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A MODEL FOR THE FRAGILITY OF THE MELTS

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Abstract

The concept of fragility has been used widely to characterize the temperature dependence of the viscosity of glass forming materials. However, the physical background that determines the degree of fragility is still not well understood. In the present study an expression for the fragility is derived 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 (E_0), coordination number (Z_0), and their fluctuations (ΔE and ΔZ). It is shown that a strong system is characterized by large value of total bond strength (Z_0E_0) and small value of its fluctuation ($(\Delta Z)^2(\Delta E)^2$). On the other hand, a fragile system is characterized by small value of total bond strength and large value of its fluctuation.

Keywords: fragility, glass forming materials, viscosity

Introduction

The temperature dependence of the viscosity for various glass forming materials is conventionally characterized by the so-called Angell's plot. 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 [1]. For highly polymerized network glass formers such as SiO_2, nearly straight lines in $\log\eta$ *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.

Although the concept of fragility has been used widely [1–14], the microscopic mechanism responsible for the degree of fragility is still not well understood [6]. In the present study, an expression for the fragility is derived based on a simple model of the melt. It is shown that the model provides a physical background to understand the fragility.

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The Model

Model of the melt

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 the next subsection, the temperature dependence of the viscosity is calculated. The model of the melt that will be used is represented schematically in Fig. 1. The small open and black circles represent atoms. Large circles represent the structural units that form the melt. Each structural unit is bound to other structural units by a certain bond strength. In Fig. 1, the bond strength is represented by the length of the sticks connecting the atoms. In the present model, the bond strength is described by using the binding energy between the structural units,

$$E=E_0+\Delta E \tag{1}$$

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 also. For instance in Fig. 1, the coordination numbers of the structural units denoted by A and B are 3 and 4, respectively. In the present model, the coordination number of the structural units is denoted as

$$Z=Z_0+\Delta Z \tag{2}$$

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

The above model of the melt seems too simple to describe a complex real system. For instance, the role of the network modifier seems to be neglected. However, that is not the case. The role of the network modifier is included in the value of E and Z. Within this sense, the term ‘structural unit’ is used in a wide form. Figure 1 illustrates the special case in which the network modifier is absent.

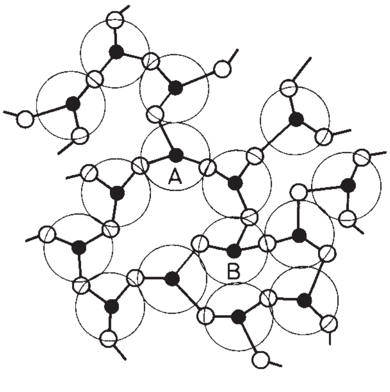

Fig. 1 A model of the melt. The small open and black circles represent atoms. Large circles represent the structural units that form the melt

Viscosity

The viscosity of the melt is well described by a thermal activation type equation. If we use the model of the melt presented in the previous subsection, the viscous flow occurs when the structural units move from one position to another by breaking the bonds connecting the structural units. By taking into consideration these facts, the viscosity is written as

$$\eta=\eta_0\langle\exp(EZ/RT)\rangle \tag{3}$$

where η_0 is the viscosity at high temperature limit, R is the gas constant and T is the temperature. η_0 is considered to be a material independent constant as the trend of the experimental data indicate [1, 14]. The parenthesis < > indicates that a statistical average of the quantity inside the parenthesis must be taken. In the present study a Gaussian distribution of binding energy E and coordination number Z is adopted. Although simple, this distribution is sufficient for the purpose of this paper, that is, provide a simple physical picture to the fragility.

Under the above conditions, Eq. (3) is written explicitly a

$$\eta=\eta_0\frac{1}{\sqrt{4\pi^2(\Delta E)^2(\Delta Z)^2}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[\frac{EZ}{RT}-\frac{(E-E_0)^2}{2(\Delta E)^2}-\frac{(Z-Z_0)^2}{2(\Delta Z)^2}\right]\mathrm{d}E\mathrm{d}Z \tag{4}$$

At a first glance, taking the integration limit from $-\infty$ to ∞ seems strange. However, this formal extension is justified physically, because the binding energy and coordination number are expected to be peaked at E_0 and Z_0, with relatively small standard deviations ΔE and ΔZ, as has been discussed by Vilgis [15].

By integrating Eq. (4), we obtain

$$\eta=\frac{\eta_0}{\sqrt{1-\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_\mathrm{g}^2}\left(\frac{T_\mathrm{g}}{T}\right)^2}}\exp\left\{\frac{\frac{Z_0E_0}{RT_\mathrm{g}}\left(\frac{T_\mathrm{g}}{T}\right)\left[1+\frac{1}{2RT_\mathrm{g}}\left(\frac{T_\mathrm{g}}{T}\right)\left[Z_0\Delta E\left(\frac{\Delta E}{E_0}\right)+E_0\Delta Z\left(\frac{\Delta Z}{Z_0}\right)\right]\right]}{1-\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_\mathrm{g}^2}\left(\frac{T_\mathrm{g}}{T}\right)^2}\right\} \tag{5}$$

A somewhat similar expression for the relaxation time has been also derived in [15]. However, in the paper by Vilgis [15], the emphasis has been put on the fluctuation of coordination number. It will be shown below that such a description is insufficient in order to characterize a real system.

If we define the quantities B and C as

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} \tag{6}$$

$$C = \frac{E_0 Z_0}{R T_g} \tag{7}$$

$$x = \frac{T_g}{T} \tag{8}$$

Equation (5) is rewritten as

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx + Cx^2 \left\{ \left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right] \frac{(1-B)}{C} - 1 \right\}}{1-Bx^2} - \frac{1}{2}\ln(1-Bx^2) \tag{9}$$

where η_{Tg} is the value of the viscosity at the glass transition temperature. For the evaluation of Eq. (9), the usual values of the viscosity at the glass transition temperature $\eta_{Tg}=10^{12}$ Pa·s and at the high temperature limit $\eta_0=10^{-5}$ Pas [14] are adopted. The behavior of Eq. (9) is shown in Fig. 2 for some set of values of *B* and *C*. We can note that the general trend of the temperature dependence of the viscosity reported for different materials [1] is reproduced by choosing appropriately *B* and *C*. The behavior of the viscosity evaluated at $x=T_g/T=0.9$ is shown in Fig. 3. We can see that the viscosity is determined by the interplay between *B* and *C*. Different set of values of *B* and *C* give the same value of the viscosity. In other words, by the fluctuation of coordination number alone (parameter *B* with fixed Δ*E),* we can not characterize the viscosity of a particular system uniquely. The same statement applies also to the fragility described in the next subsection.

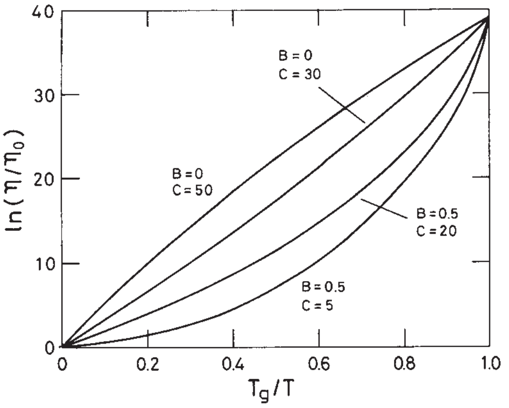

Fig. 2 Temperature dependence of the viscosity described by Eq. (9)

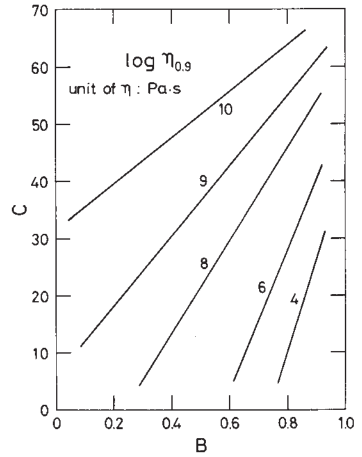

Fig. 3 Calculated viscosity at $x=T_g/T=0.9$ as functions of B and C

Fragility

The fragility is defined by the following expression [2]

$$F=\frac{R}{T_g}\left[\frac{\partial \ln \eta}{\partial(1/T)}\right]_{T_g} \tag{10}$$

By using Eq. (5) and Eqs (6)–(8), we obtain

$$F=\frac{\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_g^2}-\frac{Z_0E_0}{RT_g}+2\left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right)+\frac{1}{2}\ln\left(1-\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_g^2}\right)\right]}{\left(1-\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_g^2}\right)}R= \tag{11}$$

$$=\frac{B-C+2\left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right]}{1-B}R$$

The behavior of Eq. (11) is shown in Fig. 4. We can see that different sets of values of B and C give the same value of the fragility.

Since the fragility is obtained from the viscosity data, if we have a data on temperature dependence of the viscosity near T_g, information about microscopic quantities used in the present model can be extracted. An example is shown in Fig. 5. In this figure, the fragility and the viscosity at $x=0.9$ for four systems is shown. The crossing points give the values of B and C of the systems. An interesting trend is discernible in

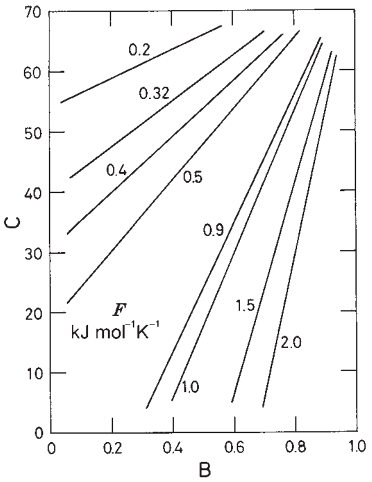

Fig. 4 Calculated fragility as functions of *B* and *C*

Fig. 5. Strong system such as SiO_2 has a large value of C and a small value of B. In other words, the total bond strength Z_0E_0 is strong and its fluctuation $(\Delta E)^2(\Delta Z)^2$ is small. On the other hand, fragile system such as ZBLA (ZrF_4–BaF_2–LaF_3–AlF_3) has a small value of C and a large value of B. Systems with intermediate fragility are located between these two sets of extreme values.

Although based on a simple analysis, the results presented in this paper provide a clear physical model for the fragility. In the present study E and Z have been assumed to be temperature independent quantities. Therefore, the values of B and C that

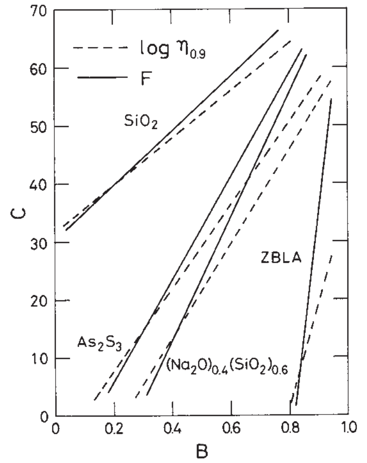

Fig. 5 Fragility (full line) and viscosity at x=0.9 (broken line) for SiO_2, As_2S_3, $(Na_2O)_{0.4}(SiO_2)_{0.6}$ and ZBLA (ZrF_4–BaF_2–LaF_3–AlF_3)

can be inferred from Fig. 5 are valid for a limited temperature range. However, this does not invalidate the general structure of the model. In order to extend the applicability of the theory to wide temperature range, we must take into account the temperature dependence of E and Z. Concerning this point a comment is given. At a glance, it seems that in the Angell's plot, the T_g scaling has been introduced to scale out the effect of bond strength in the temperature dependence of the viscosity. However, the idea that the bond strength between the constituents of the melt does not depend on temperature has not been confirmed. The absence of universality in the strong-fragile classification may be due to this fact.

Concerning the temperature dependence of the viscosity (or relaxation time), there are many studies [1, 16–21]. Among these, the model proposed by Adam and Gibbs [16] is well known. They proposed that the temperature dependence of the relaxation behavior is determined by the temperature variation of the size of the region in which the particles are rearranging cooperatively. This model has been extended and modified by some authors [18, 19]. There are also experimental results that support the Adam–Gibbs theory [19, 21, 22]. In the Adam–Gibbs theory, the important factor determining the relaxation behavior is the configurational entropy. In contrast, in the model of the present paper, the important quantities are fluctuations in the coordination number and binding energy. We may speculate that there is a link between these two theories. However, its clear relationship is unknown at present.

In a recent study, it has been shown that the ion transport properties in superionic glasses is correlated with the intermediate range structure [23]. The structure of the glass is expected to be related with the fragility. Therefore, it is probable that the model presented in this paper may enlighten the understanding of the relationship found. Concerning this point, further studies are required.

Conclusions

In the present study, an expression for the fragility has been derived based on a simple model of the melt. In the model, the melt is described as an agglomeration of structural units. These units are surrounded by $Z=Z_0+\Delta Z$ other units, and are bound each other by an energy $E=E_0+\Delta E$, where Z_0 and E_0 are the mean values, and ΔZ and ΔE are their fluctuations. By adopting a Gaussian distribution for Z and E, the viscosity is calculated from $\eta=\eta_0<\exp(EZ/RT)>$, where $<\cdots>$ means statistical average. From such a calculation of the viscosity, an expression of the fragility has been obtained. 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. By applying the model to some real systems, a microscopic interpretation of the fragility has been given.

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