

Bond Strength-Coordination Number Fluctuations and the Fragility of Some Ion Conducting Oxide and Chalcogenide Glass Forming Liquids

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Abstract. The concept of fragility has been used widely to characterize the temperature dependence of the viscosity of glass forming liquids. According to a model proposed by one of the authors, the fragility is determined by the relaxation of structural units that form the melt, and is described in terms of the bond strength, coordination number and their fluctuations. In the present contribution, the model is applied to investigate the temperature dependence of the viscosity of some ion conducting oxide and chalcogenide glass forming liquids. From the analysis of the model, physical quantities, such as the number of bonds that must be broken to observe the viscous flow is obtained. The analysis suggests also that good ionic conductors have an intermediate value of fragility.

1. Introduction

Ionic conducting glasses have attracted considerable interest for the last several years. Investigation of ionic conductivity in vitreous materials is interesting from both, academic and applied point of view. From the fundamental science point of view, despite the number of studies that have been done, no theory of ion transport in glasses has yet received general acceptance [1,2].

On the other hand, in recent years, much attention has been paid to understand liquids in the supercooled state and the glass transition phenomena [3,4]. In particular, the concept of liquid fragility put forward by Angell has motivated many studies that clarified the nature of glass forming systems [5]. Since the glasses can be considered as frozen liquids, the understanding of the properties of liquids is linked directly to the understanding of glass properties.

The temperature dependence of the viscosity for various glass forming materials is conventionally characterized by the so-called Angell's plot [5]. By plotting the logarithm of the viscosity η as a function of the reduced inverse temperature T_g/T , where T_g is the glass transition temperature, curves with different degrees of non-Arrhenius behavior may be systematized. The degree of deviation from the Arrhenius behavior is called fragility. For highly polymerized network glass formers such as SiO_2 , nearly straight lines in $\ln \eta$ vs T_g/T plot are observed. These types of materials exhibit small values of fragility and are called strong systems. On the other hand, for systems with non-directional interatomic or intermolecular bonds such as ionic or organic liquids, strong deviations from the Arrhenius behavior are found. These types of materials exhibit large values of fragility and are called fragile systems.

The degree of the fragility is quantified by the fragility index defined as

$$m = \lim_{T \rightarrow T_g} \frac{d \text{Log} \eta}{d(T_g/T)}. \quad (1)$$

In the present paper, the temperature dependence of the viscosity of some ion conducting oxide and chalcogenide glass forming liquids is studied by using a model for the viscosity proposed by one of the authors.

2. Model for the melt and the viscosity

As previously mentioned, the concept of fragility has been used widely and has played a fundamental role in understanding the relaxation behavior of supercooled liquids. However, the microscopic mechanism responsible for the degree of fragility is still not well understood. In a recent study, one of the authors has derived an expression for the fragility based on a simple model of the melt [6]. According to the model, the fragility is determined by the relaxation of structural units that form the melt, and is described in terms of the bond strength, coordination number and their

fluctuations of the structural units.

The glass forming melt is formed by an agglomeration of structural units. As the temperature of the system is lowered, the viscosity of the melt increases and at the glass transition temperature T_g , the spatial distribution of structural units is frozen. In our model, each structural unit is bound to other structural units by a certain bond strength which is denoted as

$$E = E_0 + \Delta E \quad , \quad (2)$$

where E_0 is the average value and ΔE is its fluctuation. Each structural unit is surrounded by a certain number of other structural units. The coordination number of the structural units is denoted as

$$Z = Z_0 + \Delta Z \quad , \quad (3)$$

where Z_0 is the average value and ΔZ is its fluctuation.

According to the model, the viscous flow occurs when the structural units move from one position to another by breaking the bonds connecting the structural units. Based on this picture, the temperature dependence of the viscosity has been described as

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx + Cx^2 \left\{ \left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2} \ln(1-B) \right] \frac{(1-B)}{C} - 1 \right\}}{1 - Bx^2} - \frac{1}{2} \ln(1 - Bx^2) \quad , \quad (4)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} \quad , \quad (5)$$

$$C = \frac{E_0 Z_0}{RT_g} \quad , \quad (6)$$

and

$$x = \frac{T_g}{T} \quad . \quad (7)$$

Here, R is the gas constant. η_{T_g} and η_0 are the viscosities at the glass transition temperature and at the high temperature limit, respectively. For their values, the usual values $\eta_{T_g} = 10^{12}$ Pa·s and $\eta_0 = 10^{-5}$ Pa·s were adopted [5]. Note that the expression of the viscosity given above is written in terms of the physically intuitive quantities B , C , and x . C gives the total bond strength of the structural unit and B gives its fluctuation. By using the expression for the viscosity given in Eq. (4) and the definition of the fragility index given in Eq. (1), we obtain

$$m = \frac{B - C + 2 \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1 - B) \right]}{2.3(1 - B)}. \quad (8)$$

Previous study has shown that strong system such as SiO₂ has a large value of C and a small value of B . On the other hand, fragile system such as ZBLA (ZrF₄-BaF₂-LaF₃-AlF₃) has a small value of C and a large value of B . Metallic and semiconducting chalcogenide systems exhibit intermediate behavior [7,8].

3. Application to ion conducting glass forming liquids

Concerning the temperature dependence of the viscosity of ion conducting glass forming systems, some works have been done [9-14]. However, as far as the authors are informed, no theoretical analysis has been done to systematize the behavior that these systems exhibit. For instance, naively, we expect that good ionic conducting glass forming liquids will exhibit large fragile behavior, because the bonding of fragile systems is expected to be weak. However, contrary to this expectation, the experimental data obtained for AgI-Ag₂O-M_xO_y (M_xO_y = B₂O₃, GeO₂, P₂O₅, MoO₃) systems indicate that the fragility takes an intermediate value [9,15].

The temperature dependence of the viscosity for the systems Na₂O-SiO₂ and Li₂O-2SiO₂ are shown in Fig. 1. Theoretical lines described by Eq. (4) are also shown. We can see that the model reproduces quite well the experimental data. We can also see that both systems exhibit almost the same value of the fragility. In our model the small difference is reflected in the values of the parameters B and C .

The temperature dependence of the viscosity for the system Cu-As-Se system for two different compositions is shown in Fig. 2. Here we recognize again that the model reproduces quite well the experimental behavior. The figure indicates that the fragility index of the system increases by the addition of Cu. This fact could be interpreted to arise from the fragmentation and cross linking of the layer-like structure of As₂Se₃ by the addition of Cu [16]. This kind of structural change has been observed in Ag-As-Se system [17]. The fragmentation and cross linking of the layer structure will result in the increase of the bond strength fluctuations between the structural units (As₂Se₃, in the present case).

The values of the parameters B and C , determined for the systems Na₂O-SiO₂, Li₂O-2SiO₂ and Cu-As-Se systems are shown in Fig. 3. For the sake of comparison, the values of other systems determined previously are also shown [7,8,15]. We can see clearly that strong systems are characterized by large bond strength C and small fluctuations B , whereas fragile systems are

characterized by small bond strength and large fluctuations. This observation provides a simple, but physically very sound picture for the structural relaxations occurring in supercooled liquids. From Fig. 3 we can also recognize that ion conducting glass forming systems have intermediate values of B and C . For instance, the AgI containing oxide glasses exhibit values of B and C in the range $0.4 < B < 0.6$ and $10 < C < 25$. In Fig. 3, a representative value is shown. This observation provides an important clue to understand the ion transport in glasses. In other words, these systems are not too strong as SiO_2 , nor too fragile as ZBLA. If a system is too strong, the large bond strength impedes the ion movement to occur. On the other hand, if a system is too fragile, the constituent elements of the system move collectively, inhibiting the decoupled motions of the charge carrying species from the supporting matrix. That is, the existence of certain degree of rigidity is favorable for the fast ion transport. This notion has much in common with the concept gained from the correlation found between the intermediate range ordering and the ionic conductivity in superionic glasses [18]. There it has been suggested that the network skeleton structure that originate the medium range structure influences the degree of ionic conductivity in glasses. The observation that the existence of certain degree of rigidity is favorable for the fast ion movement is also consistent with the bond fluctuation mechanism of ion transport [19], because for the occurrence of correlated ion movement by bond rearrangement, certain degree of network rigidity is necessary.

From Fig. 3, we note that there is a trend in the values of the parameters B and C determined for different type of materials. Such a trend is roughly described by the dotted curve ($\gamma = 1$, $\delta = 39.1$). This curve has been determined theoretically from Eq. (4) by assuming that the degrees of energy fluctuation and the coordination number fluctuation are the same. That is,

$$\frac{\Delta E}{E_0} = \frac{\Delta Z}{Z_0} \quad \text{or} \quad \gamma = \frac{\Delta E / E_0}{\Delta Z / Z_0} = 1. \quad (9)$$

In this case, the relationship between B and C becomes

$$C = \frac{2\gamma(1-B)}{2\gamma + \sqrt{B}(1+\gamma^2)} \left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2} \ln(1-B) \right]. \quad (10)$$

In Fig. 3, curves calculated for the case where the energy fluctuation dominates ($\gamma > 1$), and for the case where the coordination number fluctuation dominates ($\gamma < 1$) are also shown. We can see that the curves calculated for $\gamma = 10$ and $\gamma = 0.1$ coincide (curves calculated for $\gamma = 2$ and $\gamma = 0.5$ also coincide, but their locus are between the curves of $\gamma = 1$ and $\gamma = 10$). Mathematically, this coincidence arises from the symmetric form of energy and coordination number considered in the model. Superficially, it seems that we can not distinguish which factor (energy or coordination number) dominates. However, that is not true. Previous study has shown that by studying the composition dependence, we can distinguish which is the dominant factor [20].

The plausibility of the assumption expressed by Eq. (9) has been investigated by comparing the temperature dependence of the viscosity calculated by two methods. One calculation has been done based on our model with the above assumption. The other calculation has been done by using the well known Vogel-Fulcher-Tammann (VFT) equation [21],

$$\eta = \eta_0 \exp\left(\frac{B^{(VFT)}}{T - T_0}\right), \quad (11)$$

where $B^{(VFT)}$ and T_0 are the two VFT parameters. The comparison performed for 4 cases with different values of the fragility is shown Fig. 4. We can see that the agreement between the two methods of calculations is excellent. This confirms the appropriateness of Eq. (9). The observation that most of the (B, C) data are distributed around the $(\gamma = 1, \delta = 39.1)$ curve in Fig. 3 indicates that the degrees of energy fluctuation and the coordination number fluctuation is almost the same. Deviation from the curve could be understood based on the different degree of energy and coordination number fluctuations. The data points located above the $(\gamma = 1, \delta = 39.1)$ curve are due mainly to two reasons. The first is the limited temperature range in the experimental data used for the curve fitting. The second is the deviation in the value of η_{T_g} / η_0 from the adopted values of $\delta = \ln(\eta_{T_g} / \eta_0) = 39.1$. In order to see this behavior, in Fig. 3, curve calculated for the case of $(\gamma = 1, \delta = 50)$ is shown as an example.

By using the values of B and C determined, some information concerning the viscous flow can be extracted. For instance, for the case of $\text{Na}_2\text{O}-2\text{SiO}_2$, it is determined that $B \sim 0.33$ and $C \sim 27$. The reported glass transition temperature for this system is $T_g \sim 710$ K [10]. From the values of C and T_g we obtain $Z_0 E_0 = 1.6 \times 10^{12}$ erg/mol for the average total bond strength. From the ratio B/C^2 , the magnitude of the fluctuation is estimated to be $(|\Delta Z| |\Delta E|) / Z_0 E_0 = 0.02$. The measured activation energy for the viscous flow is $E_a = 5.8 \times 10^{12}$ erg/mol [10]. Since in our model the viscous flow results by breaking the bond between the structural units, the ratio $E_a / (E_0 Z_0) = 3.6$ provides a measure of the amount of bond broken. That is, for the system in consideration, the model suggests that the number of bond corresponding to about 4 structural units must be broken in order to observe the viscous flow. It is interesting to note that this quantity is equal to the number of corners of a tetrahedron, which is the shape of the dominant structural unit present in $\text{Na}_2\text{O}-2\text{SiO}_2$ [23]. For the other ion conducting glass forming systems considered in this paper, $E_a / (E_0 Z_0)$ extends from ~ 10 (AgI-containing oxide glasses) to ~ 30 (Cu-As-Se glasses) structural units. This observation indicates that the movements of the structural units in these systems are more correlated than in the $\text{Na}_2\text{O}-2\text{SiO}_2$ system.

4. Conclusion

The concept of fragility has been used widely to characterize the temperature dependence of the viscosity of glass forming materials. Recently, one of the authors has obtained an analytical expression for the fragility based on a simple model of the melt. According to the model, the fragility is determined by the relaxation of structural units that form the melt, and is described in terms of the bond strength, coordination number and their fluctuations. The model reproduces the experimental data of many types of materials that extends from covalent to ionic, molecular and metallic systems. In the present study, the model has been applied to investigate the temperature dependence of the viscosity of some ion conducting oxide and chalcogenide glass forming liquids. The analysis suggests that good ionic conductors have an intermediate value of fragility. From the analysis of the model, it has been shown that the viscous flow in ion conducting glass forming systems occurs when the bonds of about 4 ~ 30 adjoining structural units are broken. It has been also shown that for a particular case of equal magnitude of energy and coordination number fluctuations, the model reproduces the temperature dependence of the viscosity which is generated by the Vogel-Fulcher-Tammann equation.

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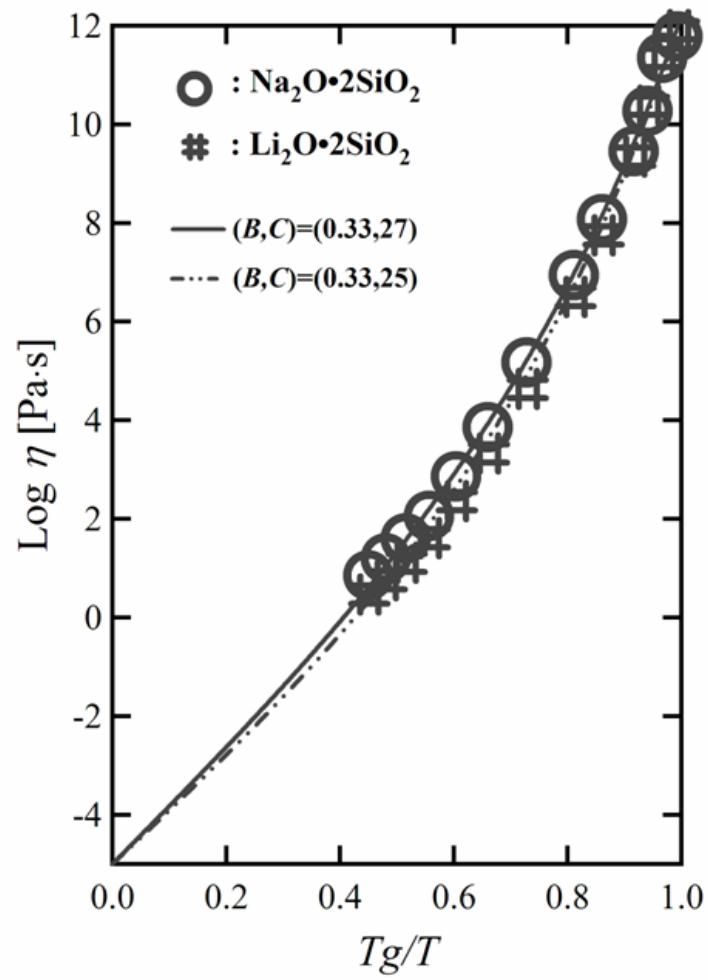


Fig. 1. Temperature dependence of the viscosity in $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. The experimental data are taken from [11].

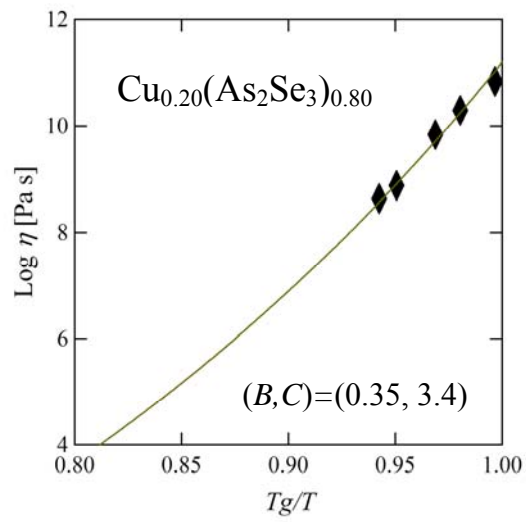
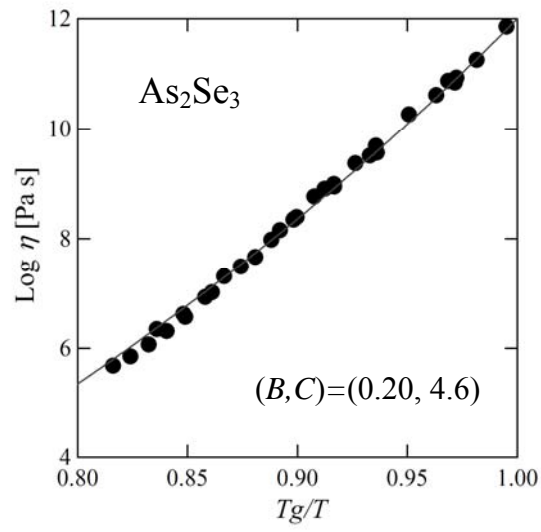


Fig. 2. Temperature dependence of the viscosity in As₂Se₃ and Cu_{0.2}(As₂Se₃)_{0.8}. The experimental data are taken from [13,14].

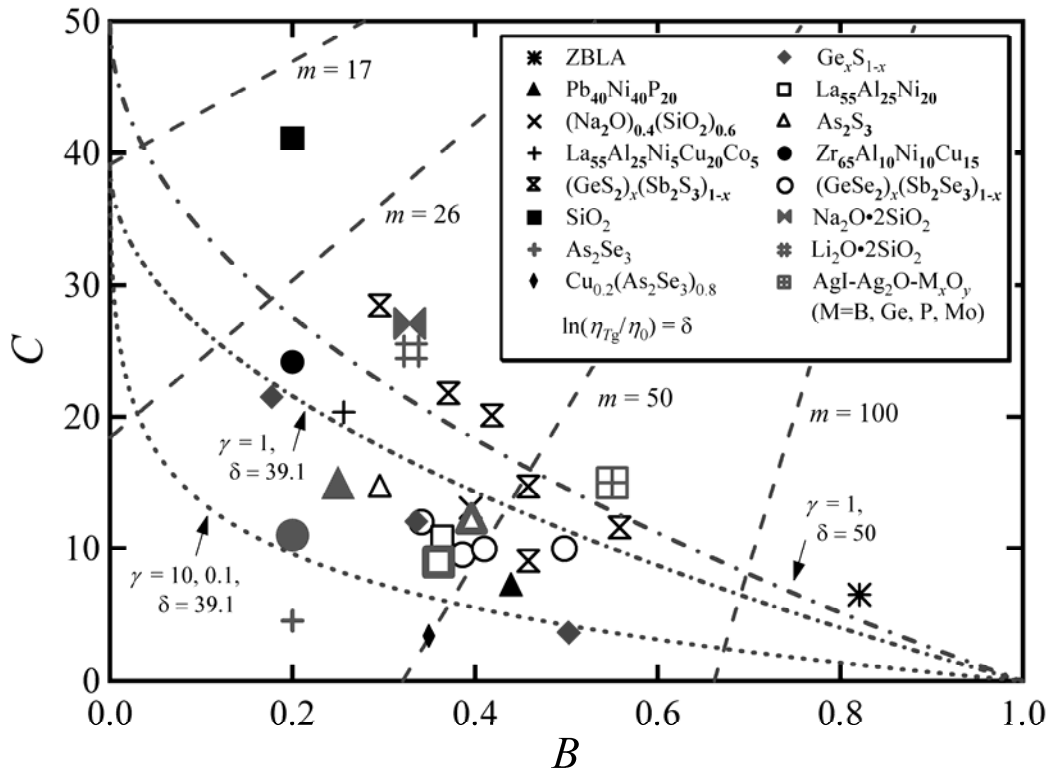


Fig. 3. Values of B and C obtained for different materials. The dotted curve ($\gamma = 1, \delta = 39.1$) is the theoretical curve determined from Eq. (4) by assuming that the degrees of energy fluctuation and the coordination number fluctuation is the same, $\gamma = 1$. Curves calculated for $\gamma = 10$ and $\gamma = 0.1$, and the effect of varying $\delta = \ln(\eta_{T_g}/\eta_0)$ are also shown. The broken lines show some lines of fixed fragility.

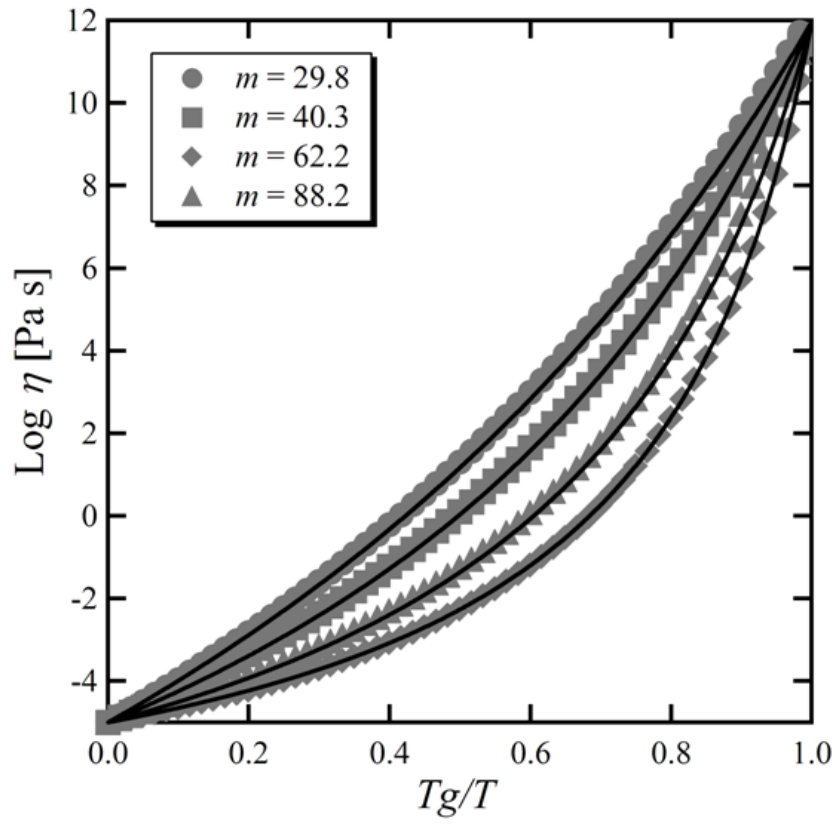


Fig. 4. Comparison between the temperature dependence of the viscosity calculated by the present model (symbols) and with the VFT equation (solid lines). The values of the VFT parameters are taken from [22].