

The Effect of Correlation in the Bond Strength - Coordination Number Fluctuation Model of Viscosity

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A model is derived for the temperature dependence of the viscosity of the melt by introducing a correlation factor between the bond strength and the coordination number in the total bond strength distribution. It is shown that the shape of the distribution function changes considerably depending on the magnitude and sign of the correlation factor.

§1. Introduction

Glass science is one of the most fascinating fields in material science from both academic and applied points of view. A wide variety of properties shown by the glasses have their origin in the microscopic bonding connectivity of the atoms that are distributed randomly.

Some years ago, a model has been proposed for the temperature dependence of the viscosity of the melt.¹⁾ The model is described in terms of the bond strength E , the coordination number Z , and their fluctuations ΔE and ΔZ . The model has been applied to study the viscosity of many kinds of glass forming liquids such as covalent, ionic, molecular and metallic systems.²⁾ It has been shown that the model reproduces quite well the viscosity data of these materials. In addition, the model provides some sort of microscopic information such as the condition of occurrence of viscous flow in glass forming liquids. It has been also shown that^{3,4)} the model is in harmony with other models such as the Adam-Gibbs model⁵⁾ and the Vogel-Fulcher-Tammann (VFT) equation.⁶⁾

In this report, the above model is extended by introducing the correlation between the bond strength and the coordination number among the structural units. We expect that the extended model will describe the chemical aspects of the glasses better than the previous model.

§2. Correlated bond strength distribution and a model of the melt

The glassy state is usually formed by quenching a liquid. In the course of lowering the temperature, the supercooled liquid is frozen at certain temperature, called "glass transition temperature T_g ". The atoms that form the glass or the supercooled liquid are bound to neighboring atoms to form certain type of clusters or structural units with different degree of randomness. The structural units move cooperatively or in

isolated form from one position to another, by breaking the bonds. Such a movement of the structural units is caused by thermally activated process and results in the viscous flow. Under this picture, we expect that there must be a correlation between the bond strength E and the coordination number Z . We consider the following Gaussian distribution

$$P(E, Z) = \frac{1}{\sqrt{4\pi^2(\Delta E)^2(\Delta Z)^2(1-\rho^2)}} \times \exp \left[-\frac{(E-E_0)^2}{2(1-\rho^2)(\Delta E)^2} - \frac{(Z-Z_0)^2}{2(1-\rho^2)(\Delta Z)^2} + \frac{\rho}{1-\rho^2} \frac{(E-E_0)(Z-Z_0)}{(\Delta E)(\Delta Z)} \right], \quad (2.1)$$

where E_0 and Z_0 are the mean bond strength and the mean coordination number, ΔE and ΔZ are their fluctuations of the structural units, respectively. The quantity ρ is the correlation factor between E and Z . In principle, it takes a value in the range of $-1 \leq \rho \leq 1$. Concerning this point further discussion is given below. The temperature dependence of the viscosity of the melt can be expressed as¹⁾

$$\eta = \eta_0 \left\langle \exp \left(\frac{EZ}{RT} \right) \right\rangle = \eta_0 \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dZ P(E, Z) \exp \left(\frac{EZ}{RT} \right), \quad (2.2)$$

where η_0 denotes the viscosity at the high temperature limit. By performing the integration of Eq. (2.2), the expression for the viscosity η is derived as

$$\ln \left(\frac{\eta}{\eta_0} \right) = \frac{Cx + Cx^2 \left\{ \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1 - B - 2\rho\sqrt{B}) \right] \frac{(1 - B - 2\rho\sqrt{B})}{C} - 1 \right\}}{1 - Bx^2 - 2\rho\sqrt{B}x} - \frac{1}{2} \ln(1 - Bx^2 - 2\rho\sqrt{B}x), \quad (2.3)$$

where

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2}, \quad C = \frac{E_0 Z_0}{RT_g}, \quad x = \frac{T_g}{T}. \quad (2.4)$$

Here η_{T_g} is the viscosity value at the glass transition temperature, R is the gas constant, B and C are the degree of the fluctuation and the mean total bond strength between the structural units, respectively. In the case of $\rho = 0$, Eq. (2.3) reduces to the previous model without the correlation.

According to Angell⁷⁾, glass forming liquids are characterized in terms of the slope of the temperature dependence of the viscosity at T_g . This quantity is called fragility index m . From Eq. (2.3), m is derived as

$$m = \lim_{x \rightarrow 1} \frac{d \text{Log } \eta}{dx} \quad (2.5)$$

$$= \frac{(B + \rho\sqrt{B}) - C + 2(1 - \rho\sqrt{B}) \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1 - B - 2\rho\sqrt{B}) \right]}{\ln(10)(1 - B - 2\rho\sqrt{B})}. \quad (2.6)$$

In our previous study, it was suggested that the values of B and C are interrelated for many kinds of glass forming materials.²⁾ Recently, the relationship between these parameters has been obtained theoretically.³⁾ By including the correlation factor ρ , such a relationship is expressed as

$$C = \frac{2\gamma(1 - B - 2\rho\sqrt{B}) \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1 - B - 2\rho\sqrt{B}) \right]}{2\gamma(1 - \rho\sqrt{B}) + \sqrt{B} \{1 + (1 + \rho^2)\gamma^2\}}, \quad (2.7)$$

where

$$\gamma = \frac{\delta E}{\delta Z}, \quad \delta E = \frac{|\Delta E|}{E_0}, \quad \delta Z = \frac{|\Delta Z|}{Z_0}. \quad (2.8)$$

Here γ is the ratio of the normalized bond strength fluctuation δE to the coordination number fluctuation δZ . Moreover, the number of structural unit N_B that provides a measure for the amount of bonds that must be broken to observe the viscous flow can be derived. This quantity is related to the fragility index m given by Eq. (2.6), and it is expressed as $N_B = (\ln(10)m)/C$. The original derivations are given elsewhere.^{2),3)}

§3. Results and Discussion

Figure 1 shows the behavior of correlated Gaussian distribution defined in Eq. (2.1) for the cases of $\rho = 0.0, \pm 0.4$ and ± 0.6 . We adopt $\gamma = 1$ in all cases. We can see that the shape of the distribution depends on the the magnitude and sign of the correlation factor. The distribution corresponding to the previous model is shown in Fig. 1(a).

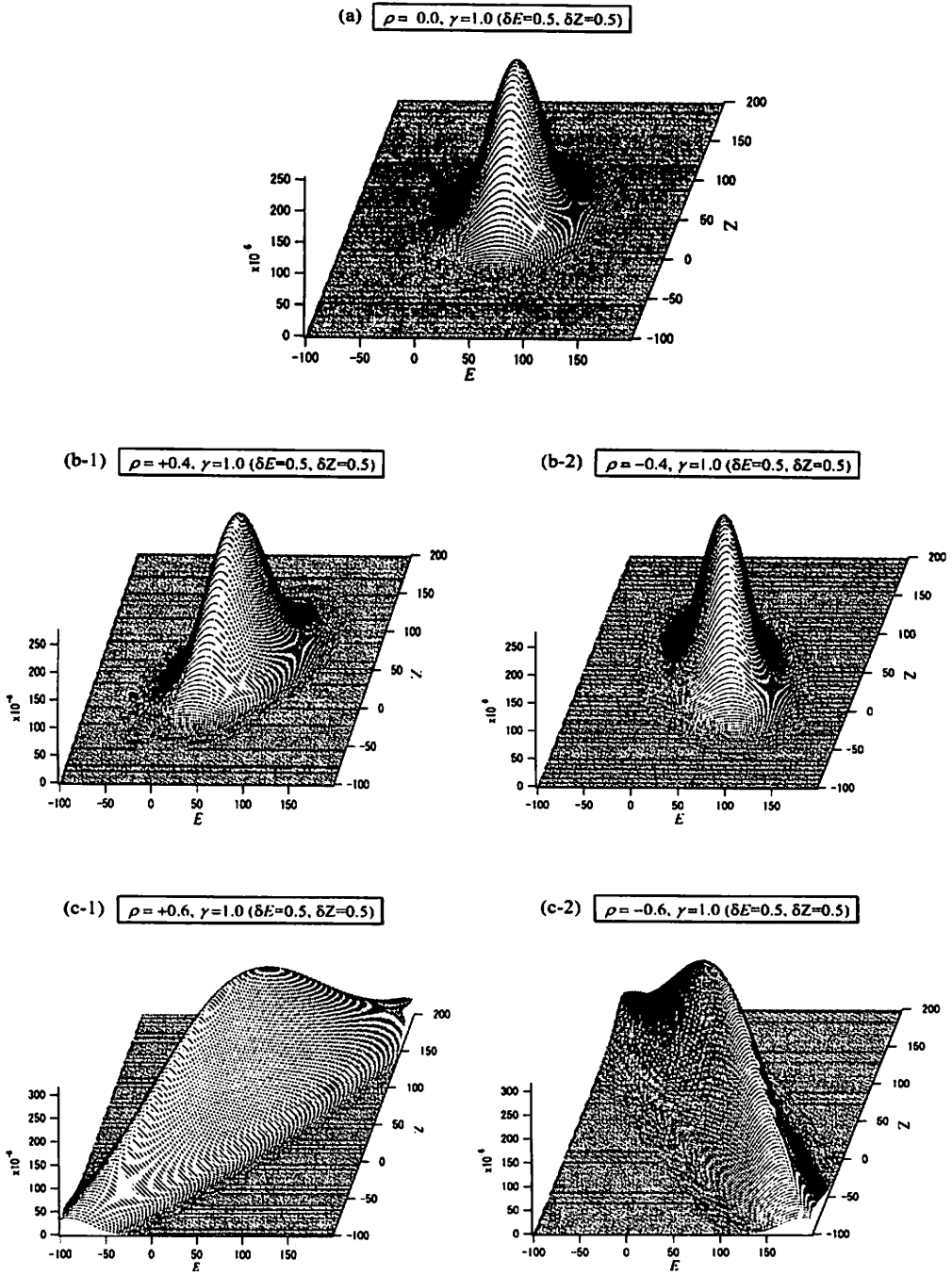


Fig. 1. Gaussian distribution including the correlation between the bond strength E and the coordination number Z .

Equations (2.3), (2.6) and (2.7) contain the factor $\ln(1 - B - 2\rho\sqrt{B})$. Since we must have $(1 - B - 2\rho\sqrt{B}) > 0$, the constraint on ρ is

$$\rho < \frac{1 - B}{2\sqrt{B}} = \rho_{\text{Max}}(B). \quad (3.1)$$

The range of permissible values of ρ and B are shown by the shaded area in Fig. 2. This figure also indicates the maximum value of the correlation factor ρ_{Max} . It is seen that the positive value of ρ diminishes as B increases.

Different types of correlation might exist in real systems. For instance, materials having a large binding energy E and a large coordination number Z between the structural units will have a large positive value of ρ . On the other hand, materials having a large value of E and a small value of Z will exhibit a negative correlation factor. This notion provides a way to describe the properties of glass forming liquids in terms of chemical bonding and the coordination number of the structural units. For the application of the model to specific materials, further studies are required.

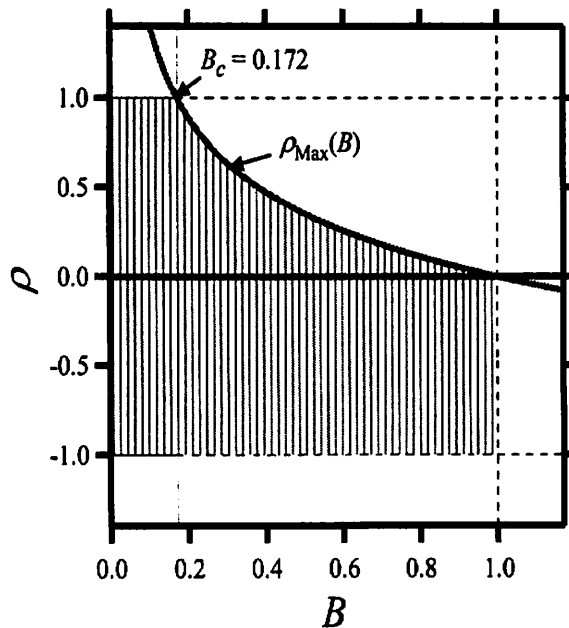


Fig. 2. Permitted values of the correlation factor ρ as a function of B .

§4. Conclusion

An extended model for the viscosity of the melt has been derived by introducing the correlation coefficient between the bond strength and the coordination number between the structural units. The new model indicates that the distributions of bond energy and coordination number change considerably depending on the magnitude and sign of the correlation factor.

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