhomogeneous cross-linked polymers [21]. In this section, we outlined three main aspects to recall its theoretical framework.

### 2.1. Relaxation inside cross-linked domains

In a typical class of domains, which obeys the power law relaxation [24], the relaxation time  $\tau(\xi)$  can be expressed in the following form, when the domain is further treated as a sufficiently large tree-like network [25],

$$\tau(\xi) = \tau_0 \left( \frac{n}{\xi} \right)^{1/\gamma} \quad (1)$$

Each domain has its maximum relaxation time  $\tau_{\max}(n)$  when  $\xi = 1$ . Thus, we can write an exponential decay form of the shear relaxation modulus  $G(t, n)$  in a domain at the time longer than its maximum relaxation time  $\tau_{\max}(n)$ ,

$$G(t; n) = \nu k T \frac{\gamma}{n} \left( \frac{\tau_{\max}(n)}{t} \right) \exp \left[ - \left( \frac{t}{\tau_{\max}(n)} \right) \right] \quad (2)$$

Note that in most situations, the power-law term  $\tau_{\max}(n) / t$  in Eq. (2) is considered as a much weaker factor than the exponential decay, and it contributes to shear relaxation modulus as a memory effect when  $t < \tau_{\max}(n)$ .

### 2.2. Size distribution of domains in inhomogeneous cross-linked polymers

In contrast to the well-known free volume model [26], the aggregate model suggests that the aggregates with different sizes are generated through the link between molecules or molecular segments [23]. Combining the kinetic equations of reversible aggregations from small to larger enough ones with a uniform reaction constant and taking the conservation of mass into account, the size distribution of the aggregates is derived as follows,

$$f(n) = C n^m e^{-(\Delta u/kT)n} \quad (3)$$

where  $C$  is the normalized constant,  $k$  is the Boltzmann constant,  $m$  is a variable influenced by the shape of aggregates and  $\Delta u$  is the aggregation

energy. On condition that the shapes of the aggregates are nearly isochoric, the value of  $m$  is determined to be 2 according to the entropy-maximum model.

### 2.3. Relaxation of inhomogeneous cross-linked polymers

A cross-linked polymer is regarded as an ensemble of noninteracting regions with finite sizes and certain internal network structure. Supposing that the cross-linked domains are uniformly embedded in the viscous medium, the different domains can relax independently due to their soft boundaries. Consequently, the integrated shear relaxation modulus can be obtained by a superposition of the relaxation modulus of different domains,

$$G(t) = \int G_0 n^m e^{-(\Delta u/kT)n} \frac{\gamma}{n} \left( \frac{\tau_{\max}(n)}{t} \right) \exp \left( - \frac{t}{\tau_{\max}(n)} \right) dn \quad (4)$$

where  $G_0$  is a general constant during the isothermal process.

## 3. Application in borosilicate glass

In this section, we attempt to use the domain approach to model the stress relaxation behavior in borosilicate glass. It should be noted that we face some critical problems in applying this approach to a phase separated glass system. The first and most important one is the feasibility of the model applied in the phase separated glass system. It is considered that the silica-rich domains (SRDs), which are separated by the boron groups in the phase separated borosilicate glass, correspond to the cross-linked domains in Gurtovenko's approach. Taking the large difference in viscosity between the silica-rich and borate-rich phases into account, it is reasonable to assume the boron groups as soft boundaries in borosilicate glass. In addition, some modifications should be made to the domain approach since the relaxation behavior in borosilicate glasses is accompanied by the phase separation. In contrast, the original approach was derived from the case where the phase separation does not exist [21]. To make the modification, we firstly analyze a possible changing trend of the SRD size based on a phase separation mechanism of oxygen vacancy motion. Then we give a dynamically quantitative description of SRD size distribution using the aggregate model. Finally, we derive a generalized domain approach for modeling the stress relaxation behavior in borosilicate glasses.

Here, the oxygen vacancy motion model is used to analyze the structure evolution of the borosilicate glass during phase separation [27]. Fig. 1 illustrates the growth of two SRDs during phase separation in borosilicate glass by combining the oxygen vacancy motion model with the physical picture of the aggregate model, namely, polymerization of the SRDs. As shown in Fig. 1(a), domains 1 and 2 are two distinct SRDs in the structure of borosilicate glass at a certain stage during phase separation while the boundaries are denoted by the dash curves. With the diffusion of oxygen vacancies, boron groups are gradually separated from the domain of the  $\text{SiO}_4$  tetrahedra as shown in Fig. 1(b). At the same time, boron–oxygen structural units bind with their adjacent ones, leading to the formation of larger boron–oxygen units. This has been partially confirmed by nitrogen adsorption, Raman spectroscopy and electron microscopy [27,28]. Thus, we can assume that the  $\text{SiO}_4$  groups have the same growing tendency with the propagation of phase separation. It is seen in Fig. 1(c) that domains 1 and 2 gradually connect with other silica-rich networks resulting in the growth of SRD. Recalling Eq. (3), we regard the term  $\Delta u / kT$  as an only temperature-dependent function  $a(T)$ , which presumably plays a minor role in the propagation of phase separation. Hence, the parameter  $m$  is the only variable in this dynamical progress. Fig. 2 shows the size distribution curves of SRDs under different  $m$  values. It is seen that the increase of  $m$  is accompanied with an increase of the average SRD size and a decrease of the size dispersion, and this is indicated by the peak shift to the longer time and thus narrowing the distribution pattern.

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