Theoretical analysis of the temperature and pressure dependences of the viscosity in supercooled liquids

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Abstract. In this paper, a method to analyze the temperature and pressure dependences of the viscosity or of the structural relaxation time in supercooled liquids is shown from the point of view of chemical bonding. The model used in this analysis is the Bond Strength–Coordination Number Fluctuation (BSCNF) model originally proposed by one of the authors. A theoretical relationship between the Vogel temperature T_0 of the well-known Vogel-Flucher-Tammann (VFT) equation and our model parameters which contain some microscopic information on bonding connectivity among the structural units that form the melt has been obtained. Using the theoretical relationship, we analyzed the dynamics of two kinds of molecular glass forming liquids under pressure, (a) 4,4'-methylenebis(N,N-diglycidylaniline), and (b) BMPC: 1,1'-di(p-methoxyphenyl)cyclohexane. The result obtained suggests that by applying pressure in these materials, the intermolecular cooperativity is suppressed due to increases in the mean total bond strength and the fluctuations of the structural units.

1. Introduction

It is known that the structural relaxation of the melt is affected by both temperature and pressure [1-5]. In the course of lowering the temperature under constant pressure, the structural relaxation known as α–relaxation takes place. In this course, the value of the viscosity increases dramatically over more than 10 orders of magnitude. It is widely accepted that materials exhibiting α–relaxation are classified into two categories, strong systems and fragile systems [6]. Strong systems exhibit the Arrhenius law. On the other hand, fragile system shows a large deviation from the Arrhenius law and obeys the Vogel-Fulcher-Tammann (VFT) equation [7],

$$\log \eta = \log \eta_0 + \frac{DT_0}{T - T_0}. \qquad (1)$$

Here, η_0 is the pre-exponential factor equivalent to the value of the viscosity at the high temperature limit. It takes approximately $\eta_0 = 10^{-5}$ Pa·s. D and T_0 are the fitting parameters and are called strength parameter and Vogel temperature, respectively. T_0 is also called "ideal glass transition temperature" at which all movements of the constituent elements of a liquid are considered to be totally frozen. By choosing adequately D and T_0, Eq. (1) can reproduce relatively well the viscosity behaviours of strong and fragile systems. Concerning the effect of pressure, however, any pressure terms are not included explicitly in Eq. (1). Nevertheless, the VFT equation has been often employed to analyze the pressure

dependence of the α–relaxation by measuring $T_0(P)$ along with $T_g(P)$ [1]. However, it must be noted that the VFT equation is a phenomenological relation whose background is not so clear. In addition, T_0 is not measured directly. Thus, the simple use of the VFT equation is not sufficient to fully understand the structural relaxation.

Based on this standpoint, recently, we have proposed an alternative model to the VFT equation, the Bond Strength–Coordination Number Fluctuation (BSCNF) model [8]. The model which have been originally derived by Aniya [9] describes the temperature dependence of the viscosity in terms of the mean values of the bond strength E_0, the coordination number Z_0, and their fluctuations ΔE, ΔZ of the structural units that form the melt. It has been shown that the model incorporates the VFT formalism, that is, under certain condition, the viscosity behavior described by the BSCNF model reproduces perfectly the behavior described by the VFT equation [8,10]. From this finding, we have obtained a new theoretical relationship which connects the Vogel temperature T_0 to our model parameters that provide some microscopic information on bonding connectivity among the structural units [8]. In the BSCNF model, the pressure terms are not included explicitly as in the VFT equation. However, the pressure effects are embodied physically in the model parameters E_0, Z_0 and ΔE, ΔZ characterizing the bond strength distribution of the supercooled liquid. Our model has an advantage that the physical meanings of the model are more clear than that of the VFT equation.

In this paper, we discussed in the light of the BSCNF model, the temperature and pressure dependences of the structural relaxation time in two kinds molecular glass forming liquids, (a) 4,4'-methylenebis(*N*,*N*-diglycidylaniline), and (b) BMPC: 1,1'-di(*p*-methoxyphenyl)cyclohexane. Experimental data analyzed in this study are taken from the literatures [11,12]. From the analysis, we evaluated the variations of $E_0 Z_0$ and $\Delta E \Delta Z$ of these materials under pressure, and discussed the intermolecular cooperativity of these glass forming liquids from a microscopic point of view.

2. Model of the supercooled liquids under pressure

2.1. Bond Strength – Coordination Number Fluctuation (BSCNF) model

The BSCNF model of the viscosity has been constructed on the physical basis that the thermally activated viscous flow occurs due to bond breaking and bond twisting of the structural units that form the melt [9,13]. The expression for the temperature dependence of the viscosity is given by

$$\eta = \frac{\eta_0}{\sqrt{1-Bx^2}} \exp\left[\frac{Cx + Cx^2 \left[\left\{ \ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right\} \frac{(1-B)}{C} - 1 \right]}{1-Bx^2} \right] , \qquad (2)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} , \quad \text{and} \quad C = \frac{E_0 Z_0}{RT_g} . \qquad (3)$$

Here, x denotes the normalized temperature, $x=T_g/T$. η_{Tg} is the value of the viscosity at T_g. Through this study we adopt $\eta_{Tg}=10^{12}$ Pa·s, as usual. R is the gas constant.

From the viscosity expression given in Eq. (2), the fragility index m, which gives the degree of deviation from the Arrhenius behavior at T_g [6], is expressed as

$$m = \frac{1}{\ln(10)} \left\{ \frac{B - C + 2\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1 - B) \right]}{1 - B} \right\} \quad . \tag{4}$$

On the other hand, by using the VFT equation given in Eq. (1), another expression for the fragility index m written as $m = DT_0T_g/(T_g - T_0)^2$ has been used in many papers. As mentioned above, in these models the pressure effects are embodied in B and C of Eq. (3) or in the temperature $T_0(P)$. Intuitively, B and C give the degrees of the fluctuations and the mean total bond strength to the thermal fluctuation at T_g, respectively. In our previous study, the following relation that connects the model parameters B and C has been found [10,13]. It is given by

$$C = \frac{2\gamma(1-B)}{2\gamma + \sqrt{B}(1+\gamma^2)} \left\{ \ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right\} \quad , \qquad \gamma = \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0} \quad , \tag{5}$$

where, γ is the ratio of the normalized bond strength fluctuation to the normalized coordination number fluctuation. Especially, in the case of $\gamma = 1$, namely when $|\Delta E|/E_0 = |\Delta Z|/Z_0$, we have found that the viscosity behavior described by Eq. (2), corresponds perfectly to that described by the VFT equation [8,10]. Moreover, from this finding, we have obtained a theoretical relationship [8],

$$\frac{T_0}{T_g} = 1 - \frac{\left(\frac{1 + \sqrt{B^*}}{1 - B^*}\right)C^* - \frac{1}{2}\ln(1 - B^*)}{\ln(10)m} \quad . \tag{6}$$

Here, (B^*, C^*) is the set of parameter satisfying Eq. (5) for the case of $\gamma = 1$. This equation is a new relationship which provides an expression to the ideal glass transition temperature from a microscopic point of view. In our recent papers, we have demonstrated the validity of Eq. (6) by applying it to some cases, such as the temperature range of cooperativity in some ion conducting polymers [14]. We have also discussed the correlation between the fragility index m and the stretched exponent β_{KWW} in the Koulrausch-Willams-Watts (KWW) function by using this relationship [8]. In what follows, we consider a method to analyze the temperature and pressure dependences of the structural relaxation in the light of the BSCNF model.

2.2. Temperature and pressure dependences of the structural relaxation time
The structural relaxation time τ obtained from the dielectric measurement is proportional to the viscosity η as given in the Maxwell relation $\eta = G_\infty \tau$, where G_∞ is the infinite frequency shear modulus. In this subsection, it is shown that the BSCNF model is applicable to fit the experimental data for the temperature and pressure dependences of the structural relaxation time. Here we considered the structural relaxations for the following two molecular glass forming liquids, (a) 4,4'-methylenebis(*N,N*-diglycidylaniline) and (b) BMPC: 1,1'-di(*p*-methoxyphenyl)cyclohexane, which have been investigated experimentally [11,12].
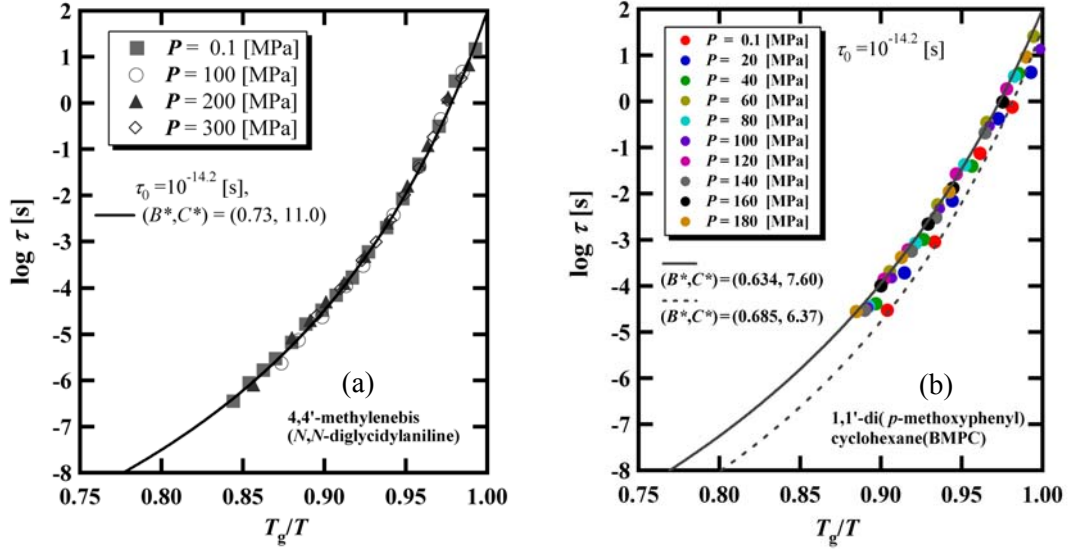
Figure 1. Temperature and pressure dependences of the structural relaxation time τ in the molecular glass forming liquids, (a) 4,4'-methylenebis, and (b) BMPC: 1,1'-di(p-methoxyphenyl)cyclohexane. The solid and dashed curves are calculated from Eq. (2). Experimental data are taken from [11,12].

Figure 1 shows the temperature and pressure dependences of the structural relaxation time τ for these two kinds of molecular glass forming liquids. We can see that in material (a), the experimental data are almost independent on pressure. Material (b) exhibits a weak pressure dependence. The fragility remains almost constant under high pressures. On this regard, Casalini *et al*. have concluded that for material (a), the origin of the increase in the molecular cooperativity due to decreasing temperature is the same to that due to increasing pressure [11]. The increase of T_0 and T_g with an increase in pressure has been also reported [11,12].

In the next section, we will discuss on the quantities $E_0 Z_0$ and $\Delta E \Delta Z$ and on the intermolecular cooperativety under pressures by using the pressure dependences of T_0 and T_g, together with the best fitted parameters (B^*, C^*) and the theoretical relationship given by Eq. (6).

3. Results and discussion

The mean total bond strength $E_0 Z_0$, and the product of the fluctuations $\Delta E \Delta Z$ for the two molecular glass forming liquids have been evaluated by using Eq. (3), (6) and the characteristic temperatures $T_0(P)$, $T_g(P)$. The result is shown in Figure 2. From the figure, we can see that $E_0 Z_0$ and $\Delta E \Delta Z$ increase with the increase in pressure. Such behaviors are understood as follows.

By increasing pressure, the structural units become more crowded due to the decrease of free volumes, leading to an increase of the average coordination number Z_0 and density. In our analysis, the degree of variation of E_0 under pressure is unclear. However, it is expected that the increment rate of Z_0 is more dominant than that of E_0. Therefore, $E_0 Z_0$ increases with pressure. Experimental data indicate that the stretched exponent β_{KWW} that gives the degree of the cooperativity remains almost constant ($\beta_{KWW} \approx 0.37$) in material (a) [11] and increases slightly ($\beta_{KWW} \approx 0.50 - 0.53$) in material (b) [12] when pressure is applied. Lower value of β_{KWW} corresponds to higher value of the fragility, indicating that a larger number of structural units are involved in the flow process [13].

In Figure 2 we can see that the values of $\Delta E \Delta Z$ for both materials increase with pressure. This result indicates that the width of the bond strength distribution become wider with the increase in pressure. Due to the increase in $E_0 Z_0$ which is the dominant factor compared to $\Delta E \Delta Z$, the degree of the intermolecular cooperativety is supressed, resulting in the nearly constant value of β_{KWW} with the increase of pressure.
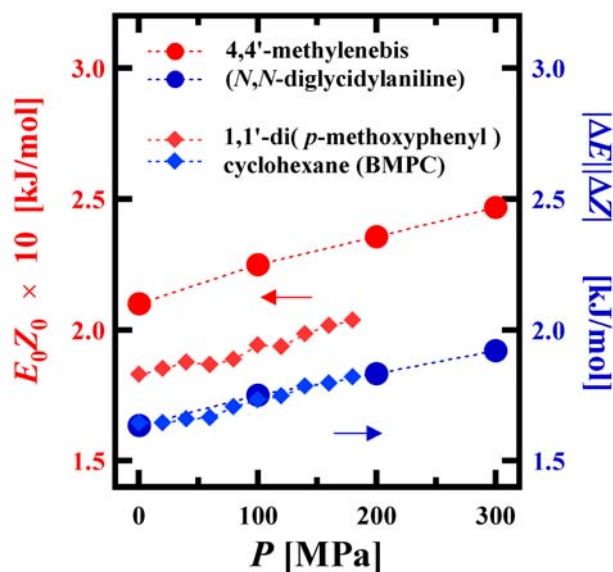
Figure 2. Mean total bond strength E_0Z_0, and the product of fluctuations $\Delta E\Delta Z$ of the structural units as a function of pressure evaluated by Eq. (3) and Eq. (6). The vertical axis in the left and right hand sides denote E_0Z_0 and $\Delta E\Delta Z$, respectively.

4. Conclusion

In this contribution, the structural relaxation under pressure of molecular glass forming liquids 4,4'-methylenebis(N,N-diglycidylaniline) and BMPC: 1,1'-di(p-methoxyphenyl)cyclohexane have been analyzed in the light of the BSCNF model. It is shown that for both systems, the mean total bond strength E_0Z_0, and the product of the fluctuations $\Delta E\Delta Z$ of the structural units increase with the increase in pressure. The variation of the stretched exponent β_{KWW} and the degree of the intermolecular cooperativity has been also discussed. The BSCNF model provides a new method to analyze both, the temperature and pressure dependences of the structural relaxation in supercooled liquids.

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