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On the viscosity change in strong and fragile glasses [1]

Yuichi Masaki *, Akio Kitagawa, Masakuni Suzuki

Department of Electrical and Computer Engineering, Kanazawa University, Kodatsuno,
Kanazawa 920, Japan

Abstract

The viscous behaviour of strong and fragile glasses has been interpreted on the basis of the fragmentation model in which it is assumed that (1) a vitreous system consists of "pseudo-molecules" and (2) the system is fragmented and the fragment size decreases with increasing temperature. The results of numerical calculations show that the size of fragments in viscous flow is constant for strong glasses whereas for fragile glasses it decreases as temperature is increased from T_g to T_m.

Keywords: Fragile glasses; Fragmentation model; Glass viscosity; Strong glasses

1. Introduction

One of the most interesting features of glasses is probably their change in viscosity (or relaxation time) during glass transition. In the glass transition region, the viscosity of many glass-forming materials changes by more than 15 orders of magnitude. The temperature-dependence of viscosity during glass transition generally enables glasses to be classified into two categories, i.e., strong and fragile glasses, a classification introduced by Angell a decade ago [1,2]. The temperature-dependence of viscosity in strong glasses obeys an Arrhenius law whereas that in fragile glasses is well fitted by an empirical Vogel–Fulcher–Tammann expression. Although the viscous behaviour of real glasses is distributed over a wide range between the above extremes of strong and fragile, network glasses such as SiO_2, GeO_2 and BeF_2 tend to be "strong", and many other glasses including industrial glasses, chalcogenide glasses and organic glasses are generally "fragile".

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* Corresponding author.

[1] Dedicated to Professor Hiroshi Suga.

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Many models have been proposed to explain such viscous behaviour. Among them, that of Vilgis recently postulated a simple model which successfully explained the difference between strong and fragile glasses [3]. According to this model, the fragility of glasses can be explained by the introduction of a fluctuation of the coordination number, Δz, i.e., viscous behaviour is "strong" when $\Delta z = 0$, as for network glasses whereas $\Delta z > 0$ always leads to fragile glasses. We have also developed a new model for the glass transition of amorphous Si in which the system becomes fragmented with increasing temperature and begins to behave like a liquid when the fragment size reaches a critical value [4,5]. In this paper, we shall describe the viscous behaviour of some glass-forming materials on the basis of the fragmentation model.

2. Model for fragile glasses

Many glass-forming materials in their molten states possess electronic properties similar to those in their vitreous states. This suggests that the unit structure which determines electronic properties is almost identical in the molten and solid states. We here denote such a unit structure in a system as a "pseudo-molecule" (or a real molecule depending on the material). The structural configuration of such pseudo-molecules is considered to be random in real glass systems. Hence, it can be thought that the cohesive energy in the system is not uniform but fluctuates from place to place. Such situations are independent of the binding mechanisms of the system. Accordingly, it is possible that the weaker bonds between pseudo-molecules begin to break with increasing temperature and consequently the system becomes fragmented. Further, it could also be thought that fragment size decreases with increasing temperature. The final stage of the fragmentation is the breaking of the system into unit structures (or pseudo-molecules); at this time the system is thought to behave as a "perfect" liquid. The cohesive energy in a fragmented system may be a weak attractive potetial due to Van der Waals interaction. In some cases, however, the interaction between fragments may still involve some of the original binding characteristics such as covalent or ionic forces, because of unsaturated bonds at the fragment surfaces.

According to the fragmentation model [4,5], the self-diffusion coefficient, D, of the fragments in a system where fragment size changes with temperature, may, by analogy with the vacancy mechanism in crystalline solids, be written as:

$$D = \frac{N_F}{N} g \nu d^2 \exp\left[-\frac{q(E_h + E_j)}{k_B T} \right] \tag{1}$$

where N_F is a fragment density, N the density of the pseudo-molecules, g a numerical factor associated with jump sites, ν the jump frequency of the fragment, d the average fragment size, q the charge on an electron, E_h the hole formation energy, E_j the fragment jump energy and k_B the Boltzman constant. The sum of the hole formation energy E_h and the fragment jump energy E_j may be written as $f d^p E_0$, where the exponent p represents a binding mechanism between fragments and is in the range of 1–2 depending on a binding mechanism; f is a numerical factor (e.g., $f = 1$ for $p = 1$ and

$f = \sim 6$ for $p = 2$) and E_0 an activation energy (in eV) for the diffusion of fragments with an average size d. The jump frequency of the fragment, ν, is given by:

$$\nu = \nu_D \left(\frac{N_F}{N}\right)^{1/3} \tag{2}$$

here ν_D is a Debye frequency of the fragments.

Eq. (1) yields:

$$D = \frac{d^{-2}}{N^{4/3}} g \nu \exp\left[-\frac{qfd^p E_0}{k_B T}\right] \tag{3}$$

Using the Stokes–Einstein relationship, the viscosity of the system is expressed by:

$$\eta = CdT \exp\left(\frac{qfd^p E_0}{k_B T}\right) \tag{4}$$

where

$$C = \frac{(Nd)^{4/3} k_B}{3\pi g \nu_D} \tag{5}$$

Further details of these expressions are described in the following section for three glass-forming materials .

3. Application of the fragmentation model to real systems

3.1. o-Terphenyl

o-Terphenyl consists of rigid real molecules between which Van der Waals weak interaction is present [6], so there is some possibility that the system becomes fragmented during the glass transition and the fragment size decreases with increasing temperature.

For simplicity, assuming the shape of fragments to be spherical with an average diameter of d and two fragments are in contact at D, the Van der Waals interaction energy is given by [7]:

$$E = -\frac{A}{6D}\frac{d}{4} \tag{6}$$

where A is a Hamaker constant with a typical value of 10^{-19} J. Therefore the exponent p in Eqs. (3) and (4) becomes unity.

3.2. SiO_2

SiO_2 is a typical strong glass and could be considered to consist of SiO_4 tetrahedral pseudo-molecules in which each oxygen atom is shared by two neighbouring Si atoms.

There are several interesting phenomena observed in this material, such as (1) no change in heat capacity at the glass transition temperature T_g (= 1173°C) [8]; (2) disappearance of a sharp peak in the Raman spectrum below 900°C [9]; (3) considerable structural change at 800°C observed by Raman spectroscopy [9]; and (4) significant volume relaxation and viscous flow at 500°C [9].

From the viewpoint of the fragmentation model, these facts suggest the following scenario for the glass transition in SiO_2. Reactions of bond breaking and rebinding of broken bonds between Si–O covalent bonds take place even at low temperature. With increasing temperature, the reaction of bond breaking becomes dominant compared with rebinding reaction. At such a temperature, large fragments may appear in an instant. However, interaction between the fragments is still so strong that the system retains characteristics of the solid and therefore this system cannot exhibit a viscosity less than 10^{12} Pa s in this state, unlike the case of *o*-terphenyl. With further increase in temperature, deformed tetrahedra (SiO_2 + 2 broken bonds) could begin to appear in the system. If a free volume (or vacancy) is simultaneously produced near the deformed tetrahedron, due to density fluctuation, the tetrahedron can jump into the free volume. At more elevated temperatures the density of vacancies increases and many more deformed tetrahedra can jump so that the system begins to show macroscopic fluidity. Thus, since the structural change occurs gradually for SiO_2, a clear glass transition with a heat capacity change is not observed. Further, a fragment is equivalent to the pseudo-molecule, i.e., the deformed tetrahedron (SiO_2 + 2 broken bonds), and the fragment size is constant above T_g. The exponent p in Eqs. (3) and (4) takes a value of 2 since to a crude approximation the number of covalent bonds is proportional to the surface area of the fragment.

3.3. $Na_2O \cdot 2SiO_2$

It is thought that when a network modifier such as Na_2O is introduced into SiO_2 the network modifer gives rise to Si–O–Si bridge rupture [10] (or chemical scissoring [2]). Hence, this material is thought to be more easily fragmented than the SiO_2 system into deformed SiO_x tetrahedra ($x = 2$, 3 or 4) with (x–2) Na ions nearby and (4–x) broken bonds. In this case, the main fragment can be regarded as a pseudo-molecule, i.e., the deformed SiO_x tetrahedron. However, the presence of larger fragments than the tetrahedra is also expected at lower temperatures because of the addition of Na_2O. Further, the interaction between fragments is also expected to be weaker than for SiO_2 and consequently E_h and E_j in this system would be smaller than those in the SiO_2 system.

When Eqs. (3) and (4) are applied to this system, the exponent p takes a value of 2 for the same reason as for SiO_2.

4. Results and discussion

Measured viscosities of *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2 as a function of reduced reciprocal temperature (taken from Ref. [2]) are shown in Fig. 1 as ■, ▲ and ◆ for *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2, respectively.

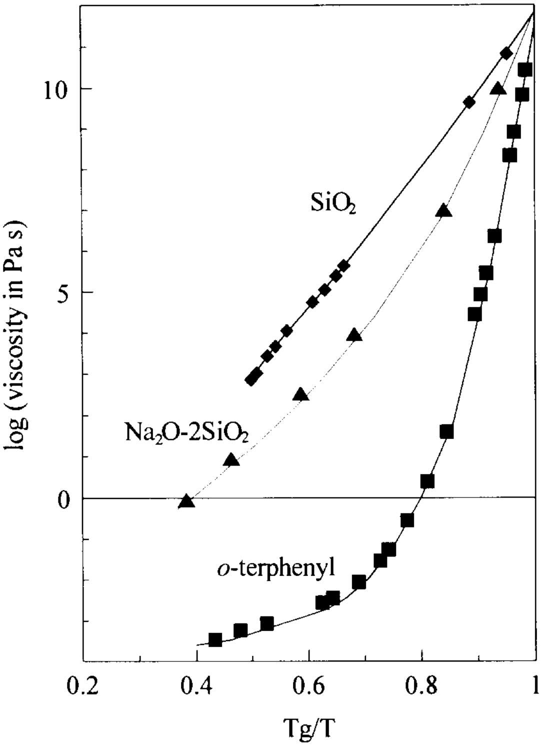

Fig. 1. Viscosities of *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2 as a function of reduced reciprocal temperature (T_g/T_m). Symbols ■, ▲ and ◆, represent measured values for *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2 and SiO_2, respectively, taken from Ref. [2]. Solid lines were calculated using the present model.

In the numerical calculations, it was first assumed that the system was fragmented into the minimum fragment size d_{min} (equivalent to the pseudo-molecular size) at the highest temperature, which was higher than the melting point T_m of each material (generally T_g/T_m is ca. 0.7). An activation energy E_0 was then determined in order to fit the viscosity given by Eqs. (3) and (4) to the measured value at the highest temperature. Finally the average fragment size, d, at various temperatures was determined by fitting Eqs. (3) and (4) to the measured viscosity values. Parameters used in the calculation are listed in Table 1. In the table, the values of T_g/T_m and Debye frequencies, ν_D for $Na_2O \cdot 2SiO_2$ and *o*-terphenyl have not been found and therefore reasonable values are assumed. The minimum fragment sizes, d_{min}, are also assumed to give reasonable results.

The calculated viscosities and fragment sizes used, as a function of reduced reciprocal temperature, are shown in Figs. 1 and 2, respectively, as solid lines for the three materials. The energy obtained for self-diffusion of fragments (or viscous flow of fragments), per fragment, are also listed as fd^pE_0 in Table 1. As shown in Fig. 2, the average fragment size d for SiO_2 does not change with temperature whereas that of

Table 1
Parameters used in the calculation and some of the results

	SiO_2	$Na_2O \cdot 2SiO_2$	o-Terphenyl
T_g/K	1446[a]	713[a]	239.7[a]
T_g/T_m	0.72[b]	0.72[d]	0.74[b]
ν_D/(1/s)	9.8×10^{12}[c]	5×10^{12}[d]	1×10^{12}[d]
C/(Pa s cm^{-1} K)	0.91	0.46	0.64
d_{min}/Å	2.6	2.7	4.2
p	2	2	1
fd^pE_0/(eV (fragment)$^{-1}$)	4.06	1.68	0.14

[a] From Ref. [2].
[b] From Ref. [6].
[c] Calculated using a Debye temperature $\theta_D = 470$ K.
[d] Assumption.

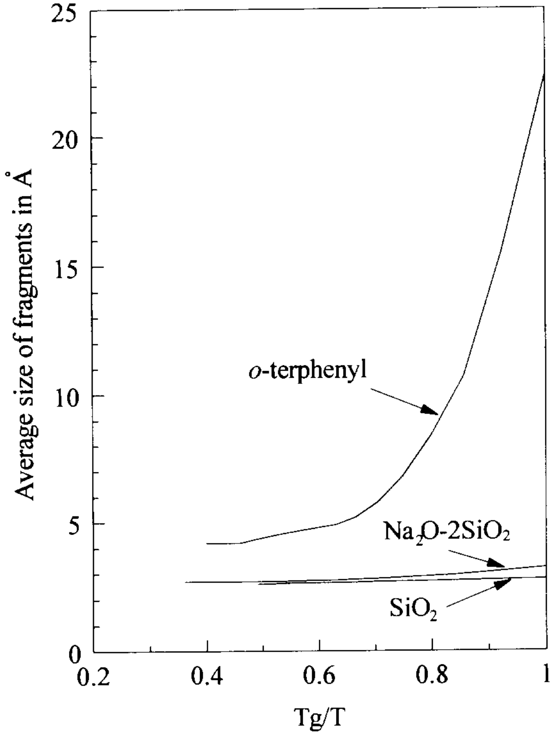

Fig. 2. Fragment sizes for o-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2 as a function of reduced reciprocal temperature (T_g/T_m), used in the calculation of the viscosities shown in Fig. 1.

o-terphenyl increases rapidly from about 0.7 with increasing T_g/T, in other words, the average fragment size in the o-terphenyl system rapidly increases with decreasing temperature below T_m. The average fragment size for $Na_2O \cdot 2SiO_2$ appears to increase slightly as temperature is decreased from T_m. This indicates that in this system the fragments are mainly SiO_x tetrahedral pseudo-molecules but some larger fragments also contribute to the viscous flow, as predicted in the previous section. On the other hand, energies obtained for the viscous flow give reasonable values, i.e., 0.14, 1.68 and 4.06 eV per fragment for *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2, respectively.

Thus, the change in viscous behaviour with temperature can be understood in terms of a fragmentation model in which the size of the main diffusant in viscous flow remains constant for strong glasses whereas for fragile glasses it decreases as the temperature is increased from T_g to T_m. Although the calculations above are rough descriptions, particularly for *o*-terphenyl because the shape of minimum fragment is not spherical, the fragmentation model can successfully give a qualitative description for the viscous flow in strong and fragile glasses.

5. Conclusions

We have explained the viscosity change for strong and fragile glasses during the glass transition on the basis of the fragmentation model. The following summarises the main results.

(1) The fragment size of *o*-terphenyl, a typical fragile glass, rapidly decreases as the temperature is increased from T_g to T_m and then becomes almost constant above T_m.

(2) The results for SiO_2, a typical strong glass, indicate that the fragment size does not change during the glass transition but has a constant which equals the pseudo-molecular size.

(3) For $Na_2O \cdot 2SiO_2$, which shows weak fragility, the fragment size decreases slightly with increasing temperature from T_g to T_m.

(4) Energies obtained for the viscous flow are 0.14, 1.68 and 4.06 eV per fragment for *o*-terphenyl, $Na_2O \cdot 2SiO_2$ and SiO_2, respectively.

Acknowledgements

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