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Thermodynamic parameters of bonds in glassy materials from viscosity–temperature relationships

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Abstract
Doremus's model of viscosity assumes that viscous flow in amorphous materials is mediated by broken bonds (configurons). The resulting equation contains four coefficients, which are directly related to the entropies and enthalpies of formation and motion of the configurons. Thus by fitting this viscosity equation to experimental viscosity data these enthalpy and entropy terms can be obtained. The non-linear nature of the equation obtained means that the fitting process is non-trivial. A genetic algorithm based approach has been developed to fit the equation to experimental viscosity data for a number of glassy materials, including SiO_2, GeO_2, B_2O_3, anorthite, diopside, $x Na_2O$–$(1-x)SiO_2$, $x PbO$–$(1-x)SiO_2$, soda-lime-silica glasses, salol, and α-phenyl-*o*-cresol. Excellent fits of the equation to the viscosity data were obtained over the entire temperature range. The fitting parameters were used to quantitatively determine the enthalpies and entropies of formation and motion of configurons in the analysed systems and the activation energies for flow at high and low temperatures as well as fragility ratios using the Doremus criterion for fragility. A direct anti-correlation between fragility ratio and configuron percolation threshold, which determines the glass transition temperature in the analysed materials, was found.

1. Introduction

The viscosities of fluids are among their most important properties. Viscosity quantifies the resistance of fluids to flow and indicates their ability to dissipate momentum. The momentum balance of Newtonian fluids is described at the macroscopic level by the Navier–Stokes equations. At the microscopic level, viscosity arises because of a transfer of momentum between fluid layers moving at different velocities as explained in Maxwell's kinetic theory. In oxide melts and glasses, viscosities determine melting conditions, working and annealing temperatures, rate of refining, maximum use temperature, and crystallization rate. In geology

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the behaviour of magma and hence volcanic eruptions and lava flow rates depend directly on the viscosities of molten silicates [1, 2].

It is commonly assumed that shear viscosity is a thermally activated process. Since the pioneering work of Frenkel [3], fluid viscosity, η, has been expressed in terms of an activation energy Q by

$$\eta(T) = A \exp\left(\frac{Q}{RT}\right) \tag{1}$$

where T is temperature in K, R is the molar gas constant and A is a constant. Two different regimes of flow have been identified with melts at high temperature having a lower activation energy for flow than melts at lower temperatures. Within the high temperature or low temperature regime an Arrhenius dependence of viscosity is observed and an appropriate activation energy, Q_H or Q_L respectively, can be defined; asymptotically, both at low and high temperatures the activation energy of viscosity is independent of temperature. This pattern has been observed with a range of melts including silicates, fused salts, oxides, and organic liquids [4]. Between the high temperature and the low temperature regimes the activation energy for flow changes and cannot be described using an Arrhenius approach. Melts are defined as strong or fragile depending on the extent of the change in the activation energy for flow, with strong melts exhibiting small changes in activation energy compared to fragile melts. The classification into strong and fragile melts uses the glass transition temperature, T_g, to separate the high and low temperature regimes. A glass transition occurs when a melt is rapidly cooled to yield a glassy structure, that has properties similar to those of crystalline solid, i.e. a glassy material is an isotropic solid material [5–7]. When the temperature, T, is greater than T_g an amorphous substance is called a liquid (even if supercooled) but if $T < T_g$ it is called a glass. T_g can be obtained by analysing the behaviour of derivative parameters, such as the coefficient of thermal expansion or the specific heat [8]. The term glass transition temperature is often used to refer to the temperature at which the viscosity attains a value of 10^{12} Pa s (10^{13} P) [9]. This definition of T_g was used by Angell to plot the logarithm of viscosity as a function of (T_g/T). In such a plot strong melts, i.e. melts that exhibit only small changes in the activation energy for flow with temperature, such as silica, have a nearly linear dependence on the inverse of the reduced temperature whereas fragile melts deviate strongly from a linear dependence [10]. The activation energies of fragile liquids significantly change with temperature so their viscosity deviates significantly from Arrhenius behaviour. Doremus indicated that the changes that occur in the activation energy can be unambiguously characterized by the ratio of the high and low temperature activation energies, which can be used as a fragility criterion [1]:

$$R_D = \frac{Q_H}{Q_L}. \tag{2}$$

The higher the value of R_D the more fragile the melt. Doremus's fragility ratio ranges from 1.45 for silica to 4.52 for anorthite melts (for more details see table 2).

2. Viscosity equations

Many different equations to model the viscosity of liquids have been proposed. The most popular viscosity equations are those of Vogel, Tamman and Fulcher (VTF), Adam and Gibbs (AG) and Avramov and Milchev (AM) [4, 12]. The VTF equation of viscosity is an empirical expression which describes viscosity data over many orders of magnitude with accuracy better than 10%:

$$\ln[\eta(T)] = A_{VTF} + \frac{B_{VTF}}{R(T - T_V)} \tag{3}$$

where A_{VTF}, B_{VTF} and T_{V} (Vogel temperature) are constants determined by fitting equation (3) to experimental data. The VTF equation can be derived from the free volume model which relates the viscosity of the melt to free (or excess) volume per molecule V_{f}. The excess volume is considered to be the specific volume of the liquid minus the volume of its molecules. This molecular volume is usually derived from a hard sphere model of the atoms in the molecules. Molecular transport is considered to occur when voids having a volume greater than a critical value form by redistribution of the free volume [13]. The flow unit or molecule is imagined to be in a structural cage at a potential minimum. As the temperature increases there is an increasing amount of free volume that can be redistributed among the cages, leading to increased transport, and this leads to an exponential relationship between viscosity and free volume [13]:

$$\eta = \eta_0 \exp\left(\frac{BV_0}{V_{\mathrm{f}}}\right) \tag{4}$$

where V_0 is the volume of a molecule, η_0 and B are constants. In terms of the specific volume V per molecule it can be shown that $V_{\mathrm{f}} = V - V_0 = V_0(T - T_0)/T_0$, for some constant and low temperature T_0. Clearly equation (4) is the same as equation (3) if we define $A_{\mathrm{VTF}} = \ln \eta_0$, $B_{\mathrm{VTF}} = BT_0$ and $T_{\mathrm{V}} = T_0$.

The Adam and Gibbs equation is obtained assuming that, above the glass transition temperature, molecules in a liquid can explore many different configurational states over time, and that as the temperature is raised higher energy configurational states can be explored. In contrast, below the glass transition temperature it is assumed that the molecules in the glass are trapped in a single configurational state. The resulting AG equation for viscosity is similar to the VTF equation [14]:

$$\ln[\eta(T)] = A_{\mathrm{AG}} + \frac{B_{\mathrm{AG}}}{TS_{\mathrm{conf}}(T)} \tag{5}$$

where A_{AG} and B_{AG} are adjustable constants and $S_{\mathrm{conf}}(T)$ is the configurational entropy. Assuming in equation (5) that $S_{\mathrm{conf}}(T) = \Delta C_p(T - T_{\mathrm{V}})/T$, where ΔC_p is the relaxational part of the specific heat, one can see that equation (5) is the same as (3) if $A_{\mathrm{AG}} = A_{\mathrm{VTF}}$ and $B_{\mathrm{AG}} = \Delta C_p B_{\mathrm{VTF}}/R$. The configurational entropy model of Adam and Gibbs fits a large number of viscosity data, but like the free volume theory it does not provide an accurate fit over the entire temperature range. At high and low viscosities equation (5) does not describe the experimental temperature dependence of viscosity and increasingly large deviations from the experimental values are produced. In addition, the configurational entropy model gives discontinuities in the first differential of the entropy at the glass transition, despite the fact that that there are no discontinuities in experimentally measured viscosities in this temperature range.

The Avramov and Milchev (AM) viscosity model gives an excellent description of viscosity within the temperature range where the activation energy of viscosity changes with temperature. The AM model assumes that due to existing disorder, activation energy barriers with different heights occur and that the distribution function for heights of these barriers depends on the entropy. Thus viscosity is assumed to be a function of the total entropy of the system which leads to the temperature dependence of equilibrium viscosity [12]:

$$\ln[\eta(T)] = A_{\mathrm{AM}} + 2.3(13.5 - A_{\mathrm{AM}})\left(\frac{T_{\mathrm{g}}}{T}\right)^{\alpha} \tag{6}$$

where in this case T_{g} is defined by $\ln[\eta(T_{\mathrm{g}})/(\mathrm{d\ Pa\ s})] = 13.5$, A_{AM} is a constant and α is Avramov's fragility parameter. Strong liquids have a value of α close to unity and as α increases the fragility of the melt increases.

Priven [15] has developed an empirical equation, which he indicates is superior to the VTF equation, namely

$$\log[\eta(T)] = \log\eta_0 + \left[\frac{\beta}{\log T - \log\theta_0}\right]^{1/n} \tag{7}$$

where $\log(\eta_0) = -3.5$, β and θ_0 are fitting parameters and n is a composition dependent parameter. Priven reports that for the majority of silicate melts $n = 1.0 \pm 0.1$ and for the majority of borate melts $n = 0.9 \pm 0.4$. However, for high-silica melts (>90 mol%SiO_2) the values of n are reported to be significantly smaller than unity and do not exceed 0.5, whereas for high boron oxide melts (>90 mol% B_2O_3) the values of n are reported to be significantly greater than unity, ranging from 1.5 to 2.5 [15]. Priven states that this equation reasonably describes the temperature dependence of viscosity for silicate and aluminosilicate melts in the range $1 \leqslant \eta \leqslant 10^{12}$ Pa s, but that a limit of applicability is reached for viscosities <1 Pa s.

All of the above equations can only be used within limited temperature ranges that essentially correspond to the range of temperatures where the activation energy for flow changes with temperature. None of equations (3) or (5)–(7) correctly describe the asymptotic low and high temperature Arrhenian viscosity behaviour [4]. In addition, the non-physical character of the fitting parameters does not give a clear understanding of changes that occur with temperature or composition. Therefore, equations (3) and (5)–(7) may be useful for fitting experimental measurements over limited temperature ranges, but they cannot explain the temperature dependences of viscosity.

It is well known [4, 16] that mathematically the viscosity of amorphous materials can most exactly be described by

$$\eta(T) = AT\exp\left(\frac{B}{RT}\right)\left[1 + C\exp\left(\frac{D}{RT}\right)\right] \tag{8}$$

where A, B, C and D are all constants. In addition to the fact that equation (8) provides a good fit to the experimental data across the entire temperature range, it correctly gives Arrhenian type asymptotes at high and low temperatures [4] with $Q_H = B + D$ and $Q_L = B$. For the low viscosity range ($\log(\eta/\mathrm{d\,Pa\,s}) < 3$) Volf gives $Q_L = 80$–300 kJ mol^{-1} and for the high viscosity range $\log(\eta/\mathrm{d\,Pa\,s}) > 3$ and $Q_H = 400$–800 kJ mol^{-1} [16]. Within narrow temperature intervals equation (8) can be easily approximated to many types of curves, such as those given by equations (3)–(6). However, in contrast to them, equation (8) gives a correct asymptotic Arrhenius-type dependence of viscosity with temperature at low and high temperatures when the activation energy of viscosity becomes constant.

It can be shown that equation (8) follows immediately from Doremus's ideas concerning the role of defects in viscous flow [4, 6, 17, 18]. Moreover, equation (8) has been derived by Douglas for silicate glasses by assuming that the oxygen atoms between two silicon atoms could occupy two different positions, separated by an energy barrier [19], with flow being limited by the breaking of Si–O–Si bonds.

3. Doremus's model of viscosity

The Doremus model assumes that viscous flow in amorphous materials is mediated by broken bonds, which can considered to be quasi-particles termed configurons. Doremus analysed the diffusion and viscosity in amorphous silica and showed that viscous flow is mediated by defects of the amorphous silica network such as SiO molecular defects [4]. Formation of these defects occurs via breaking of covalent Si–O bonds and attachment of an additional oxygen atom which leads to Si being in fivefold coordination with oxygen atoms. Experimental evidence for fivefold coordination of oxygen around silicon has been found in silicates [4]. Doremus's approach returns to Mott's ideas on the role of defects in the viscous flow; Mott suggested that the concentration of broken silicon–oxygen bonds in vitreous silica increases as the temperature increases, enabling easier flow [20].

Consider a material that forms an ideal disordered network such as amorphous SiO_2. In this case the three-dimensional disordered network is formed by $[SiO_4]$ tetrahedra interconnected via bridging oxygens so that we have $\equiv$Si • O • Si$\equiv$, where • designates a bond between Si and O and thus •O• designates a bridging oxygen atom with two bonds. The ideal network can also contain some point defects in the form of broken bonds $\equiv$Si ◦ O • Si$\equiv$, where ◦ designates a broken bond between Si and O. Each broken bond, which is typically associated with strain-release and local adjustment of centres of atomic vibration, is treated as an elementary configurational excitation in the system of bonds and is termed a configuron [21]. Using Angell's bond lattice model we can represent condensed phases by their bond network structures [6, 7, 21, 22]. Thus we can analyse the system of interconnecting bonds of a disordered material rather than the system of atoms. In this approach the initial set of N strongly interacting cations such as Si^{4+} is replaced by the congruent set of weakly interacting bonds of the system. At absolute zero ($T = 0$ K) the material contains no broken bonds; however, at any finite temperature ($T > 0$ K) the material will contain thermally activated defects, i.e. configurons. The formation of defects in a network is governed by the formation Gibbs free energy $G_d = H_d - TS_d$, where H_d is the enthalpy and S_d is the entropy of formation of network defects, e.g. broken Si ◦ O bonds. The temperature-induced formation of network breaking defects in a disordered network can be represented by the reaction involving the breaking of a covalent bond, e.g. in amorphous silica:

$$\equiv\mathrm{Si} \bullet \mathrm{O} \bullet \mathrm{Si}\equiv \xrightarrow{T} \equiv\mathrm{Si} \circ \mathrm{O} \bullet \mathrm{Si}\equiv \tag{9}$$

The higher the temperature, the higher the concentration of thermally created defects, including configurons. Because the system of bonds has two states, namely a ground state corresponding to unbroken bonds and the excited state corresponding to broken bonds, it can be described using the statistics of two-level systems [6, 7, 18]. The two states of the equivalent two-level system are separated by the energy interval G_d governing equation (9). The statistics of two-level systems leads to the well known relationship for equilibrium concentrations of configurons, $C_d = C_0 f(T)$, and unbroken bonds, $C_u = C_0[1 - f(T)]$ [6, 7, 18, 19, 21–23], with

$$f(T) = \frac{\exp(-G_d/RT)}{\left[1 + \exp(-G_d/RT)\right]} \tag{10}$$

where C_0 is the total concentration of elementary bond network blocks or the concentration of unbroken bonds at absolute zero $C_u(0) = C_0$.

The viscosity of an amorphous material is related to the diffusion coefficient, D, of the configurons, which mediate the viscous flows via the Stokes–Einstein equation:

$$\eta(T) = \frac{kT}{6\pi r D} \tag{11}$$

where k is the Boltzmann constant and r is the radius of the configuron. The configuron moving through material will perform jumps between different energy minima in a potential energy landscape. In a crystalline material these minima are associated with lattice or interstitial sites; similarly, in an amorphous material these minima are associated with network sites. At each minimum in the energy–distance diagram, the configuron is in an equilibrium position. The energy G_m which is required to enable the configuron to jump across a barrier equals the difference in energy between the energy associated with the configurons being in equilibrium positions and the energy associated with the diffusing configuron (along with its neighbours, which must move apart to allow the jump) being in a saddle point configuration at a maximum in the energy–distance curve. The probability of the energy gathered is given by the Gibbs distribution [23]:

$$w = \frac{\exp(-G_m/RT)}{[1 + \exp(-G_m/RT)]} \tag{12}$$

where $G_m = H_m - TS_m$ is the Gibbs free energy of motion associated with a jumping configuron; H_m and S_m are the corresponding enthalpy and entropy of configuron motion. Assuming that the mean jump time of configurons is short compared with the mean residence time $\tau(T)$ in network sites, the trajectory of a configuron is composed of a sequence of elementary jumps with average jump length λ. From these microscopic quantities the configuron diffusion coefficient can be defined by

$$D = fg\lambda^2\nu(T) \tag{13}$$

where f is the correlation factor, g is a geometrical factor close to $1/6$ and $\nu(T) = 1/\tau(T)$ is the total jump frequency. The correlation factor equals unity for purely random hopping, and in general $0 < f \leqslant 1$. For defect mediated jumps the equation for the total jump frequency is given by

$$\nu(T) = zp_0 f(T)\nu_0 w \tag{14}$$

where z is the number of nearest neighbours, p_0 is a configuration factor (in simple cases $p_0 = 1$), $f(T)$ is the relative concentration of configurons given by equation (10), and ν_0 is the configuron vibrational frequency or the frequency with which the configuron attempts to surmount the energy barrier to jump into a neighbouring site. Hence the viscosity of amorphous materials is directly related to the thermodynamic parameters of configurons via equation [6]:

$$\eta(T) = A_1 T\left[1 + A_2 \exp\left(\frac{B}{RT}\right)\right]\left[1 + C\exp\left(\frac{D}{RT}\right)\right] \tag{15}$$

where

$$A_1 = k/6\pi r D_0 \tag{16a}$$

$$A_2 = \exp(-S_m/R) \tag{16b}$$

$$B = H_m \tag{16c}$$

$$C = \exp(-S_d/R) \tag{16d}$$

$$D = H_d \tag{16e}$$

and $D_0 = fg\lambda^2 zp_0\nu_0$. Experiments show that in practice four fitting parameters suffice [16] and the viscosity is well described by equation (8), which follows from (15), assuming, as is commonly the case, that $A_2\exp(B/RT) \gg 1$ (see below data from table 1) and taking $A = A_1A_2$.

Equation (15) can be fitted to practically all available experimental data on viscosities of amorphous materials. Moreover, equation (15) can be readily approximated within a narrow temperature interval by known empirical and theoretical models such as VTF (equation (3), AG (equation (5), or Kohlrausch-type stretch–exponential relationships [12]. In contrast to such approximations, equation (15) can be used over wider temperature ranges and gives the correct Arrhenian-type asymptotes at high and low temperatures, namely $\eta(T) \cong A_1A_2(1 + C)T\exp(B/RT)$ and $\eta(T) \cong A_1A_2CT\exp[(B + D)/RT]$ respectively. Equation (15) shows also that at extremely high temperatures when $T \to \infty$ the viscosity of melts changes to a non-activated, e.g. non-Arrhenian, behaviour $\eta(T) \xrightarrow{T\to\infty} A_1(1+A_2)(1+C)T$, which is characteristic of systems of almost free particles [23].

Table 1. Thermodynamic parameters of configurons in amorphous materials.

Amorphous material	H_d (kJ mol^{-1})	S_d/R	H_m (kJ mol^{-1})	S_m/R
Silica (SiO_2)	237 (220[a])	17.54 (16.13[a])	522 (525[a])	11.37
Germania (GeO_2)	129	17.77 (17.84[a])	272	2.49
B_2O_3	258	44.2	113	9.21
$75.9SiO_{2}24.1PbO$	262	36.25	234	5.44
$66.7SiO_{2}33.3PbO$	197	25.40	274	7.3
$65SiO_{2}35PbO$	231	30.32	257	8.53
$59.9SiO_{2}40.1PbO$	236	31.12	258	6.55
$80SiO_{2}20Na_{2}O$	155	17.98	207	7.79
$75SiO_{2}25Na_{2}O$	233	30.62	203	4.22
$70SiO_{2}30Na_{2}O$	258	34.84	205	5.22
$65SiO_{2}35Na_{2}O$	300	40.71	186	7.59
SLS (mass%): $70SiO_{2}21CaO9Na_{2}O$	331	44.03	293	24.40
$52SiO_{2}30Li_{2}O18B_{2}O_{3}$	420	52.06	194	0.227
Anorthite ($CaAl_2Si_2O_8$)	884	79.55	251	0.374
Diopside ($CaMgSi_2O_6$)	834	88.71	240	0.044
Salol ($HOC_6H_4COOC_6H_5$)	145	68.13	118	0.114
α-phenyl-*o*-cresol (2-hydroxydiphenylmethane)	172	83.84	103	0.134

[a] Data from [6, 7].

Table 2. Asymptotic Arrhenian activation energies for viscosity and corresponding Doremus fragility ratios.

Amorphous material	Q_L (kJ mol^{-1})	Q_H (kJ mol^{-1})	R_D
Silica (SiO_2)	522 (525[a])	759 (745[a])	1.45 (1.42[a])
Germania (GeO_2)	272	401	1.47
B_2O_3	113	371	3.28
$75.9SiO_{2}24.1PbO$	234	506	2.16
$66.7SiO_{2}33.3PbO$	274	471	1.72
$65SiO_{2}35PbO$	257	488	1.9
$59.9SiO_{2}40.1PbO$	258	494	1.91
$80SiO_{2}20Na_{2}O$	207	362	1.75
$75SiO_{2}25Na_{2}O$	203	436	2.15
$70SiO_{2}30Na_{2}O$	205	463	2.26
$65SiO_{2}35Na_{2}O$	186	486	2.61
SLS: $70SiO_{2}21CaO9Na_{2}O$	293	634	2.16
$52SiO_{2}30Li_{2}O18B_{2}O_{3}$	194	614	3.16
Anorthite ($CaAl_2Si_2O_8$)	251	1135	4.52
Diopside ($CaMgSi_2O_6$)	240	1084	4.51
Salol ($HOC_6H_4COOC_6H_5$)	118	263	2.23
α-phenyl-*o*-cresol (2-hydroxydiphenylmethane)	103	275	2.67

[a] Data from [6, 7].

The five coefficients A_1, A_2, B, C, and D in equation (15) can be treated as fitting parameters derived from the experimentally known viscosity data. By use of equations (16*a*)–(16*e*) the thermodynamic parameters of the configurons (network breaking defects) can be obtained from the fitting parameters. Hence the experimentally measured viscosity–temperature relationships of amorphous materials can be used to characterize the configuron thermodynamic parameters.

4. Thermodynamic parameters from viscosity data

An exact determination of thermodynamic parameters of configurons becomes possible from the known viscosity behaviour with temperature using relationships (15) and (16*a*)–(16*e*). As the number of parameters to be found via the fitting procedure is high (five parameters when using equation (15) or four parameters when using equation (8)) we used a dedicated genetic algorithm[1] (GA) to achieve the best fit of theoretical viscosity–temperature relationships with experimental data on viscosity.

Genetic algorithms are a particular class of evolutionary algorithms that use techniques based on evolutionary biology. These techniques are known as genetic operators, of which there are three main types: selection, crossover, and mutation. GAs are a powerful search and optimization technique with a diverse range of applications.

The first stage of a GA involves encoding the problem and mapping it to a set of abstract chromosomes. In our case we have employed a GA to find the best choice of fit parameters in the 5(4)-parameter glass viscosity equation. One chromosome is subdivided into 5(4) parts; one for each of the different parameters in the model. Each of these 'genes' is then taken to be a sequence of binary digits or bits. An initial population of chromosomes is created (typically we used 80 chromosomes) and these contain randomly generated bit strings for all five genes. It is not necessary to have the same number of bits for each parameter, but we used 24-bit encoding throughout for simplicity. Each of the binary bit strings may be converted to its denary equivalent at any stage. These base ten numbers are then rescaled to a number lying within a range chosen for that particular parameter. The wider the allowable range, the larger the search space, and the longer it takes for the GA to converge. The narrower the range, the more precision can be given on the parameters for a given bit string length. During a typical GA fitting exercise we re-adjusted the range of each parameter to gradually narrow the search space and allow greater precision in the values we report.

For each member of the population of chromosomes we calculated a fitness value. This value was determined by calculating the residual or sum of the squared errors (SSE),

$$\chi^2 = \sum_{i=1} (\eta_{\mathrm{exp}} - \eta_{\mathrm{fit}})^2, \tag{17}$$

which measures the deviation of the fitted viscosity to that of the experimental viscosity. Fitter chromosomes were deemed to be those with lower χ^2 values.

Having established the initial generation of chromosomes we then applied a selection operator to determine which pairs of chromosomes are to 'mate'. There are a plethora of different selection operators, including roulette wheel, rank, steady state selection, etc, but we found that the optimum choice for our problem involved tournament selection. In tournament selection subgroups of chromosomes are randomly sampled from the main population and these compete against each other using a simple stochastic rule. Once a pair of 'champion' chromosomes is selected, these go on to mate. This method of selection allows some of the weaker chromosomes a chance to survive to the next generation and maintain diversity. In addition, we employed 'elitism', which ensures that the fittest member of each population always survives to the next generation. With one member of the next generation already determined (by elitism), the remaining members are then determined by tournament based selection followed by application of the crossover operator. For the crossover algorithm we spliced each gene on a particular chromosome at a single randomly determined point, creating two subsets of binary bits per gene. The rightmost sequence or subset of one gene on one of the selected pair of chromosomes is then exchanged with the leftmost sequence on the

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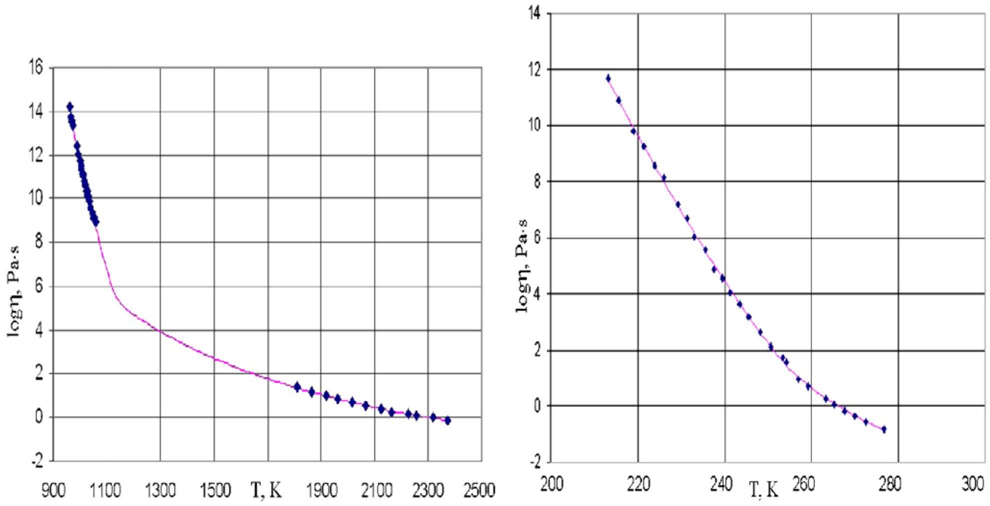
[1] Our genetic algorithm was constructed using a code written in Fortran 77 adapted from one appearing in [24].



(a) (b)

Figure 1. Viscosity–temperature relationships for (a) diopside and (b) salol.
(This figure is in colour only in the electronic version)

mating chromosome. This is continued for all 5(4) genes and then this newly formed pair of chromosomes is added to the new population. The process continues until a full population is achieved. Crossovers do not occur for every selected pair of chromosomes; sometimes a chosen mating pair is copied into the new population unchanged. For our GA work, we employed a crossover probability of 0.6. Following application of the crossover operator we then applied a mutation operator. Our mutation operator consisted of randomly choosing bits along a chromosome and changing 1s to 0s and vice versa. Mutations were carried out with a probability of 0.083 33.

With the new population constructed, the fitness of each chromosome is evaluated and the process of selection–crossover–mutation is then continued for another cycle. The GA is terminated once the average fitness of the population ceases to change. Our GA runs typically required 2000 generations to achieve a limiting value [24].

An example of such evaluation is demonstrated in figure 1, which shows viscosity–temperature relationships for amorphous diopside and salol along with the associated best fit curves calculated using equation (15). Experimental data for the viscosity of diopside were taken from [25] and for salol from [26]. Similar fits to the viscosity–temperature data for amorphous silica and germania were recently presented in [6, 7].

Calculations show that the description of experimental data using equation (15) is excellent, with very low and uniformly scattered deviations. Although equation (8) is also known to give a very good description of the viscosity–temperature behaviour of most melts [16], it was recently found that for SLS (mass% $70SiO_221CaO9Na_2O$) and B_2O_3 melts at very high temperatures equation (8) gives slightly but systematically lower results compared to the experimental data [27]. Thus viscosities of these two materials at very high temperatures are better described using the complete equation (15) rather than the approximate equation (8) [28].

The enthalpies and entropies of formation and motion of the configurons (bond system) in these amorphous materials were obtained from the fitting parameters using equations (16*a*) to (16*e*) and the results are given in table 1.

Table 3. Glass transition temperatures of amorphous materials.

Amorphous material	R_D	T_g (K)	θ_c
Silica (SiO_2)	1.45	1475	0.15
Germania (GeO_2)	1.47	786	0.15
SLS (mass%): $70SiO_221CaO9Na_2O$	2.16	870	1.58×10^{-3}
B_2O_3	3.28	580	9.14×10^{-5}
Diopside ($CaMgSi_2O_6$)	4.51	978	6.35×10^{-7}
Anorthite ($CaAl_2Si_2O_8$)	4.52	1126	3.38×10^{-7}

From table 1 one can see that practically for all materials the entropy of formation is significantly higher than the entropy of motion $S_d \gg S_m$. Taking into account the values of H_m this means that $G_m/RT \gg 1$ and thus it is legitimate to simplify equation (15) to the simpler equation (8), i.e. four fitting parameters are usually sufficient to correctly describe the viscosity–temperature behaviour of a melt. Notable exceptions are the SLS glass considered (mass% $70SiO_221CaO9Na_2O$) and B_2O_3, which, at high temperatures, can exhibit deviations from equation (8) [27, 28].

5. Discussion

Configuron thermodynamic data obtained can be used to calculate the asymptotic Arrhenian activation energies for high and low temperature viscosity. Table 2 gives these data along with the Doremus fragility ratio, which can be obtained from

$$R_D = 1 + \frac{H_d}{H_m}. \tag{18}$$

Melts with a higher enthalpy of formation for defects compared with their enthalpy of motion thus have a higher Doremus fragility ratio; conversely, melts with a lower H_d have a lower fragility. An ideal strong liquid for which $R_D \to 1$ would have a very small enthalpy of formation for defects mediating mass transport (H_d/H_m) $\to 0$, whereas an ideally fragile material would have an enthalpy of formation of defects incommensurably higher than the enthalpy of motion (H_d/H_m) $\to \infty$. Thus the fragility of melts is a thermodynamic parameter that is directly related to thermodynamic parameters of the network defects, i.e. enthalpies of formation and motion of network defects H_d and H_m [11].

The thermodynamic parameters of configurons can also be used to estimate the glass transition temperatures which are related to changes in the symmetry of topological disorder (Hausdorff dimension of bond system [29]) when percolation clusters of configurons are formed. T_g is directly related to the configuron thermodynamic parameters via [6, 7, 29]

$$T_g = \frac{H_d}{S_d + R\ln[(1-\theta_c)/\theta_c]} \tag{19}$$

where θ_c is the percolation threshold for configurons in the material. For strong melts such as silica or germania $\theta_c = \vartheta_c = 0.15 \pm 0.01$, where ϑ_c is the Scher–Zallen critical density in 3D space [30–32]. Complex oxide systems are typically fragile and described by a modified random network model comprising network modifying cations distributed in channels [33, 34]. The value of θ_c in these systems is significantly lower compared with strong melts (see table 3).

Table 3 shows that the higher the fragility ratio, the lower the threshold for the formation of percolation clusters of configurons in the material. Thus there is a direct anti-correlation between the fragility ratio and configuron percolation threshold, which determines the glass transition temperature. Networks that exhibit only small changes in the activation energy for flow with temperature form percolation clusters of configurons at the classical Scher–Zallen critical density. In contrast, fragile liquids, which are characterized by a higher density of configurational states, have a very low percolation threshold, which decreases with increasing fragility.

6. Conclusions

The Doremus model of viscosity is based on assumption that viscous flow in amorphous materials is mediated by broken bonds (or quasi-particles termed configurons). The theoretical equation of viscosity resulting from this approach (equation (15)) contains four coefficients, which are directly related to thermodynamic parameters of the bond system: (i) $A_2 = \exp(-S_m/R)$, (ii) $C = \exp(-S_d/R)$, (iii) B and (iv) D, where S_m and S_d, are the entropies of motion and formation, and B and D are the enthalpies of motion and formation of configurons. We have analysed the viscosity–temperature relationships for a number of glassy materials including SiO_2, GeO_2, B_2O_3, anorthite, diopside, $x\mathrm{Na_2O}$–$(1-x)\mathrm{SiO_2}$, $x\mathrm{PbO}$–$(1-x)\mathrm{SiO_2}$, soda-lime-silica glasses, salol, and α-phenyl-*o*-cresol. A dedicated genetic algorithm was used to fit equation (15) to experimental viscosity data obtained from the literature. It was found that equation (15) provides an excellent description of the viscosity of glassy materials at all temperatures, which enables quantitative determination of the enthalpies and entropies of formation and motion of configurons in the analysed systems. In addition, the asymptotic Arrhenian activation energies for high and low temperature viscosities and the Doremus fragility ratios were determined. It was found that there is a direct anti-correlation between fragility ratio and configuron percolation threshold which determines the glass transition temperature in the analysed materials.

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References

[1] Doremus R H 2003 *Am. Ceram. Soc. Bull.* **82** 59–63
[2] Viscardy S and Gaspard P 2003 *Phys. Rev.* E **68** 041204
[3] Frenkel Y I 1946 *Kinetic Theory of Liquids* (Oxford: Oxford University Press)
[4] Doremus R H 2002 *J. Appl. Phys.* **92** 7619–29
[5] *IUPAC Compendium of Chemical Terminology* 1997 vol 66, p 583
[6] Ozhovan M I 2006 *J. Exp. Theor. Phys.* **103** 819–29
[7] Ojovan M I and Lee W E 2006 *J. Phys.: Condens. Matter* **18** 11507–20
[8] Zarzycki J 1982 *Glasses and the Vitreous State* (New York: Cambridge University Press)
[9] Richert R 2002 *J. Phys.: Condens. Matter* **14** R703–38
[10] Angell C A 1988 *J. Phys. Chem. Solids* **49** 863–71
[11] Ojovan M I and Lee W E 2005 *Phys. Chem. Glasses* **46** 7–11
[12] Avramov I 2005 *J. Non-Cryst. Solids* **351** 3163–73
[13] Turnbull D and Cohen M H 1961 *J. Chem. Phys.* **45** 120
[14] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **3** 139
[15] Priven A I 1999 *Glass Phys. Chem.* **25** 491–7
[16] Volf M B 1988 *Mathematical Approach to Glass* (Amsterdam: Elsevier)
[17] Ojovan M I 2004 *J. Exp. Theor. Phys. Lett.* **79** 85–7

[18] Ojovan M I and Lee W E 2004 *J. Appl. Phys.* **95** 3803–10
[19] Douglas R W 1949 *J. Soc. Glass Technol.* **33** 138–62
[20] Mott N F 1987 *Phil. Mag.* B **56** 257
[21] Angell C A and Rao K J 1972 *J. Chem. Phys.* **57** 470–81
[22] Angell C A and Wong J 1970 *J. Chem. Phys.* **53** 2053–66
[23] Landau L D and Lifshitz E M 1984 *Statistical Physics* part 1 (London: Butterworth-Heinemann)
[24] Coley D A 1999 *An Introduction to Genetic Algorithms (Complex Adaptive Systems)* (Singapore: World Scientific)
[25] Sipp A, Bottinga Y and Richet P 2001 *J. Non-Cryst. Solids* **288** 166–74
[26] Laughlin W T and Uhlmann D R 1972 *J. Phys. Chem.* **76** 2317
[27] Al-Mahrouqi M 2004 Defect mediated model for glass *Final Year BEng Project Report* (Sheffield: University of Sheffield)
[28] Shi L 2006 High-temperature viscosity of melt oxides based on Doremus approach *MSc Project Thesis* (Sheffield: University of Sheffield)
[29] Ojovan M I 2004 *J. Exp. Theor. Phys. Lett.* **79** 632–4
[30] Scher H and Zallen R 1970 *J. Chem. Phys.* **53** 3759
[31] Isichenko M B 1992 *Rev. Mod. Phys.* **64** 961
[32] Sahimi M 1994 *Applications of Percolation Theory* (London: Taylor and Francis)
[33] Greaves G N 1985 *J. Non-Cryst. Solids* **71** 203–17
[34] Varshneya A 1994 *Fundamentals of Inorganic Glasses* (Boston, MA: Academic)