

Viscosity of strong and fragile glass-forming liquids investigated by means of principal component analysis

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Abstract

The Vogel–Fulcher–Tammann–Hesse (VFTH) equation has been the most widespread tool for describing the temperature dependence with viscosity for strong, moderate and fragile glass-forming liquids. In this work, the VFTH equation was applied over a wide temperature range (between the glass transition temperature, T_g , and the melting point, T_m) for 38 oxide glasses, considering simple, binary and ternary compositions of silicate and borate systems. The Levenberg–Marquart non-linear fitting procedure was used to assess VFTH viscosity parameters B and T_0 , maintaining $A = -5$ fixed (in Pa · s) to reduce the number of adjustable parameters. Regarding this restriction, the VFTH formula has shown to adjust very well to experimental data in a wide temperature range. Previous assertions revealed that there is statistical correlation between B and T_0 . Principal component analysis (PCA) was used in the present study to verify the correlation between the B and T_0 parameters [J. F. Mano, E. Pereira, *J. Phys. Chem. A* 108 (2004) 10824], as well as between T_g and T_m . In brief, PCA is a mathematical method aimed at reorganizing information from data sets. The results have shown that it is possible to map either borate (and almost fragile) or silicate (usually strong up to near fragile) systems. As a statistical tool, PCA justifies the use of B , T_0 and T_g as the main parameters for the fragility indexes $m = d(\log_{10}\eta)/d(T_g/T)|_{T=T_g}$ and $D = B/T_0$, where η is the viscosity and T the absolute temperature.

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1. Introduction

Viscous flow theory of glass-forming and dense liquids is still a very active field in physics [1]. Viscosity varies strongly with temperature in the supercooled regime of glass-forming liquids. In these systems, as the temperature is lowered from melting (T_m), the material becomes more viscous, and rigidity begins to set in, if crystallization is prevented. At T_g , rigidity percolates and the glassy state is formed, which corresponds to a viscosity value of approximately 10^{12} Pa s.

At thermodynamic equilibrium, i.e., above T_g , the dependence of viscosity on temperature $\eta(T)$ in these systems often deviates strongly from the simple activated (or Arrhenius) behavior. The most accurate three-parameter

relation for viscosity is the Vogel–Fulcher–Tammann–Hesse (VFTH) equation:

$$\log_{10} \eta = A + \frac{B}{T - T_0}, \quad (1)$$

where A , B and T_0 are constants and T is the absolute temperature.

From a historical perspective, in 1921 Hans Vogel [2] stated in a German journal of physics that Eq. (1) was useful for describing the viscosity of water, mercury and oil, but no data was presented. Vogel anticipated by four years the more complete work of Gordon Fulcher [3], which compared viscosity data of many oxide glasses from the literature with a variety of empirical formulas, and finally selected Eq. (1) as the most appropriate. Although Vogel's paper was unnoticed by Tammann and Hesse [4], the latter presented the same equation in 1926 in a study of viscosity of organic liquids and cited Fulcher's work.

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Nevertheless, Tammann and Hesse claimed to have discovered Eq. (1) independently.

VFTH provides a practical representation of the complex dependence of viscosity on temperature $\eta(T)$ for many different materials. The applicability of the VFTH equation for glasses in a wide temperature range has been recently tested and compared with other established models, such as Avramov–Milchev [5], Cukierman–Lanne–Uhlmann [6] and Bendler–Shlesinger [7], and published elsewhere [8].

The viscosity models are widely used for the study of cooperative thermal relaxation processes. This work is an attempt to clarify relevant issues related to the use of the VFTH equation. It is intended to extract the corresponding parameters and possible correlations from the fitting of reliable, experimental viscosity data of 21 silicate and 17 borate glass systems measured near T_g to T_m , covering *circa* 12 (or more) decades in viscosity. As far as the authors know, this is the first study that presents viscosity data in such a systematic way. The fragile/strong characters obtained from VFTH fitting in these systems was also evaluated using the Principal Component Analysis, which provided a new data set organization.

2. Briefing on the principal component analysis theory

Principal component analysis (PCA) is a mathematical method of reorganizing information from data sets. It is used in many branch of science, such as biology and public health [9], chemistry [10], physics [11] and materials science [12]. In brief, what PCA does is to discover new variables, termed principal components (PCs), which account for the majority of the variability in the data. The rules for computing PCs are rather simple. The first PC is the direction throughout the data that explains the most variability. The second and subsequent PCs must be orthogonal to the previous PC and describe the maximum amount of the remaining variability [13].

PCA is a special case of transforming the original data into a the new coordinate system. If the original data involve n different variables, then each observation may be considered as a point in a n -dimensional vector space. From a practical point of view, data from Table 1 could be represented by a matrix \mathbf{Z} composed of $n = 4$ variables (B , T_0 , T_g and T_m) and $t = 38$ objects. PCA is, in simple terms, a rotation of the system of original axes that attempts simultaneously (i) to find in the space of dimension n a certain direction in which data spread is at maximum and in which it is expected to find a pattern and (ii) to protect the maximum original information from this procedure. This is made through a covariance matrix \mathbf{ZZ}^T , where \mathbf{Z}^T is the transpose matrix of original data \mathbf{Z} . Briefly, variance is a “measure of data spread” considering a unique data set. Covariance is similar to variance, but it considers different data sets. From this procedure, the eigenvectors represent the cosine directors (or the contribution which each one of the original axes makes to the composition of the new

axes), named *main* components. The eigenvalues, in turn, represent the amount of original variance for the respective eigenvectors.

2.1. Matrix algebra derivation of the principal component analysis

The mathematics of the PCA is expressed more succinctly in terms of matrix operations. The basics of the matrix approach is given below. Let the data be represented as a matrix \mathbf{Z} with n rows and t columns, where n is the number of variables and t is the number of observations. The matrix of approximations of the data based upon the vector of coefficients \mathbf{M} and the vector of the PC \mathbf{P} is obtained by multiplying the $n \times 1$ vector \mathbf{M} times the $1 \times t$ vector, which is the transpose of the vector \mathbf{P} ; that is,

$$\mathbf{MP}^T. \quad (2)$$

The matrix of deviations of the actual data from the values based upon \mathbf{M} and \mathbf{P} is:

$$\mathbf{Z} - \mathbf{MP}^T. \quad (3)$$

The sum of the squared deviations can be obtained in terms of matrix operations by multiplying the deviations matrix times the transpose of the deviations matrix itself; i.e.,

$$(\mathbf{Z} - \mathbf{MP}^T)(\mathbf{Z} - \mathbf{MP}^T)^T. \quad (4)$$

The result is a $n \times n$ matrix. The sum of the elements on the principal diagonal is the sum of the squared deviations for all of the variables. The constraint on the choice of \mathbf{M} is

$$\mathbf{M}^T\mathbf{M} = 1. \quad (5)$$

The first-order condition for a minimum with respect to the elements of \mathbf{P} is, in matrix form

$$\mathbf{P}^T = \mathbf{M}^T\mathbf{Z} \quad (6)$$

or, equivalently,

$$\mathbf{P} = \mathbf{Z}^T\mathbf{M}. \quad (7)$$

The first-order condition for a minimum with respect to the elements of \mathbf{M} is, in matrix form,

$$\lambda\mathbf{M}^T = \mathbf{Z}\mathbf{P}, \quad (8)$$

or, equivalently, since $\mathbf{P} = \mathbf{Z}^T\mathbf{M}$,

$$\lambda\mathbf{M} = \mathbf{ZZ}^T\mathbf{M}. \quad (9)$$

Letting $\mathbf{N} = \mathbf{ZZ}^T$ (the covariance matrix),

$$\lambda\mathbf{M} = \mathbf{N}^T\mathbf{M}. \quad (10)$$

Thus, \mathbf{M} is an eigenvector of the matrix \mathbf{N} . The equation defining eigenvalues and eigenvectors is:

$$(\mathbf{N} - \lambda\mathbf{I})\mathbf{M} = 0, \quad (11)$$

where \mathbf{I} is an identity matrix and the zero on the right side represents a vector of zeroes. For this equation to

Table 1

VFTH viscosity parameters B and T_0 (A was fixed as -5 , η in Pa · s unities, plus χ^2 test), T_g and T_m values, the measured viscosity temperature range and the corresponding parameters m and D

Glass	B (K)	T_0 (K)	T_g (K)	T_m (K)	T range (K)	m	D	χ^2
SiO ₂	21,254	139	1450	2000	1377–2000	17.9	152.91	0.0011
Li ₂ O · SiO ₂	5744	276	593	1573	593–1823	33.9	20.81	1.458
Li ₂ O · 2SiO ₂	5752	380	727	1306	718–1720	34.7	15.14	0.094
Li ₂ O · 3SiO ₂	8218	255	734	1306	747–1873	26.3	32.23	0.130
Na ₂ O · SiO ₂	4999	395	687	1362	687–1623	40.3	12.66	0.129
Na ₂ O · 2SiO ₂	5538	393	728	1146	684–1173	35.9	14.09	0.208
Na ₂ O · 3SiO ₂	7484	287	743	1084	689–1773	26.7	26.08	0.177
Na ₂ O · 4SiO ₂	7618	323	765	1423	691–1811	29.8	23.59	0.723
K ₂ O · SiO ₂	4395	416	675	1248	675–1301	44.2	10.56	0.134
K ₂ O · 2SiO ₂	7461	333	768	1313	748–1679	30.3	22.41	0.125
K ₂ O · 3SiO ₂	8334	253	760	1353	773–1673	24.6	32.94	0.046
K ₂ O · 4SiO ₂	8471	255	766	1408	764–1673	24.8	33.22	0.151
Na ₂ O · Al ₂ O ₃ · 6SiO ₂ (Albite)	12,281	347	1087	1393	1062–2660	24.4	35.39	0.066
CaO · MgO · 2SiO ₂ (Diopside)	4826	710	995	1664	960–2066	59.1	6.80	0.028
CaO · Al ₂ O ₃ · 2SiO ₂ (Anorthite)	5802	785	1113	1825	1082–1973	60.0	7.39	0.041
2MgO · 2Al ₂ O ₃ · 5SiO ₂ (Cordierite)	8244	583	1088	1740	1073–1798	35.2	14.14	0.073
15.45Na ₂ O · 12.81CaO · 71.74SiO ₂ (Soda Lime)	6785	421	819	1283	773–1761	35.1	16.12	0.093
2BaO · TiO ₂ · 2SiO ₂ (Fresnoite)	3896	750	983	1714	1000–1792	70.5	5.19	0.016
PbO · SiO ₂	3694	454	673	1037	685–1616	51.8	8.14	0.302
PbO · 2SiO ₂	6001	390	749	1190	646–1073	34.9	15.39	0.059
2PbO · SiO ₂	2496	473	613	1016	611–1477	78.1	5.28	0.068
B ₂ O ₃	4695	252	540	723	545–1077	30.6	18.63	0.268
Li ₂ O · B ₂ O ₃	2557	542	693	1116	690–1333	77.7	4.72	0.067
Li ₂ O · 2B ₂ O ₃	2497	616	763	1190	758–1292	88.2	4.05	0.013
Li ₂ O · 3B ₂ O ₃	2850	599	768	1155	764–1481	76.6	4.76	0.102
Li ₂ O · 4B ₂ O ₃	2908	579	751	1108	748–1173	73.8	5.02	0.033
Na ₂ O · 2B ₂ O ₃	2405	600	748	1015	727–1351	82.1	4.01	0.129
Na ₂ O · 3B ₂ O ₃	3121	557	746	1039	718–1323	65.2	5.60	0.104
Na ₂ O · 4B ₂ O ₃	3172	539	727	1087	708–1333	65.2	5.88	0.078
K ₂ O · 2B ₂ O ₃	2888	520	705	1063	654–1317	59.5	5.55	0.174
K ₂ O · 3B ₂ O ₃	3403	512	709	1140	709–1369	62.2	6.65	0.025
K ₂ O · 4B ₂ O ₃	3588	463	691	1130	644–1393	47.7	7.75	0.197
Cs ₂ O · 3B ₂ O ₃	3363	491	693	1110	684–1141	57.1	6.85	0.063
BaO · 2B ₂ O ₃	3262	619	810	1183	807–1184	72.4	5.27	0.042
SrO · 2B ₂ O ₃	2592	755	911	1270	906–1362	97.0	3.43	0.017
PbO · B ₂ O ₃	2171	525	658	983	643–1473	80.8	4.14	0.397
PbO · 2B ₂ O ₃	3020	545	738	1048	722–1473	59.8	5.54	0.059
PbO · 3B ₂ O ₃	2656	569	728	1023	712–1053	76.5	4.67	0.237

have a non-trivial solution, the determinant of the coefficient matrix $(\mathbf{N} - \lambda \mathbf{I})$ must be zero. This is the condition determining the eigenvalues. It reduces to a n -th degree polynomial equation. Once an eigenvalue is known, the system of equations can be solved for the components of \mathbf{M} by setting one component equal to an arbitrary non-zero value and solving for the rest. The solution can be normalized and put it into any desired form. Eqs. (2)–(11) summarize the PCA standard procedure.

3. Results and discussion

The dynamics of supercooled liquids is an intricate problem that continues to be the focus of many investigations. Most studies dealing with the dynamics of liquids above or close to T_g use the VFTH equation to treat the dependence of viscosity on temperature. As well known,

VFTH needs three parameters to fit (Eq. (1)), but it is possible to use only two of them if one considers $A = -5$ (considering η in Pas unities). Previous tests considering the applicability of VFTH were done and published in a thesis (Ref. [8]). Fig. 1 presents the frequency distribution of pre-exponential VFTH A values considering the same compositions presented in Table 1, but considering A , B and T_0 as free parameters. The average value found was $A_{\text{avg}} = -5.1 \pm 2.0$, and more than half values were situated between $-5 < A < -4$. This fixed average value was supported previously by Barrer [14] and Angell [15,16].

From a theoretical point of view, at least two reasonable approximations to estimate A could be given. First, from Maxwell's definition of shear viscosity, experimental η data from some sources do apply well if one considers A between -1 and -3 with a reasonable accuracy (see [17] references cited therein). Another way to find the average A value is to consider the theoretical value estimated via

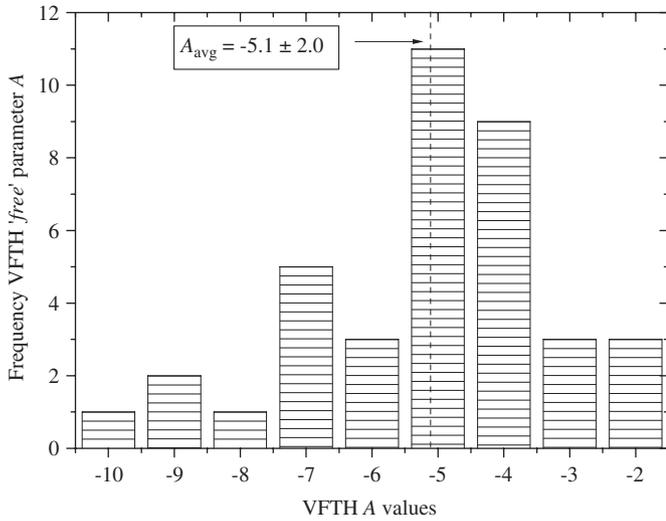


Fig. 1. Frequency distribution of A from VFTH equation (in Pa · s) in 38 silicate and borate systems (the same presented in Table 1), considering it as a free parameter (as also B and T_0). Dashed vertical line represents the average value. Results from Ref. [8].

Eq. (12), as recently explained [17]:

$$\eta_0 = 10^A = \frac{k_B T}{\lambda^3} \tau_0, \quad (12)$$

where $\tau_0 = h/k_B T$ is a characteristic time of the period of atomic vibrations, h is Planck's constant and λ has a value of the order of O^{2-} radius. Using $\lambda = 2.7 \text{ \AA}$, one could obtain $A = -4.5$.

Thus, from theory, it is possible to expect a pre-exponential fixed value for A . The distribution frequency presented in Fig. 1 provided an average value equal to -5 , but the theoretical validity of a fixed pre-exponential factor A still remains (i.e., from $A = -1$ to -5 , there is an increment of four orders of magnitude in η_0). The main task of this manuscript was to study the statistical correlations between B and T_0 VFTH parameters in systematic way by using PCA (maintaining A fixed) will be presented below. The main purpose of fixing A as constant was just to help on the analysis.

Therefore, the main physical reason to consider A fixed is that at high temperatures there is a decrease in structural complexity of the glassy melts [14]. A third point to be considered is that recent theories demonstrated that $\log_{10} \eta(T_g) - A \approx 17$ thus $A = -5$ [18]. This third point would be clearer considering the fragility index m , as explained below. The results of VFTH fitting in 21 silicates and 17 borates are shown in Table 1. Values of B and T_0 were obtained from VFTH fitting, and T_g and T_m are experimental data. The accuracy of this approximation (using A fixed) is also presented in Table 1, which presented reasonable values (see χ^2 values). Viscosity measurements included the use of different methods, as beam bending, falling ball, torsion, rotating viscometer and fiber elongation. Data mining on these viscosity and thermal properties results can be found elsewhere [8].

A useful measure of the viscosity dependence on temperature is the fragility parameter m , proposed by Angell [15,16] and is defined by:

$$m = \left. \frac{d(\log_{10} \eta)}{d(T_g/T)} \right|_{T=T_g} \quad (13)$$

Eq. (1) indicates the sensitivity of the liquid structure to temperature changes. Some results in Table 1 are plotted in Fig. 2 for silicates (a) and borates (b), wherein m seems to increase with T_g/T , which is the normalized reciprocal temperature. These glasses are characterized as *strong*, *moderate* or *fragile* depending on the m index. The limiting cases are those of SiO_2 , which shows almost Arrhenius behavior (Fig. 2a), as well as nearly all borate glasses presenting a non-Arrhenius behavior (Fig. 2b). Strong liquids exhibit lower m values at T_g , and fragile liquids exhibit higher values at T_g . For silicates and borates, the fragility index nearly corresponds to the depolymerization

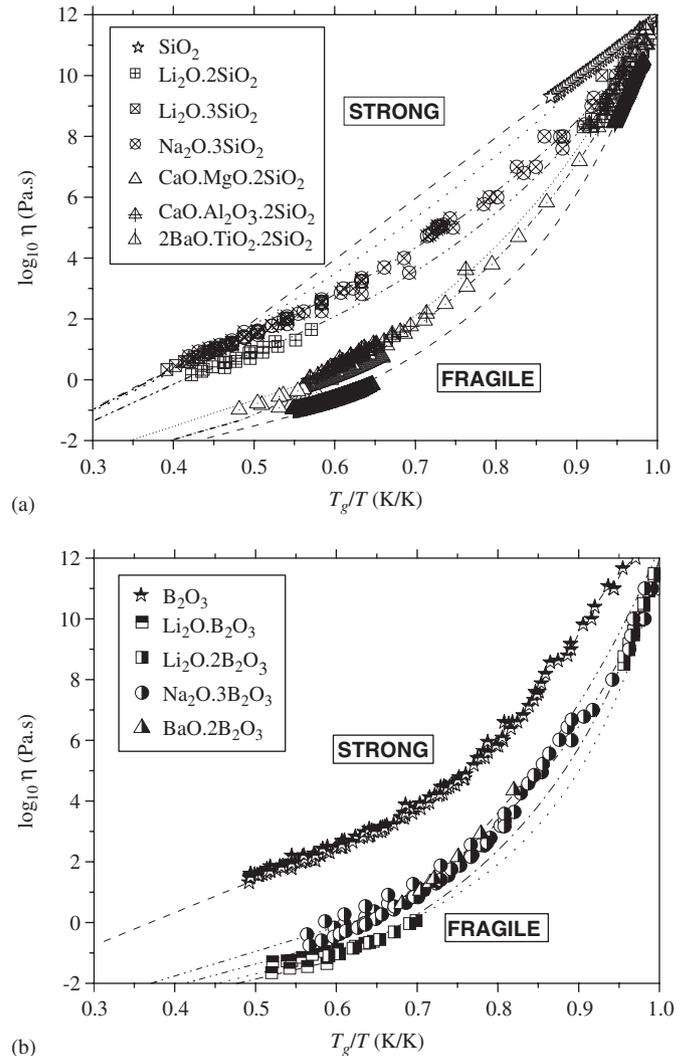


Fig. 2. Experimental viscosity of silicate (a) and borate (b) systems as a function of the normalized temperature T_g/T , showing the range from “strong”, characteristic of open tetrahedral network liquids, to “fragile”, typical of ionic and molecular liquids.

degree, or the increase in alkali content, according to Avramov's recent findings [19]. This could be observed in the binary (and ternary) silicate and also binary borate data presented in Fig. 2.

According to the VFTH equation, T_0 is a diverging temperature, close to the so-called Kauzmann temperature, and $D = B/T_0$ is the strength parameter, which can also be related to fragility in the classification proposed by Angell [15,16]: a D value higher than 30 represents a *moderate* or *strong* behavior, and a low D (below 30) characterizes a *fragile* system. Relevant information may be obtained from these parameters associated to a given system; this includes insights about the glassy structure itself. Moreover, VFTH parameters may be used to predict system dynamics at temperatures beyond limited experimental procedures. Values of m and D are also presented in Table 1.

About viscosity data used, an extensive analysis was carried out in all systems presented in Table 1. When there were two (or more) data sets measured at the same temperature from the same system (probably due to impurity effects), we chose the more viscous system (e.g. $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and B_2O_3). Some systems such as silica required close attention. SiO_2 is largely affected by impurity. Thus, we selected some of the purest viscosity data. A recent review on this particular problem can be found elsewhere [20]. Other systems, such as diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), present a de-polymerized chain structure where the viscosity behavior could not be affected by any impurity added in a wide T [21]. This fact could explain the great agreement in 12 orders of magnitude from different data sources.

Unfortunately, no viscosity data were available near T_g for some systems, as in $\text{Li}_2\text{O} \cdot 3\text{SiO}_2$, $\text{Li}_2\text{O} \cdot \text{SiO}_2$, $\text{K}_2\text{O} \cdot \text{SiO}_2$, soda lime silica, $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ and $\text{SrO} \cdot 2\text{B}_2\text{O}_3$. In these cases, an approximation was

done considering the measured T_g as the temperature when viscosity reaches 10^{12} Pa s.

Some criticisms have been addressed on the VFTH equation when applied in a wide temperature range [22,23]. According to those authors, VFTH shows a high divergence near T_0 . This poses a minor problem, however, as viscosity is certainly a finite quantity and it is very high and out of practical interest at temperatures below T_g . The important point is that VFTH could be applied in a wide temperature range, and the agreement with experimental data is excellent (covering 12 orders of magnitude with an accuracy higher than 10%, see χ^2 values from VFTH fitting in Table 1). As expected, from VFTH results in Table 1, stronger glasses present higher B and lower T_0 , in opposition to the fragile ones. The B parameter also diminishes with alkali content in the lithia–silica, soda–silica and potassium–silica systems, showing the influence of depolymerization degree.

Böhmer and Angell [24] established a relation between m and the characteristic temperatures T_g and T_0 :

$$\frac{m}{m-17} = \frac{T_g}{T_0}, \quad (14)$$

where $\log_{10}\eta(T_g) - A \approx 17$ is the *lower fragility limit* [18]. Fig. 3 shows the resulting plot. One should note that SiO_2 nearly corresponds to this limit, and the opposite can be expectedly observed for all borate glasses. Thus, from Fig. 3, the agreement of fragility index m with T_g and T_0 parameters of 38 oxide glasses confirmed the validity of $A = -5$ in the present calculations. In other words, the choice of $A = -5$ is critical considering fragility classification.

Following Angell's classification, another way to classify liquids is to use the PCA. A recent publication [25] shows that statistical correlation exists between VFTH parameters, mainly B and T_0 , considering just dielectric

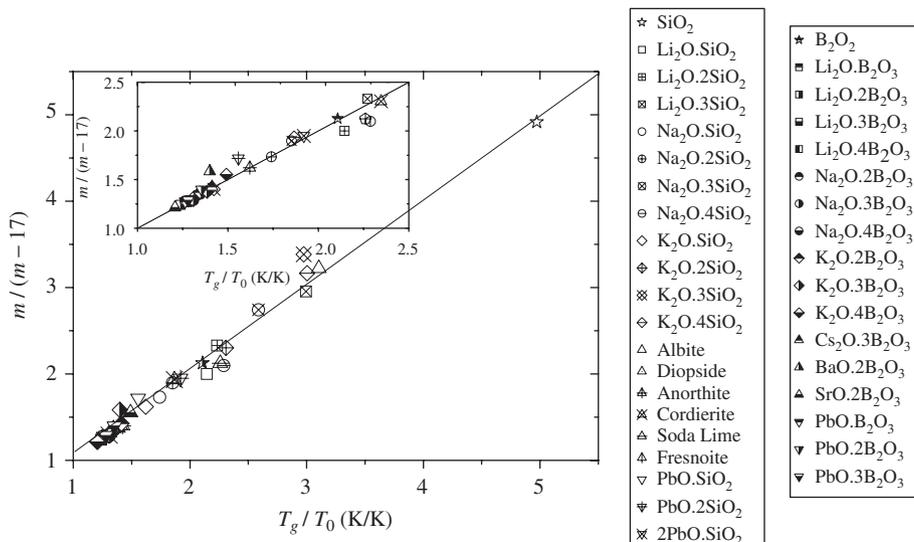


Fig. 3. Observation of the characteristic ratio T_g/T_0 for 38 oxide glasses. Data were determined from experimental T_g and T_0 values and also m from Table 1, considering the VFTH equation for viscosity.

relaxation in *poly (vinyl acetate)*. This paper presents results considering 38 oxide glass systems, in which viscosity was analyzed in a wide temperature range (from near T_g to T_m).

Table 1 presents data used for the PCA procedure. According to the PCA theory, high variance corresponds to high B values ranging from 2100 to 21,000 K. By definition, B values correspond to the first PC, and the second one to T_0 . From Table 1, 94.35% of the data could be represented by the first two axes (related to B , representing 61.94% of variability; and T_0 , representing 32.42% of variability, respectively—see Table 2). Positive eigenvalues occurred due to the use of medium values from the original data. The centered correlation matrix corresponding to Table 1 is

$$\begin{pmatrix} 1 & -0.631 & 0.691 & 0.639 \\ -0.631 & 1 & 0.124 & 0.00094 \\ 0.691 & 0.124 & 1 & 0.798 \\ 0.639 & 0.00094 & 0.798 & 1 \end{pmatrix}. \tag{15}$$

Table 2 shows the total and cumulative percentages and respective eigenvalues of each axis considered, whereas Table 3 presents values of B , T_0 , T_g and T_m in the corresponding four axis.

Fig. 4 shows the mapping distribution of PC 1 (related to B) and PC 2 (related to T_0). Some systems are well distributed, such as the borate glasses that are localized on first and fourth quadrants (excluding B_2O_3 , a relatively strong glass) ternary silicate glasses on the second and third quadrants; binary silicate glasses, on the third and fourth quadrants and the stronger glasses SiO_2 and albite, near the abscissa. The main reason for the distribution observed in the map may be related to the weight of the PCs: in the first PCA, the highest weights come from the high B values of SiO_2 , albite and B_2O_3 . Borates are distinguishable because of their lower B and (relative) intermediate T_0 values.

Fig. 5 shows that T_g (PC3) and B (PC1) also present correlation, and it is possible to distinguish a borate (or fragile) region. Binary and ternary silicates are mixed, but strong glasses such as silica and albite are also noticeable.

Table 2
Total and cumulative percentages and respective eigenvalues of each axis considered

PC axis	Eigenvalue	Total percent	Cumulative percent
1	2.477	61.94	61.94
2	1.297	32.42	94.35
3	0.225	5.63	99.99
4	0.00058	0.01	100.00

Table 3
Values of B , T_0 , T_g and T_m of the corresponding four PC axis

Parameter	PC 1	PC 2	PC 3	PC 4
B	-0.586	-0.320	-0.271	0.694
T_0	0.203	0.830	-0.134	0.502
T_g	-0.556	0.360	-0.544	-0.516
T_m	-0.553	0.282	0.783	-0.032

4. Conclusions

The fragility concept is usually applied for the classification of glass-forming liquids, but PCA proved to be a complementary tool to interpret liquid properties. There are strong correlations between the VFTH B and T_0 parameters, and thermodynamic properties such as T_g and T_m in the 38 oxide glass systems analyzed. The PCA gave another way to interpret VFTH parameters, distinguishing strong from fragile systems, and also differentiating

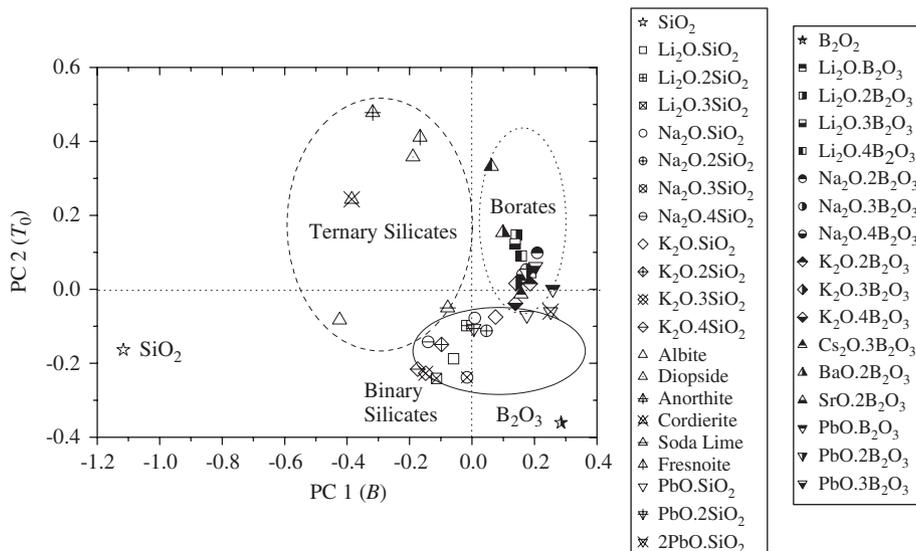


Fig. 4. Plot of principal component 1 (related to B parameter) versus principal component 2 (T_0).

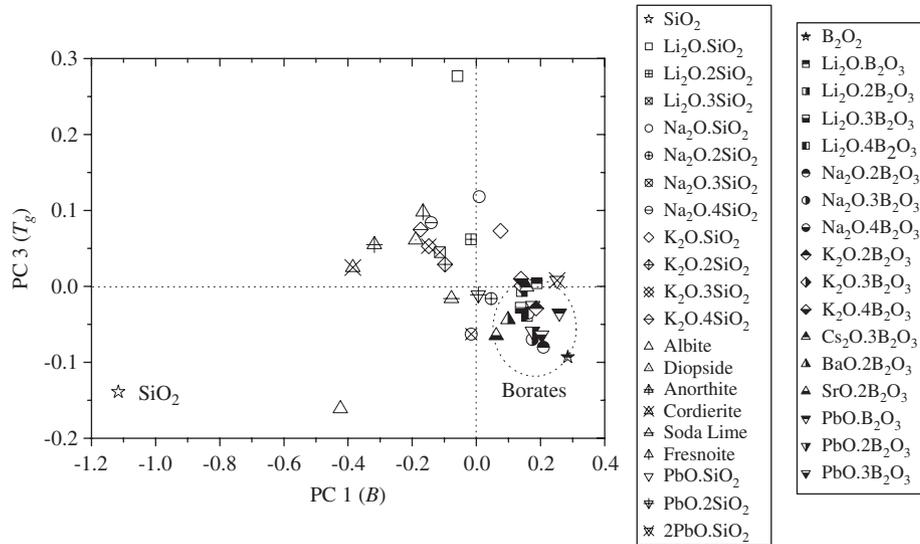


Fig. 5. Plot of principal component 1 (related to B parameter) versus principal component 3 (T_g).

borates from silicates. The fragility parameter m ranged from 17.9 (SiO₂) to 97.0 (SrO·2B₂O₃). The main PCA advantage is to allow an easy graphical criterion to classify glass-forming liquids. It partially justifies the use of B , T_0 and T_g as key parameters to define fragility. These results also validates the use of VFTH equation in many silicate and borate glass-forming systems. The combined use of Angell's classification of glass-forming liquids and PCA may provide a better understanding about viscous flow phenomena.

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