Research article

On temperature dependence of the activation energy of viscous flow of chalcogenide glasses

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Abstract: The temperature dependence of the activation energy of viscous flow U(T) of As-Se, Ge-Se, Sb-Ge-Se chalcogenide glasses in the glass transition range is calculated using the Williams-Landel-Ferry (WLF) equation. A method is proposed for determining the activation energy of viscous flow in the glass transition range as a function of temperature by expanding the function U(T) in the Taylor series. The estimates made are in satisfactory agreement with the experiments. The nature of the dependence U(T) is briefly discussed.

Keywords: glass transition; viscosity; activation energy; WLF equation; chalcogenide glasses

1. Introduction

Viscosity arises because of a transfer of momentum between material layers moving at different velocities and quantifies the resistance of material to flow with Frenkel equation generically used for the temperature dependence of viscosity [1-5]:

\[ \eta = \eta_0 \exp \left( \frac{U}{RT} \right), \]  

(1)

where \( \eta_0 \) is the preexponential coefficient, \( U \) is the activation energy of viscous flow, \( T \) is the temperature, and \( R \) is the universal gas constant. For glass forming melts the activation energy of
viscosity is a well-defined constant only asymptotically at high temperatures at which the viscosities are low, i.e. $\log(\eta/\text{Poise}) < 3$ and $U = U_L = 80–300 \text{kJ/mol}$ [2], whereas the pre-exponential coefficient $\eta_0$ was shown to be the high-temperature viscosity limit within logarithmic approximation [4]. In the glass transition range of temperatures $T \sim T_g$, where $T_g$ is the glass transition temperature, the activation energy of viscous flow of glass-forming melts has a strong temperature dependence $U = U(T)$ increasing on decrease of temperature from its lowest value $U_L$ in the melts ($T >> T_g$) to its highest value in the glassy state ($T < T_g$) $U_H = 400–800 \text{kJ/mol}$ [2]. Following [3,5] we observe hence that the viscous flow in glass forming melts exhibits three temperature ranges as illustrated by Figure 1.

**Figure 1.** The viscosity regimes of glasses and glass forming melts [3].

Namely, the temperature regimes of viscosity are as follows:

I. Low temperatures $T < T_g$: isostructural Arrhenius-type law viscosity of the glass ($U = U_H$);  
II. Intermediate temperatures $T_g < T < T_A$: non-Arrhenius-type law formally expressed with an exponent $U$ with variable activation energy of viscosity $U = U(T)$;  
III. High temperatures $T > T_A$: Arrhenius-type law viscosity ($U = U_L$).

The crossover temperature $T_A$ is assumed to be close to $T_{liq}$ [5]. In line with earlier results of [6,7] it was recently shown [8] that regardless of the type of glass-forming liquid the crossover temperature is given by the universal equation (2):

$$T_A = kT_m,$$

where $T_m$ is the melting temperature and $k = 1.1 \pm 0.15$ (see for details Figure 3(b) of reference [8]).

This work is devoted to estimating the temperature dependence of the activation energy of viscous flow for several chalcogenide compositions within temperature range II: $T_g < T < T_A$. We chose chalcogenide glasses as objects of study as having experimental data on viscosity in a wide temperature range for which we apply expansion of the $U(T)$ function in a Taylor series. The method proposed could be expanded to other glass forming compositions.
2. Modelling the viscosity

Many useful models of the viscosity of amorphous materials have been proposed for the temperature range II (see the overviews [1-5]), among which we can note the two most developed and frequently used models, namely the Vogel – Fulcher – Tammann (VFT) equation [9-11], and the Williams-Landel-Ferry (WLF) equation [12,13]:

\[ \eta = \eta_0 \exp \left( \frac{B_{VFT}}{T - T_{VFT}} \right), \]  
\[ \log a_T = -C_1 \frac{T - T_0}{T - T_0 + C_2}, \]

where \( \eta_0 \) and \( B_{VFT} \) are temperature independent constants – material dependent parameters, \( a_T \) is the relative viscosity \( a_T = \eta(T)/\eta(T_0) \), \( C_1 \) and \( C_2 \) are empirical temperature independent constants, \( T_0 \) is the reference temperature typically taken as the glass transition temperature \( T_0 = T_g \). The validity of these equations has been demonstrated in many works for various glass forming systems, e.g. see Refs. [1-5,14-19]. We note that the activation energy of viscous flow starts to decrease exactly at temperatures exceeding \( T_g \), see e.g. Figure 1 Ref. [5] and Figures 1, 2 and 4 of Ref. [18]. The WLF equation is successfully used to analyze various aspects of molecular kinetic processes in the glass transition region correctly describing the temperature dependence of relaxation time \( \tau(T) \) and viscosity \( \eta(T) \) in the glass transition region for amorphous polymers, organic and inorganic glasses, and metallic amorphous alloys [14-19]. It was derived in [16] without specifying function \( \eta(T) \) based on series expansion of function \( \ln(\eta(T)) \) near the \( T_g \) with respect to the small dimensionless parameter \( \lambda = (T - T_g)/T_g << 1 \). This led to following equation (5) in terms of natural logarithms (\( \ln \)) rather than decimal (\( \log \)) logarithms while assuming \( T_0 = T_g \):

\[ \ln a_T = -(A^2_B) \frac{T - T_g}{T - T_g + (B_g/A_g)} \text{, where } A = -\left. \frac{\partial \ln \eta}{\partial (\tau/T_g)} \right|_{T=T_g} \text{, and } B = \frac{1}{2} \left. \frac{\partial^2 \ln \eta}{\partial (\tau/T_g)^2} \right|_{T=T_g} \]

(5)

From here the WLF equation constants \( C_1 \) and \( C_2 \) acquire a physical meaning, expressed through the derivative parameters \( A \) and \( B \):

\[ C_1 = \frac{A^2}{B}, \text{ and } C_2 = \frac{A}{B} T_g, \]

(6)

Additionally, we observe that the VFT and WLF equations are equivalent if we suppose that:

Either \( B_{VFT} = C_1 C_2 \ln 10 \) for equation (4) or \( B_{VFT} = C_1 C_2 \) for equation (5), and

\[ T_{VFT} = T_g - C_2 \]

(7)

Equating formulas (1) and (3) and taking into account that \( \eta_0 = \text{const.} \), we obtain the dependence of the activation energy of viscous flow on temperature as:

\[ U(T) = B_{VFT} \tau T_{VFT} - TVFT \]

(8)
Accounting for (7) we can rewrite it relying on (5) as:

\[ U(T) = \frac{C_1 C_2 R T}{T - T_g + C_2} \]  

(9)

We conclude from (9) that in order to calculate the activation energy of viscous flow within temperature range II it is necessary to know the values of three parameters: \( C_1 \), \( C_2 \) and \( T_g \). From equation (9) it follows the relation for calculating the activation energy of the glass transition process \( U_g = U(T_g) \):

\[ U_g = C_1 R T_g. \]  

(10)

Applicability of equations (9) and (10) was checked for several chalcogenide materials as described below.

3. Materials and methods

We have analyzed the activation energies of the viscous flow within temperature range II for the following three families of glasses: As-Se, Sb-Ge-Se, Ge-Se. The content of elements was as follows: As – 3 mol. %, Se – 97 mol. %; Sb – 20 mol. %, Ge – 10 mol. %, Se – 70 mol. %; Ge – 92 mol. %, Se – 8 mol. %. Figures 2 (a), 2 (b) and 2 (c) show the temperature dependence of the activation energy \( U(T) \) with curves calculated using the equation (9), and the points in the plots are the experimental data.

Figure 2. Temperature dependence of the activation energy of viscous flow \( U(T) \) for As-Se glass. As content – 3 mol. %, Se – 97 mol. %. Points – experimental data, curve – calculation using formula (9).
Figure 3. Temperature dependence of the activation energy of viscous flow $U(T)$ for Sb-Ge-Se glass. Sb content – 20 mol. %, Ge – 10 mol. %, Se – 70 mol. %. Points – experimental data, curve – calculation using formula (9).

Figure 4. Temperature dependence of the activation energy of viscous flow $U(T)$ for Ge-Se glass. Ge content – 92 mol. %, Se – 8 mol. %. Points – experimental data, curve – calculation using formula (9).

The experimental points were obtained from viscosity data $\log(\eta(T))$ following data of Reference [19] and using the equation:
\[ U(T) = \ln10 \times RT [\log (\eta (T)) - \log(\eta_0)]. \]  \tag{11}

From Fig. 2 – 4 it is seen that the experimental points fall on the calculated curve, confirming the good applicability of the WLF formula. Table 1 shows the values of the parameters used \((C_1, C_2 \text{ and } T_g)\) for the compositions analyzed, as well as the activation energy of the glass transition process at the glass transition temperature, calculated using formula (10).

**Table 1.** Parameters of the WLF equation (4) and activation energy of the glass transition process at \(T = T_g\) (data from [19] were used).

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<th>№</th>
<th>Composition, mol. %</th>
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<th>(C_2), K</th>
<th>(U_g)</th>
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4. Theoretical

Let us expand the function \(U(T)\) near \(T_g\) into a series in terms of a small temperature increment with small parameter \(\lambda = (T - T_g)/T_g \ll 1\) and limit ourselves to the first three terms of the series [20]:

\[ U = U_g - D_1(T - T_g) + D_2(T - T_g)^2 \text{ where } D_1 = -\left(\frac{\partial U}{\partial T}\right)_{T_g}, D_2 = \frac{1}{2}\left(\frac{\partial^2 U}{\partial T^2}\right)_{T_g}. \]  \tag{12}

The small parameter in expansion (12) is the dimensionless quantity \(\lambda\) but \(T_g\) to the first and second powers is hidden in the coefficients \(D_1\) and \(D_2\). From equation (1) it follows that:
\[-\frac{\partial \ln \eta}{\partial (T/T_g)} = -\frac{T_g}{R} \left[ \frac{1}{T} \frac{\partial U}{\partial T} - \frac{U}{T^2} \right] \] (13)

According to equation (5), for parameter $A$ we obtain the relation:

\[ A = \left. -\frac{\partial \ln \eta}{\partial (T/T_g)} \right|_{T=T_g} = -\frac{1}{R} \left[ \frac{\partial U}{\partial T} \right] \frac{T_g}{T_T} \frac{U_g}{T_g} = \frac{D_1}{R} + \frac{U_g}{RT_g} \] (14)

where we accounted the definition of $D_1$ from (12). The parameter $A$ is given following equations (5) and (6) by:

\[ A = \frac{C_1}{C_2} T_g \] (15)

Equating the right-hand sides of equalities (14) and (15), we arrive at the relation:

\[ D_1 = \frac{C_1 R T_g}{C_2} - \frac{U_g}{T_g} \] (16)

which taking into account $U_g = C_1 R T_g$ transforms into the following equation:

\[ D_1 = C_1 R \left( \frac{T_g}{C_2} - 1 \right) \] (17)

We find the formula for coefficient $D_2$ from the calculations as follows:

\[ \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial (T/T_g)^2} = \frac{T_g^2}{2} \frac{\partial}{\partial T} \left( \frac{\partial \ln \eta}{\partial T} \right) = \frac{T_g^2}{2 R} \frac{\partial}{\partial T} \left[ \frac{1}{T} \frac{\partial U}{\partial T} - \frac{U}{T^2} \right] = \frac{T_g^2}{2 R} \left\{ \frac{1}{T} \left( \frac{\partial^2 U}{\partial T^2} \right) - \frac{1}{T^2} \left( \frac{\partial U}{\partial T} \right) - \frac{1}{T^2} \left( \frac{\partial U}{\partial T} \right) + \frac{2 U}{T^3} \right\} \] (18)

The coefficient $B$ is given accordingly by:

\[ B = \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial (T/T_g)^2} \bigg|_{T=T_g} = \frac{T_g}{R} \left\{ D_2 + \frac{D_1}{T_g} + \frac{U_g}{T_g^2} \right\} \] (19)

Further, in this relation for $D_1$ we take into account expression (16) resulting in:

\[ B = \frac{T_g}{R} \left\{ D_2 + \frac{1}{T_g} \left( \frac{C_1}{C_2} R T_g - \frac{U_g}{T_g} \right) + \frac{U_g}{T_g^2} \right\} = \frac{T_g}{R} \left\{ D_2 + \frac{C_1 R}{C_2} \right\} \] (20)

From (6) and (15) we have equality $B = C_1 (T_g/C_2)^2$ which on substitution into (20) gives finally for $D_2$:

\[ D_2 = \frac{C_1 R}{C_2} \]
\[ D_2 = \frac{C_1}{C_2} R \left( \frac{T_g}{C_2} - 1 \right) \]  

(21)

The same result can be obtained by directly substituting series (12) into the formula for viscosity (1) and calculating the derivatives \(A\) and \(B\). The final Taylor series expansion of the activation energy of viscous flow in the temperature range II is as follows:

\[
U = U_g \left[ 1 - \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) + \frac{1}{C_2} \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g)^2 \right] = \\
= U_g \left\{ 1 - \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) \left( 1 - \frac{1}{C_2} \right) (T - T_g) \right\} 
\]

(22)

The quadratic term of the series can be neglected if it is significantly less than the linear one, i.e. when:

\[
(T - T_g) \ll C_2
\]

(23)

Thus, based on data on three quantities \((C_1, C_2 \text{ and } T_g)\), using equations (12), (18) and (22), it is possible to calculate the dependence of the activation energy of viscous flow on temperature in the temperature range II. Table 2 shows the coefficients \(D_1\) and \(D_2\) for the chalcogenide glasses analyzed, which are compared with the characteristics of the \(U(T)\) versus \((T - T_g)\) curves obtained directly from experimental data on the temperature dependence of viscosity.
<table>
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<th>Calculated using (17) and (21)</th>
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Note: dimension of coefficients $[D_1] = [kJ/mol\cdot K]$; $[D_2] = [kJ/mol\cdot K^2]$

The coefficients of the curve $U(T)$ from $(T - T_g)$ as a polynomial of the second degree, were calculated using Microsoft Excel (Fig. 4).
Figure 4. Results of processing the temperature dependence of the activation energy of viscous flow for As-Se glass using Microsoft Excel. The content of As – 3 mol. %, of Se – 97 mol. %. Points – experimental data, curves – polynomials.

It is taken into account that in a wide temperature range the role of the cubic term in the Taylor series expansion of \( U(T) \) may begin to be important and this affects the estimate of the effective value of \( D_2 \). For this purpose, the temperature dependence of the activation energy was approximated as a third-degree polynomial. Within the framework of the considered approximation, a satisfactory agreement between the theoretical and experimental values is nevertheless observed.

We come hence to the conclusion that the temperature dependence of the activation energy in a wide temperature range for chalcogenide glasses Ge-Se, As-Se, P-Se, AsSe-TlSe and AsSe is satisfactorily described by a polynomial of the second degree, and for Sb-Ge-Se glass by a polynomial of the third degree.

5. Discussion

The basic laws of the glass transition process are qualitatively the same for the vast majority of amorphous substances, regardless of their nature: for inorganic glasses, amorphous organic polymers, amorphous metal alloys, aqueous solutions, chalcogenides, which is confirmed by the presence of universal equations and rules in the glass transition region [1-4, 14-18, 21-25]. The physical reason for the sharp increase in the activation energy of the viscous flow with decreasing temperature is the configuration change in the structure of the glass-forming melt [3,23-26]. It is known [3] that the activation energy of viscous flow can be expressed in form of sum of two components – that due to bond breaking processes (defect formation after Mott [27]) and that due to motion of broken bonds termed configurons [23]. The idea of dividing the activation energy of fluidity into two components was expressed by Ya. I. Frenkel [1]. It was further developed in the works of Duglas [28], Angell and Rao [23], Filipovich [29], Nemilov [30], Doremus [31], and later by Sheffield school of glass [32]. In
a more rigorous approach, \( U(T) \) should be understood as the free energy of activation, as is customary in the classical works of Eyring [33].

Within the framework of the model of delocalized atoms [34-36], for glass-forming liquids, the activation energy of viscous flow \( U(T) \) in the equation (1) is the sum of two terms:

\[
U(T) = U_\infty + U_s(T)
\]

where \( U_\infty \) is the potential for the transition of a structural kinetic unit (atom, molecule) to a new local position, \( U_s(T) \) is the potential for a configurational change in structure, which is a function of temperature [24,34,35]:

\[
U_s(T) = RT \left[ \exp \left( \frac{\Delta \varepsilon_e}{RT} \right) - 1 \right]
\]

Here \( \Delta \varepsilon_e \) is the energy of delocalization of the atom (assuming its maximum displacement from the local equilibrium position). Atom delocalization is caused by the rearrangements of neighboring particles (short-range order fluctuations) and reflects a local configurational change in the structure.

At elevated temperatures \( RT \gg \Delta \varepsilon_e \), the potential for configurational structural change is zero \( U_s(T) = 0 \) and the viscosity equation (1), taking into account (24) and (25), transforms into the usual Arrhenius (Frenkel) dependence with constant activation energy \( U(T) = U_\infty \).

\[
\eta = \eta_0 \exp \left( \frac{U_\infty}{RT} \right)
\]

From this point of view, the value of \( U_\infty \) turns out to be the high-temperature limit of the activation energy of viscous flow i.e. \( U_\infty = U_H \).

At low temperatures approaching the glass transition region the delocalization energy of an atom \( \Delta \varepsilon_e \) becomes comparable to the energy of thermal vibrations of the lattice (\( \sim 3RT \)) and the relative number of delocalized atoms \( (N_e/N) \), responsible for fluidity above \( T_g \), significantly decreases according to the law \( \exp(-\Delta \varepsilon_e/kT) \) [24,35]. The structure of the melt becomes denser and for the activation jump of an atom to a new position, a preliminary local configurational change in the structure near it is required: the potential for a configurational structural change \( U_s(T) \) increases sharply. This explains the almost exponential increase in the activation energy of fluidity observed in the glass transition region and the configurational change in the structure, which is described within the framework of the model of delocalized atoms, turns out to be responsible for the temperature dependence of the activation energy of the glass transition process in the region of transition from the liquid to the glassy state.

6. Conclusions

For chalcogenide glasses, methods for calculating the temperature dependence of the activation energy of the viscous flow \( U(T) \) were considered. The \( U(T) \) dependence is satisfactorily described near \( T_g \) using the well-known Williams-Landel-Ferry equation for viscosity. It is shown that there is a way to estimate \( U(T) \) using the Taylor series expansion of the function \( U(T) \) near the glass transition temperature. Within the framework of the model of delocalized atoms, a sharp increase in the activation energy in the glass transition region is explained by an increase in the potential for configurational changes in the structure upon cooling of the glass-forming melt.
Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

Conflict of interest

Authors declare no conflict of interests.

References


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