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Viscosity-temperature Relation Based on the Evolution of Medium-range Structures of Silica

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Abstract

The viscosity of glass is the most important technological property to glass manufactures and various applications. Practically, finding an accurate equation to express the glass viscosity behavior in the entire glass transition temperature range is tremendously challenge because it spans more than ten orders of magnitude. After a brief review of existing empirical viscosity equations, this work focuses on the correlating silica viscosity behavior with the evolution of glass medium-range structure, based on the recently proposed nanoflake model. From this new model, a new equation is constructed, which correctly describes the Arrhenius-type behavior of silica viscosity η above the melting temperature T_m , and non-Arrhenius-type behavior from T_m to a critical temperature T_c . At temperature lower than T_c , the equation predicts Arrhenius-type behavior again for the viscous flow with increased activation energy. The new equation agrees with experimental data in the entire temperature spanned from extremely high to extremely low. The application of the new equation is shown to extend to other silicate glasses as well.

1. Introduction

Viscosity is the most important property of liquids and melts. In glass manufacture, it determines the melting conditions, the working and annealing temperatures, and the maximum usage temperature for the materials. In geology, the magma behavior, volcanic eruptions, and lava flow rate are all dependent on the silicate viscosity.

Understanding the temperature dependence of viscosity is key to improve the knowledge of the nature of glass and the glass transition process¹. The viscosity-temperature relation of glass materials has been investigated over the past hundred years, and many physical models with associated viscosity equations have been proposed. The most common one is the Vogel-Fulcher-Tamman (VFT) equation, which uses three empirical parameters²⁻⁴:

$$\eta = \eta_0 \exp[B/(T-T_0)] \quad (1)$$

Where η_0 , B , T_0 are temperature-independent constants. Although the equation has the theoretical basis of the free volume theory⁵ and the entropy theory⁶, it exhibits systematic error at low temperatures due to a mathematical divergence at $T = T_0$, where it predicts infinite viscosity. In 2002, Doremus provided a critical assessment of existing experimental data from various research groups, and concluded that there are two temperature regions separated at 1400°C. Each region has an Arrhenius dependence with a different activation energy⁷.

Doremus also found that Eq.1 does not fit the experimental viscosity data of silica correctly at the extremes of both high and low temperature regions⁷. Based on this analysis, a four parameters equation for the viscosity-temperature relation of silica was proposed:

$$\eta = A \exp(B/RT) [1 + C \exp(D/RT)] \quad (2)$$

Where R is a molar gas constant, and A, B, C and D are temperature-independent constants. Equation 2 is a sum of two exponential terms. Each term fits the Arrhenius temperature dependence of viscosity data at the high and the low temperature regions, respectively. However, the sharp boundary of the regions with different activation energies at 1400°C is difficult to explain. The theoretical basis of Eq. 2 is that the silica viscous flow results from motion of line defects composed of SiO molecules^{7,8}. In 2009 the MYEGA equation was proposed⁹. This is a more sophisticated equation based on the temperature dependence of the configurational entropy and has no the singularity at finite temperature. After many decades of research on the glass transition process, quantitative understanding of the extraordinary viscous flow slow-down that accompanies supercooling and glass formation is still a major scientific challenge¹. The details of the subject can be found in several books and comprehensive review papers¹⁰⁻¹⁴.

The purpose of this work is to present a new viscosity equation for silica glass based on the nanoflake medium-range structural model,

proposed in 2017¹⁵⁻²⁰. One fundamental principle in materials science and engineering is that the macroscopic properties of material originate from the internal structures of that material. With this principle the viscosity-temperature behavior of glass must be highly sensitive to the structure-temperature relation of the glass. Previously, the most common structural model for vitreous silica is the continuous random network theory (CRN)^{21,22}. Although the original CRN model is presented in many textbooks, it has to be regarded as a first order approximation of the glass structure. While the CRN model is hardly challenged for its description of short-range structure as a SiO₂ tetrahedron and the long-range structure as a random network, the model contains no description on the structure-temperature relation of glasses. Thus, the CRN model cannot provide useful guidance for the viscosity-temperature relation. The newly proposed nano-flake model describes the medium-range ordering structure in silica and the evolution of the ordering structure in the glass transformation^{15,16}. This model is expected to be useful in understanding various properties of silica, including the viscosity behavior in the silica glass transition process.

2. A new equation from the nanoflake model

The new model describes the medium-range ordering structure in silica as ‘nanoflakes’. A nanoflake is formed by two layers of SiO₄ tetrahedra with a thickness of about 0.8 nm and lateral extension of about 2 nm. The cross-section of these layers is shown in Fig. 1(a).

While looking from the direction perpendicular to the layers, the nanoflake has a structure described by CRN theory, shown in Fig. 1(b).

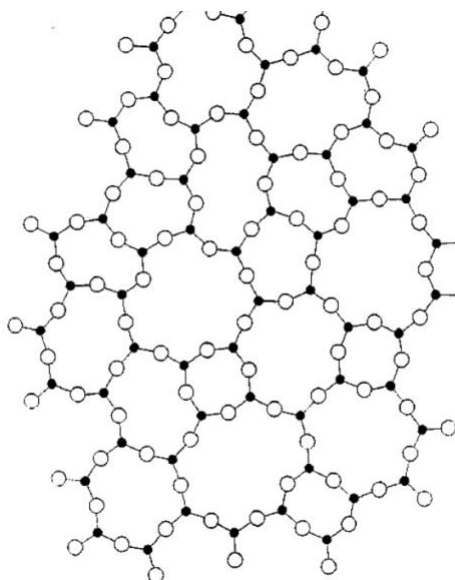
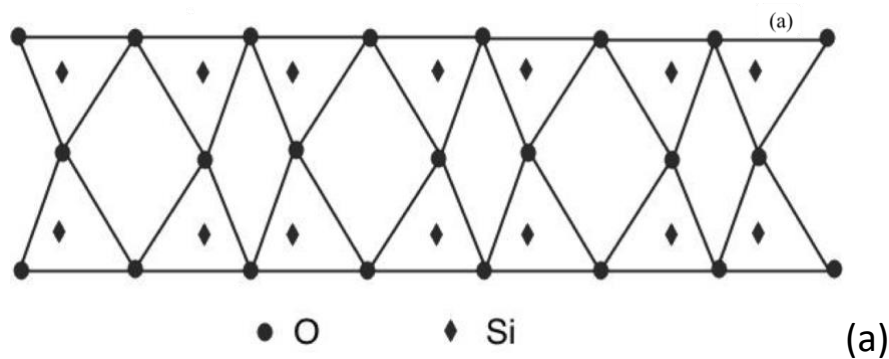


Figure 1: Illustration of medium range ordering structure in vitreous silica, as proposed by the nanoflake model. (a) Side view of the nanoflake model: two layers of SiO_4 tetrahedra with a thickness of about 0.8 nm and lateral extension of about 2 nm. (b) Top view of the structure: various membered-rings as described in Zachariasen's continuous random network theory.

Adjacent nanoflakes intersect each other forming a cluster with a shape that is approximately octahedral¹⁵. The clusters are randomly orientated and distributed in the system such that bulk isotropy is preserved. According to the nanoflake model, there are three distinct regions in the entire temperature range¹⁶. Within each region, silica has a different internal structure, and a different formula is needed to describe the viscosity behavior:

(1) The first is the high temperature region, defined as above 1723°C, the melting temperature T_m of silica. In this region, the structure of silica described by the nanoflake model is not different from the CRN theory, and there is no cluster formed in the liquid. Like a normal liquid, the viscosity η of silica has exponential dependence to temperature and can be described by the Arrhenius equation:

$$\eta = \eta_1 \exp(Q_1/RT) \quad (3)$$

Where η_1 and Q_1 are temperature-independent constants, called the pre-exponential factor and the activation energy, respectively.

(2) The second is the medium temperature region from T_m of 1723°C to the critical temperature T_c of 1470°C, which is the transition temperature between β -cristobalite and tridymite¹⁶. In this temperature region, the silica liquid is unstable, and the SiO_4 tetrahedra in the supercooled silica liquid adjust continuously to form the β -cristobalite crystal. To obtain glass, the cooling rate has to be fast enough to avoid the crystallization. However, no matter how high

the cooling rate is, a certain number of clusters with approximately octahedral shape, will form in the liquid^{15,16}. These clusters would not disappear unless the glass temperature rises above the melting temperature. As the temperature cools from high to the critical temperature of 1470°C, the numbers of clusters and the average size of the clusters increase, resulting in the continuous increase of the activation energy of the viscous flow. Since the activation energy is Q_1 at T_m of 1723°C, one may use ΔQ , which is positive energy, to define the increase of activation energy with the decreasing temperature T . Thus, the viscosity of silica can be written as:

$$\eta = \eta_3 \exp[(Q_1 + \Delta Q)/RT] \quad (4)$$

Where η_3 and ΔQ are temperature-dependent, and will be further explained and computed later. At the low end of the medium temperature region of 1470°C (1743°K), the activation energy would be increased to $Q_1 + \Delta Q(T_c)$, which is designated as Q_2 .

(3) The third is the low temperature region, where the temperature is lower than T_c , 1470°C. The response of the glass structure to the reduced temperature in this region is to form nanoflakes, i.e. one-dimension ordering structure on the facets of the clusters¹⁵. As the temperature decreases further, the number of nanoflake increases, and the medium-range structure of the silica becomes more ordered. Consequently, various physical properties, such as optical transmission, X-ray scattering et al., change as the temperature

decreases²³⁻²⁵. However, formation of the medium-range ordering structure does not influence the activation energy of the liquid flow. This is because the size and the shape of the clusters do not change by ordering on facets, and the energy barriers in the liquid flow stay the same. Thus, after the activation energy increases to Q_2 at the critical temperature of 1470°C, it stays unchanged in the whole low-temperature region, and the behavior of viscosity is Arrhenius-type:

$$\eta = \eta_2 \exp(Q_2/RT) \quad (5)$$

Where η_2 , Q_2 are temperature-independent constants. The activation energy Q_2 is larger than Q_1 .

In summary, the nanoflake model predicts that in the high, medium and low temperature regions, the viscosity of silica behaves following Eqs. 3, 4, 5, respectively. Placing these three equations together, Eq. 6 describes the viscosity-temperature relation of silica in the entire temperature zone from extreme high to extreme low:

$$\eta = \eta_1 \exp(Q_1/RT) + \eta_3 \exp[(Q_1 + \Delta Q)/RT] + \eta_2 \exp(Q_2/RT) \quad (6)$$

where η_1 and Q_1 , as well as η_2 and Q_2 are the temperature independent constants in the high and low temperature range, respectively. The temperature dependent parameters ΔQ and η_3 in Eq. 6 can be computed as follows. Since the activation energy and the viscosity of silica are continuous functions in the entire temperature region, their

values at T_m and T_c obtained by equations 4 should match that obtained from equations 3 and 5, respectively. Thus, using the linear approximation formulas ΔQ , $\log \eta_3$, and η_3 can be calculated as:

$$\Delta Q = [(T_m - T)/(T_m - T_c)](Q_2 - Q_1) \quad (6a)$$

$$\log \eta_3 = \log \eta_1 + [(T_m - T)/(T_m - T_c)](\log \eta_2 - \log \eta_1),$$

$$\eta_3 = 10^{\log \eta_3} \quad (6b)$$

The parameter η_1 , Q_1 can be derived from any two points of viscosity data at the high-temperature region. Similarly, η_2 , Q_2 can be determined from any two points of viscosity data in the low-temperature region. Using Eqs. 6a and 6b, ΔQ and η_3 , which determines the viscosities in the medium temperature range, can be computed. Therefore, the temperature behavior of silica in the entire temperature interval can be determined by 4 parameters. Equation 6 with two additional Eq. 6a and 6b appears more complicated than VFT equation (Eq. 1) or Doremus equation (Eq. 2), but it avoids the inherent drawbacks of them, and is also more accurate than both.

3. Comparison with experimental data

Substantial experimental data on silica viscosity have been generated in the past by many research groups. In 2002, Doremus summarized previous data and provided a critical assessment⁷. In the high-

temperature region, there are measurements made by Bacon et al. and by several other groups²⁶⁻²⁸. These measurements show that the viscosity of silica has Arrhenius-type behavior with the activation energy near 515 kJ/mole^{26, 7}. As shown in Fig. 2(a), the viscosity data of Bacon et al., from 1935°C to 2322°C, are slightly scattered, but contain more data points in this region than other groups.

In the low-temperature region, the measurements of other independent research groups indicated that the viscosity of silica also has Arrhenius-type relation with temperature²⁹⁻³¹, with an activation energy of about 712 kJ/mole, which is higher than that in the high-temperature region. Data of the research group of Hetherington et al. were produced under the special care of stabilizing the silica in an “equilibrium” condition, and are also plotted in Fig. 2(a).

In the medium temperature region, the silica is in an unstable state. Most research groups did not provide experimental data in this temperature region. Only two data points were produced by Urbain et al²⁷. The experimental data of silica viscosity in the entire temperature region, produced by Bacon et al., Hetherington et al. and Urbain et al. are shown together in Fig. 2(a). To compare these experimental data with the predictions of Eq. 6, the logarithm of silica viscosity as a function of reciprocal temperature is plotted in Fig. 2(b). According to Eq. 6, the logarithm of viscosity as a function of reciprocal temperature should yield straight lines in both high and low temperature region. The line in the low-temperature region should have a higher slope than the line in the high-temperature region, and

the two lines should join smoothly with the curve in the medium temperature region. These predictions are in an agreement with the experimental data presented in Fig. 2(b).

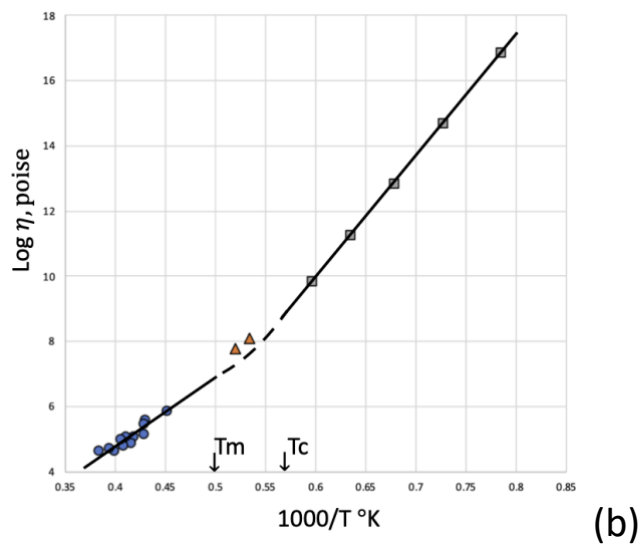
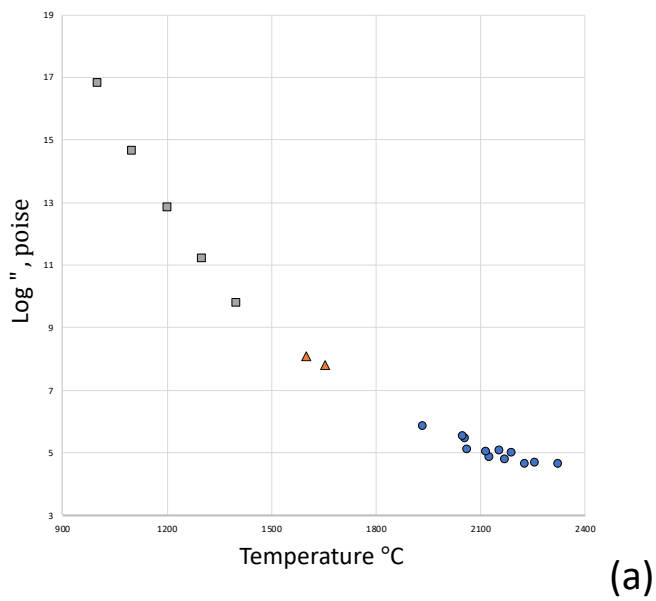


Figure 2: Experimental data of the viscosity temperature relation of silica. Data are taken from Ref. 24 (O), Ref. 25 (Δ) and Ref. 27 ().
 (a) The logarithm of silica viscosity as a function of the temperature.
 (b) The logarithm of silica viscosity as a function of reciprocal temperature.

The correlation coefficient of linear regression is better than 99.99% for the low temperature data and is about 85% for the high

temperature data. The activation energies and the pre-exponential factors of silica in both high and low temperature regions can be calculated from the slopes and the intercepts of the straight lines in Fig. 2(b). The results are 371 kJ/mole and 715 kJ/mole, and $1.1(10)^{-3}$ poise and $3.24(10)^{-13}$ poise, respectively. The determined activation energy is almost the same as reported by Hetherington et al. in the low temperature region⁷; but is lower than that reported by Bacon et al. in the high temperature region. The difference might be caused by that Bacon et al. combined the data in the high temperature regions with the data from a low temperature range (1265°C to 1465 °C) together to calculate the activation energy²⁷. In the medium temperature region, there are two experimental data points at 1599°C and 1652°C in Fig. 2(b). Using Eq. 6 with Eqs. 6a and 6b, the values of $\log \eta$ at these two temperatures are calculated to be 7.46 and 7.02 in poise. Compared with the experimental data of 8.08 and 7.79 in poise, the error of using Eq. 6 in predicting the silica viscosity in the medium temperature range is about 10%. A larger scatter in the experimental data in this region is expected since silica in the medium temperature region is unstable, and the measured value of viscosity not only depends on the temperature but also on the cooling rate. Thus, Eq. 6 is found in reasonable agreement overall with the experimental data, as published by various research groups.

4. Discussions

The application of Eq. 6 is not limited to silica. It can be applied to other silicate glasses, as long as the melting temperature T_m and the critical temperature T_c are known. Both T_m and T_c can be obtained from the silicate phase diagram. As an example, Fig. 3(a) is the experimental data of the viscosity of a $\text{Na}_2\text{O-SiO}_2$ glass³². The composition of the sodium silicate is 20 mol. %. Two characteristic temperatures of T_m as 1140°C and T_c as 870°C can be extracted from the phase diagram of the $\text{Na}_2\text{O-SiO}_2$ glass system³³. The logarithm of viscosity of this silicate glass is plotted as a function of reciprocal temperature, shown as the solid lines in Fig. 3(b). The results are similar to Fig. 2(b): there are two straight solid lines showing the linear dependence of the logarithm of this silicate viscosity with reciprocal temperature, in both high and low temperature regions. The line in the low-temperature region has a higher slope than the line in the high-temperature region. The activation energies and the pre-exponential factors of the $\text{Na}_2\text{O-SiO}_2$ glass in both high and low temperature regions can be calculated from the slopes and the intercepts of the straight lines in Fig. 3(b), which are 170 kJ/mole and 349 kJ/mole, and $6.9(10)^{-4}$ poise and $3.98(10)^{-12}$ poise, respectively. The correlation coefficient of linear regression for both lines is better than 97%. In the medium temperature region, there are three experimental data points. Using Eq. 6 with Eqs. 6a and 6b, the values of $\log \eta$ at these three temperatures are found to be smaller than the experimental data by from 8 to 17%. The viscosity data in Fig. 3 were produced by two different groups³². It is possible that a systematic

error exists in one set of data. The systematic error does not change the linearity of the data set, but can introduce a large error in the data fitting in the medium temperature range.

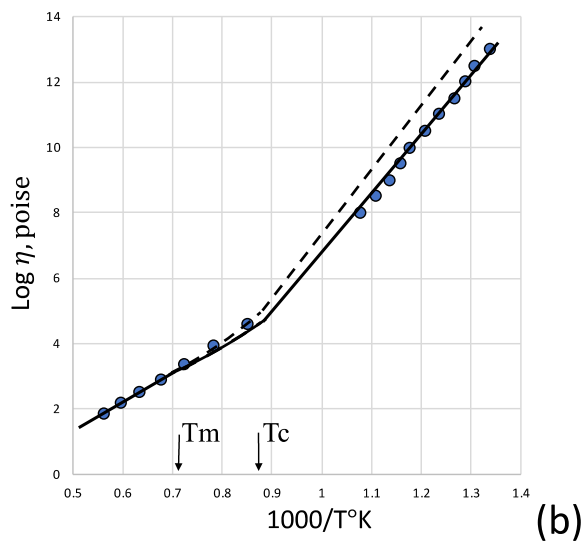
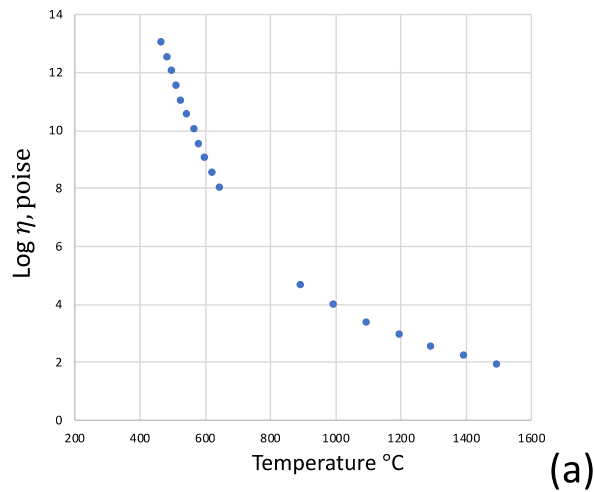


Figure 3: The relations of the viscosity and temperature of sodium silicate. Data are taken from Ref. 30 (O). (a) The logarithm of the sodium silica viscosity as a function of the temperature. (b) The logarithm of sodium silicate viscosity as a function of reciprocal temperature. The solid line represents the existed experimental data. The dashed line represents experimental data with assumed lower cooling rate.

It is well known that the cooling rate plays an important factor in determining various physical and chemical properties of silica and other silicate glasses. However, from Eq. 1 and Eq. 2 and their underlying theories, one cannot see how the cooling rate influences the temperature dependence of glass viscosity. In contrast, the nanoflake model predicts that viscosity temperature relation is cooling rate dependent, which is reflected by parameters ΔQ and Q_2 in Eq. 6. According to the nanoflake model, as the silica remains in the medium temperature region for longer period of time due to slower cooling rate, the number of the clusters and the average size of the clusters in the supercooled glasses will increase, and result in the higher activation energy of $Q_1 + \Delta Q$ in the medium temperature region and the higher activation energy of Q_2 , i.e. $Q_1 + \Delta Q(T_c)$, in the low temperature region. Thus, the value of Q_2 is cooling rate dependent, and this can be seen from experimental results. For example, the solid line in Fig. 3(b) is the viscosity temperature relation of $\text{Na}_2\text{O-SiO}_2$ glass at the set-up experimental cooling rate. Assuming these glass specimens cooled with slower rate while all other experimental parameters are kept the same, Eq. 6 predicts that the temperature behavior of glass viscosity in the medium and the low temperature regions will follow the dashed line shown in Fig. 3(b). Such prediction can be verified by future experiments.

5. Concluding remarks

This work demonstrates the essential correlations between the macroscopic properties and the internal microstructures of the glasses. A new equation is derived from the nanoflake medium-range structure model and correctly predicts silica viscosity behavior in the entire temperature range. The application of the new equation and its underlying physical model is not limited to the silica glass and can be extended to complex silicate glasses. However, its validity to other types of glasses, such as metallic glasses and organic glasses et al., needs to be further investigated.

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References

1. P.W. Anderson, Through a glass lightly. *Science*. 1995;267:1615.
2. G.S. Fulcher, Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram. Soc.* 1925;8(6):339-355.

3. H. Vogel, The law of temperature dependence of the viscosity of fluids. *Phys. Z.* 1921;22;645-646.
4. G. Tamman and W. Hesse, The dependence of viscosity on temperature for undercooled fluids. *Z. Anorg. Allg. Chem.* 1926;156: 245-257.
5. A.K. Doolittle, Studies in Newtonian Flow. I. The Dependence of the Viscosity of Liquids on Temperature. *J. Appl. Phys.* 1951;22: 1031-1035.
6. G. Adam and J.H. Gibbs, On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J. Chem. Phys.* 1965;43:139-146.
7. R.H. Doremus, Viscosity of Silica. *Journal of Applied Physics.* 2002; 92, 12:7619-7629.
8. M.I. Ojovan and W.I. Lee, Viscosity of network liquids within Doremus approach. *Journal of Applied Physics.* 2004; 95, 7:3803-3810.
9. J.C. Mauro, Y. Yue, A.J. Ellison, P.K. Gupta & D.C. Allan, Viscosity of glass-forming liquids. *Proc. Natl. Acad. Sci. U.S.A.* 2009;106:19780–19784.
10. U. Fotheringham, Viscosity of Glass and Glass-Forming Melts. In Eds. J.D. Musgraves, J. Hu and L. Calvez, *Handbook Springer of Glass.* 2019; P.104-108.
11. D.S. Sanditov and M.I. Ojovan, On relaxation nature of glass transition in amorphous materials. *Physica B.* 2017;523:96–113.

12. Q. Zheng and J.C. Mauro, Viscosity of glass-forming systems. *J. Am. Ceram. Soc.* 2017;100: 6-25.
13. I.S. Gutzow & J.W.P. Schmelzer, *The Vitreous State*, Second edition, Springer-Verlag Berlin Heidelberg 2013, P. 35-41.
14. A.K. Varsheneya & J.C. Mauro, *Fundamentals of Inorganic Glasses*, Third edition, Elsevier Inc. 2019, P. 225-239.
15. S. Cheng, A nanoflake model for the medium range structure in vitreous silica. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 2017; 58 (2): 33-40.
16. S. Cheng, Medium Range Ordering Structure and Silica Glass Transition. *Glass Physics and Chemistry.* 2019;45(2): 91-97.
17. A.C. Wright, The Cheng nanoflake model for the structure of vitreous silica: a critical appraisal. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 2017; 58(5):226-228.
18. S. Cheng, Comments on “The Cheng nanoflake model for the structure of vitreous silica: a critical appraisal”. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 2018;59(2):114-117.
19. A.C. Wright, Further Comments on the Cheng nano-flake Model for the Structure of Vitreous Silica. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 2018;59(5):251-252.
20. S. Cheng, “Response to the letter ‘Further comments on the Cheng nano-flake model for the structure of vitreous silica’”. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B.* 2019; 60(3):125-127.

21. W.H. Zachariasen, The Atomic Arrangement in Glass. *J. Amer. Chem. Soc.* 1932;54:3841-3851.
22. B.E. Warren, X-Ray Determination of the Structure of Glass. *J. Am. Ceram. Soc.* 1934;17:249-254.
23. B. Champagnon, V. Martinez, C. Martinet, R. Le Parc and C. Levelut, Density and density fluctuations of SiO₂ glass: comparison and light-scattering study. *Phil. Mag.* 2007;87:691-695.
24. S. Cheng, S. Schiefelbein, L.L. Moore, M. Pierson-Stull, S. Sen and C. Smith, Use of EELS to Study the Absorption Edge of Fused Silica. *J. Non-cryst. Solids.* 2006;352:3140-3146.
25. S. Cheng, The Measurements of Frozen-in Disorder and Thermal Disorder of Fused Silica by EELS. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 2009;50(5):329-331.
26. J.F. Bacon, A.A. Hasapis and J.W. Wolley, Viscosity and density of molten silica and high silica content glasses. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 1960;1(3):90-98.
27. G. Urbain, Y. Bottinga and P. Richet, Viscosity of liquid silica, silicates and alumino-silicates. *Geochim. Cosmochim. Acta* 1982;46:1061-1072.
28. D.W. Bowen and R.W. Taylor, Silica viscosity from 2300°K to 2600°K *Ceram. Bull.* 1978;57:818-819.
29. G. Hetherington, K.H. Jack and J.C. Kennedy, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B.* 1964;5:130.

30. E.H. Fontana and W.A. Plummer, A study of viscosity-temperature relationships in the GeO₂ and SiO₂ systems. Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B. 1966;7:139-145.
31. T. Kimura, Viscosity Measurement of Synthetic Fused Quartz by Beam-Bending Method. Jpn. J. Appl. Phys. 1969;8:1397-1403.
32. N.P. Bansal and R.H. Doremus, Handbook of Glass Properties, Academic Press, Inc. (1986) p.233
33. F.C. Kracek, The system sodium oxide-silica, J. Phys. Chem. 1930;34:1588-1599.