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The Temperature Interval of the Liquid–Glass Transition of Amorphous Polymers and Low Molecular Weight Amorphous Substances

Migmar V. Darmaev [1,2] , Michael I. Ojovan [3,*] , Alexey A. Mashanov [1] and Timur A. Chimytov [1,2]

1 Department of General and Theoretical Physics, Banzarov Buryat State University, Ulan-Ude 670000, Russia
2 Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences, Ulan-Ude 670047, Russia
3 Department of Radiochemistry, Lomonosov Moscow State University, Moscow 119991, Russia
* Correspondence: m.ojovan@imperial.ac.uk

Abstract: We present calculation results of the temperature interval δT_g characterizing the liquid–glass transition in amorphous materials obtained on the basis of available data of the empirical parameters C_1 and C_2 in the Williams–Landel–Ferry (WLF) viscosity equation. We consider the unambiguous dependence of the relative transition temperature interval $\delta T_g/T_g$ on the fraction of the fluctuation volume f_g frozen at the glass transition temperature T_g utilizing Sanditov's model of delocalized atoms. The parameter $f = \Delta V_e/V$, which determines the molecular mobility characteristic of delocalized atoms in the liquid–glass transition region, is weakly dependent on the nature of most vitreous substances and can be found as $f_g = 1/C_1$. We show that the temperature interval δT_g is less than 1% of the T_g for most amorphous substances. This result conforms with Simon's classical idea of a small temperature range in which the structure freezes. The structural relaxation time τ_g at T_g of polymers and chalcogenide glasses is also calculated.

Keywords: kinetic criterion for glass transition; amorphous polymers; viscosity in the glass transition region; Williams–Landel–Ferry equation; fluctuation volume fraction; vitrification

1. Introduction

Currently, one of the urgent tasks of modern materials science is the search and development of functional materials with desired properties. Vitreous polymers occupy a special place among such functional materials and have a number of unique advantages that allow them to be used in electronics as binders for nanocomposites, etc. An important direction in the study of the structure and properties of polymers and nanocomposites is the study of the regularities of the liquid–glass transition process (vitrification), which is qualitatively similar in polymers, inorganic substances, amorphous metals, and aqueous systems, including biological species, etc., regardless of their nature and confirmed by the presence of universal rules and equations in the glass transition region [1–5]. In this case, it can be noted that for different classes of substances, the mobility of kinetic units at the glass transition temperature T_g is frozen, implying a different nature of interaction with each other. Thus, the glass transition process (vitrification) of linear amorphous polymers is associated with a relaxation process and a loss of segmental mobility at the glass transition temperature, while in inorganic glasses with a fundamentally different structure, this process is associated with chemical relaxation (bond formation or configuron annihilation [6,7]) and freezing of switching valence chemical bonds process. The presence of such universal regularities allows us to assume that the vitrification of liquids of different natures can be described by a unified theory. We have utilized in this paper the model of delocalized atoms developed by Sanditov [8], aiming to calculate the temperature interval δT_g characterizing the liquid–glass transition in amorphous polymers and low molecular weight amorphous substances.

2. Materials and Methods

This work is based on an analysis of the kinetic criterion of glass transition in amorphous polymers and chalcogenide glasses As-S, Se-Ge, and As-Se. It is known that when a glass-forming liquid is cooled at temperatures in the region of the glass transition temperature, the viscosity of substances increases sharply. Conventionally, the liquid–glass transition (i.e., vitrification) occurs when the viscosity reaches $\eta_g = \eta(T_g)$, where

$$\eta_g \approx const \approx 10^{12} \text{ Pa} \cdot \text{s} \tag{1}$$

Relation (1) is an approximate rule for the constancy of the logarithm of viscosity at the glass transition temperature T_g, i.e., this relation (1) can be considered as a logarithmical approximate phenomenological criterion for glass transition [9]. Mazurin [10] states that, for most of the studied glasses, the value of T_g corresponds to temperatures at which the viscosity η_g takes values in the range from 10^{11} to 10^{12} Pa·s, and its value fluctuates in the region of the approximate value (1) with some scatter. However, this is not always the case, as can be seen from Table 4 of Ref. [11], which reveals that the actual viscosities at glass transition temperatures vary from $10^{8.8}$ to 10^{13} Pa·s, which is far different from arbitrarily agreed viscosity (1). The constancy of $log(\eta_g)$ is better fulfilled for glassy systems of the same class [10]. In the scientific literature, it is also generally accepted that the liquid–glass transition for amorphous substances, including the studied polymers, occurs at viscosity values $\eta(T_g)$ in the range of 10^{12}–10^{13} Pa·s [10]. Attempts were made to determine the temperature dependence of the viscosity of amorphous substances using the Arrhenius equation, but they were unsuccessful in view of the fact that the activation energy of a viscous flow in the region of the glass transition temperature depends on temperature and can be determined only in a narrow temperature range [10,12]. For simple low-viscosity liquids, the Frenkel equation is used for the temperature dependence of viscosity [1–3,13]:

$$\eta = \eta_0 \exp\left(\frac{U}{RT}\right) \tag{2}$$

where the activation energy U is taken as a constant value, and η_0 is the high-temperature viscosity limit [14]. However, as mentioned above, for glass-forming melts, the activation energy of viscous flow in the glass transition region depends quite noticeably on the temperature $U = U(T)$. In this regard, the scientific community considers it most successful in determining the temperature dependence of the viscosity of amorphous materials, including polymers using the Williams–Landel–Ferry (WLF) equation [1–3,15–17]:

$$\ln a_T = -C_1 \frac{T - T_g}{T - T_g + C_2}, \quad a_T = \frac{\eta(T)}{\eta(T_g)} \cong \frac{\tau(T)}{\tau(T_g)}, \tag{3}$$

where a_T is the relative viscosity, and τ is the structural relaxation time. The values of the parameters of the WLF equation C_1 and C_2 and some characteristics of the glass transition process calculated on their basis for various chalcogenide glasses and polymers are shown in Table 1 [5,18].

At the same time, C_1 in Equation (3) is, in the first approximation, a universal constant for various classes of amorphous substances, including the studied polymers.

It is noteworthy that the WLF equation is practically equivalent to the Vogel–Fulcher–Tammann (VFT) equation:

$$\eta(T) = A \cdot \exp\left[\frac{B}{T - T_0}\right], \tag{4}$$

while substituting $B = C_1(T - T_g)$, $T_0 = T_g - C_2$.

Table 1. The parameters of the WLF Equation (3) C_1 and C_2 and the characteristics of the glass transition process for polymers and glasses As-S, Se-Ge, and As-Se [5,18].

Material			C_1	C_2, K	T_g, K	δT_g, K	f_g	τ_g, s
Polyisobutylene			38	104	202	2.7	0.026	54
Polyvinyl acetate			36	47	305	1.3	0.028	26
Polyvinyl chloroacetate			40	40	296	1.0	0.025	20
Polymethyl acrylate			42	45	276	1.1	0.024	22
Polyurethane			36	33	238	0.9	0.028	18
natural rubber			38	54	300	1.4	0.026	57
Methacrylate polymers:								
ethyl			40	65	335	1.6	0.025	32
n-butyl			39	97	300	2.5	0.026	50
n-octyl			37	107	253	2.9	0.027	58
No	**As, mol%**	**S, mol%**			**Chalcogenide glasses**			
1	12.5	87.5	12.0	81.20	318.5	6.7	0.083	134.8
2	15.0	85.0	13.0	101.5	326.0	7.8	0.077	156.3
3	17.5	82.5	12.3	86.50	337.5	7.0	0.081	140.1
4	20.0	80.0	13.9	112.8	351.5	8.1	0.072	162.5
5	25.0	75.0	14.5	120.7	379.1	8.3	0.069	166.6
6	27.0	73.0	17.2	174.8	386.7	10.1	0.058	202.8
7	28.6	71.4	19.2	216.7	391.6	11.3	0.052	225.4
8	30.0	70.0	18.9	210.6	396.4	11.2	0.053	223.2
9	32.5	67.5	18.2	210.4	403.5	11.6	0.055	231.4
10	35.0	65.0	22.2	286.9	418.8	12.9	0.045	258.2
11	36.7	63.3	22.7	303.9	423.4	13.4	0.044	267.4
12	37.6	62.4	26.3	364.2	432.2	13.8	0.038	276.8
13	39.0	61.0	25.6	350.5	441.3	13.7	0.039	273.4
14	40.0	60.0	27.0	355.7	449.6	13.2	0.037	263.2
15	40.6	59.4	27.8	379.2	446.1	13.7	0.036	273.0
16	41.1	58.9	26.3	359.7	444.2	13.7	0.038	273.4
17	42.1	57.9	27.0	360.5	440.4	13.3	0.037	266.8
18	42.7	57.3	27.0	359.7	433.5	13.3	0.037	266.2
No	**Se, mol%**	**Ge, mol%**			**Chalcogenide glasses**			
1	97	3	12.8	63.7	317	5.0	0.078	99.3
2	95	5	11.8	41.8	330	3.5	0.085	71.0
3	92	8	12.7	64.0	352	5.1	0.079	101.2
4	90	10	19.6	183.9	356	9.4	0.051	187.6
5	85	15	19.2	225.4	396	11.7	0.052	234.4
6	83	17	18.5	243.9	411	13.2	0.054	263.4
7	80	20	21.7	354.1	430	16.7	0.046	325.8
8	75	25	13.5	200.4	487	14.8	0.074	296.6
No	**As, mol%**	**Se, mol%**			**Chalcogenide glasses**			
1	3	97	11.8	41.8	316	3.5	0.085	71.0
2	5	95	12.7	48.8	320	3.9	0.079	77.2
3	10	90	17.5	108.4	331	6.2	0.057	123.5
4	14.9	85.1	16.7	110.6	344	6.6	0.060	132.7
5	25	75	23.3	238.6	364	10.3	0.043	205.2
6	26.5	73.5	25.0	299.5	365	12.0	0.040	239.6
7	28.6	71.4	29.4	368.2	370.5	12.5	0.034	250.4
8	40	60	18.5	169.9	443	9.2	0.054	183.5
9	42.2	57.8	21.7	245.0	437	11.3	0.046	225.4
10	43.3	56.7	21.3	247.9	435	11.7	0.047	233.0
11	45	55	20.4	244.3	433	12.0	0.049	239.4
12	48.5	51.5	20.0	245.0	425.5	12.3	0.050	245.0
13	49	51	22.7	278.0	431	12.2	0.044	244.6
14	50	50	15.6	138.9	440	8.9	0.064	177.8
15	50.6	49.4	17.2	185.3	426	10.8	0.058	215.0
16	51	49	16.1	165.8	425	10.3	0.062	205.6
17	52.7	47.3	16.4	153.4	422	9.4	0.061	187.2
18	53.7	46.3	15.2	135.5	415	8.9	0.066	178.9

It is worth noting that we are using the WLF empirical equation to identify the temperature interval where different liquids transform into glasses because the activation energy of flow starts changing, namely, at T_g (see, e.g., [19] and Figures 1, 2 and 4 of [20]). Indeed, the viscous flow in glass-forming melts exhibits three regimes [19]: Stage I ($T < T_g$):

isostructural Arrhenius law viscosity of the non-relaxed liquid, the upper and lower lines referring to the two limiting fictive temperatures; Stage II ($T_{liq} > T > T_g$): variable activation energy of viscosity, with a VFT or WLF fitting through the data; and Stage III ($T > T_{liq}$): Arrhenius law viscosity, with a crossover temperature T_A assumed to be close to T_{liq} [19] or more exactly, $T_A = kT_m$ (where $k = 1.1-0.15$) regardless of the type of glass-forming liquid [21] in line with the results of Refs. [22,23]. Indeed, the VFT and WLF empirical equations are successfully used to consider various aspects of molecular kinetic processes in the glass transition region (see, e.g., [19,24,25]). The WLF equation also describes the temperature dependence of relaxation time $\tau(T)$ and viscosity $\eta(T)$ in the glass transition region for amorphous polymers, inorganic glasses, and metallic amorphous alloys [15,16,26,27].

3. The Temperature Interval of the Liquid–Glass Transition

If we rewrite the WLF Equation (3) as a straight line equation and draw graphs in the coordinates $y = -[(T - T_g)/\ln(a_T)]$ and $x = (T - T_g)$; then, we can get a linear dependence of y on x. Figure 1 shows that the dependence y(x) in the glass transition region is linear, which confirms the applicability of the WLF equation.
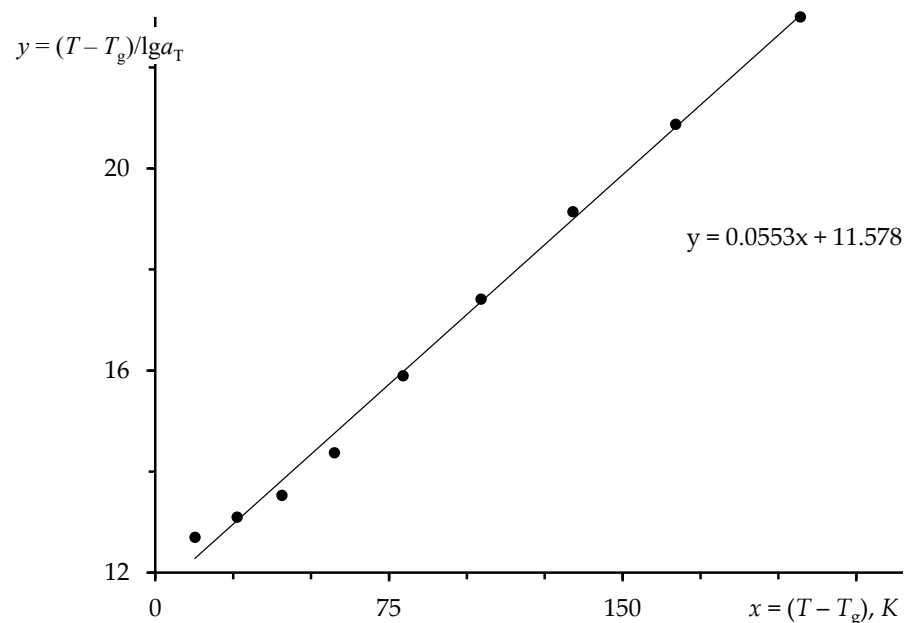
Figure 1. Temperature dependence of the viscosity of As-S glasses in coordinates corresponding to the Williams–Landel–Ferry equation. The data of [18] were used where the composition is as follows: As—32.5 mol%; S—67.5 mol%.

Experimental data on the temperature dependence of the viscosity of chalcogenide glasses were used from the electronic database SciGlass [18], which are shown in Table 2.

Similarly, graphs were constructed for all compositions of studied polymers. From these straight lines y–x, the values of the parameters of the WLF equation C_1 and C_2 are determined (Table 1).

Within Sanditov's model of delocalized atoms [8,17,28], an interpretation of the WLF equation is proposed, from which it follows that the parameter C_1 is the reciprocal of the fraction of the fluctuation volume f_g frozen at the glass transition temperature:

$$C_1 = \frac{1}{f_g} \tag{5}$$

The fluctuation volume of an amorphous substance ΔV_e is due to thermal displacements of atoms (kinetic units) [17,28]

$$\Delta V_e = N_e \Delta v_e, \tag{6}$$

where N_e is the number of delocalized atoms, and Δv_e is the elementary fluctuation volume required for the delocalization of an atom, i.e., its maximum displacement from the local equilibrium position.

Table 2. Temperatures of As-S glasses of composition in mol%, temperature in K, at which the viscosity $\log[\eta(T)$, poise] takes given values.

As	S	13	12	11	10	9	8	7	6	5	4
12.5	87.5	318.5	324.7	333.0	345.3	362.0	384.0	410.5	440.5	476.5	531.0
15.0	85.0	326.0	333.3	344.0	357.6	373.9	392.5	418.0	450.0	489.5	539.0
17.5	82.5	337.5	344.0	353.0	365.3	381.3	403.5	429.4	458.7	496.0	546.0
20.0	80.0	351.5	360.8	370.6	380.9	395.5	415.2	439.0	467.5	504.5	561.5
25.0	75.0	379.1	389.1	399.4	410.2	421.6	438.0	461.0	491.0	532.5	586.0
27.0	73.0	386.7	398.3	410.7	424.0	438.5	454.5	473.0	500.0	537.5	593.0
28.6	71.4	391.6	404.3	417.8	432.2	447.6	464.3	484.0	511.5	547.5	599.0
30.0	70.0	396.4	409.0	422.4	436.6	451.9	468.3	489.0	516.5	552.0	603.0
32.5	67.5	403.5	416.2	429.7	444.1	461.0	483.0	508.0	537.5	570.5	610.5
35.0	65.0	418.8	432.7	447.6	463.6	480.8	500.6	524.9	552.0	583.0	620.0
36.7	63.3	423.4	437.7	453.1	469.6	487.4	507.0	531.0	557.8	588.8	626.5
37.6	62.4	432.2	446.8	462.6	479.4	497.6	516.9	538.4	562.7	591.0	630.0
39.0	61.0	441.3	455.8	471.3	487.9	506.0	525.6	546.2	569.7	598.0	639.0
40.0	60.0	449.6	463.7	478.7	494.1	510.6	528.5	548.7	571.0	599.3	636.5
40.6	59.4	446.1	460.5	475.8	492.3	510.6	528.5	548.7	571.0	599.3	636.5
41.1	58.9	444.2	458.7	474.3	490.9	508.7	527.5	549.0	573.0	601.5	641.0
42.1	57.9	440.4	454.5	469.6	485.7	503.0	521.4	542.0	565.2	592.0	629.0
42.7	57.3	433.5	477.7	462.7	478.8	496.0	514.5	533.7	555.5	583.0	624.5

The volume fraction of the fluctuation volume f_g, obtained from the data on the parameter C_1, of course, weakly depends on the nature of amorphous substances [8,17] (Table 1) and is no higher than 10%.

$$f_g = \left(\frac{\Delta V_e}{V} \right)_{T=T_g} \approx const \approx 0.03 - 0.08 \tag{7}$$

During cooling in the glass transition region, due to the slowing down of molecular rearrangement, the change in the structure of the melt does not have time to follow the change in temperature. In the glass transition region, the viscosity of the melt sharply increases, as well as the relaxation time $\tau(T)$, which, in turn, is related to the liquid cooling rate $q = (dT/dt)$. According to relaxation theories [5,29–34], the relationship between the relaxation time and the melt cooling rate plays a decisive role in the glass transition process. Bartenev [29], in 1951, from general considerations based on experimental data, proposed an equation relating these quantities in the following form:

$$q\tau_g = C, \tag{8}$$

where τ_g is the structural relaxation time at the glass transition temperature T_g, and C is an empirical parameter with the dimension of temperature. The rate q in this equation implies the absolute value of the rate of temperature change $|q|$ when the melt is cooled or when the glass is heated. The relationship (8) gave good results in terms of determining the dependence of the glass transition temperature on the cooling rate using the methods of relaxation spectrometry of amorphous polymers and other glassy systems [33].

A rigorous physical theory about the behavior of kinetic units that can be in two states with different states separated by an energy barrier was developed by Volkenstein and Ptitsyn [30]. The solution of the kinetic equation shows that the glass transition of the system occurs at a certain temperature T_g when the fraction of particles in the excited state freezes. The temperature T_g satisfies the condition:

$$\left(\frac{d\tau}{dT}\right)_{T=T_g} = -\frac{1}{q} \tag{9}$$

The kinetic criterion for the liquid–glass transition in this theory is the glass transition equation [28]:

$$q\tau_g = \delta T_g \tag{10}$$

The value of δT_g, which was proposed in this notation by Nemilov [31], characterizes the temperature range of the transition from liquid to glass upon cooling.

To estimate this parameter of the glass transition equation δT_g for the glasses and polymers under study, we turn to expressions (3) and (9) discussed earlier. Substituting the dependence $\tau(T)$ from the WLF Equation (3) into relation (9) leads to the equality:

$$q\tau_g = \frac{C_2}{C_1}, \tag{11}$$

a comparison of which with the glass transition Equation (10) allows one to obtain a formula for calculating the temperature interval δT_g from the data on the parameters of the WLF equation:

$$\delta T_g = \frac{C_2}{C_1}. \tag{12}$$

For the studied materials (Table 1), the values of δT_g are as follows: As-S: 6.7–13.8 K; Se-Ge: 3.5–16.3 K; As-Se: 3.5–13.4 K; polyisobutylene: 2.7 K; polyvinyl acetate: 1.3 K; natural rubber: 1.4 K; polymethyl methacrylate: 1.1 K; polyurethane: 0.9 K, etc.

While the first empirical parameter C_1 of the WLF equation, as noted above, is equal to the reciprocal of f_g; then, the second parameter C_2 is equal to the ratio of f_g to the thermal expansion coefficient of the fluctuation volume at the glass transition temperature β_f [17]

$$C_2 = \frac{f_g}{\beta_f}. \tag{13}$$

Moreover, the product $\beta_f \cdot T_g$ is a single-valued function of f_g:

$$\beta_f T_g = f_g \ln(1/f_g) \tag{14}$$

From equalities (5), (12) and (13), taking into account (14), it follows that the parameter of the glass transition Equation (10) δT_g can be determined by the glass transition temperature and the fluctuation volume fraction f_g:

$$\delta T_g = \frac{f_g}{\ln(1/f_g)} T_g \tag{15}$$

Formula (15) implies a linear correlation between the temperature interval δT_g and the glass transition temperature T_g since fg ~ const for glasses of the same class (see Table 1). The slope of the straight lines $\delta T_g - T_g$ is determined by the value f_g. The value of f_g, although weak, depends on the nature of the glasses, which is sometimes quite strong and can cause a deviation from the linear dependence of δT_g on T_g. The possibility of some inaccuracies in the experimental data on the temperature dependence of viscosity is also not ruled out. Since materials of the same class have $f_g \approx$ const, one can expect a linear correlation between the values of δT_g and T_g. Indeed, as we see from Figures 2 and 3, for

As-S and Se-Ge glasses, the temperature interval δT_g, within which the transition from liquid to glass occurs, depends linearly on the glass transition temperature T_g.
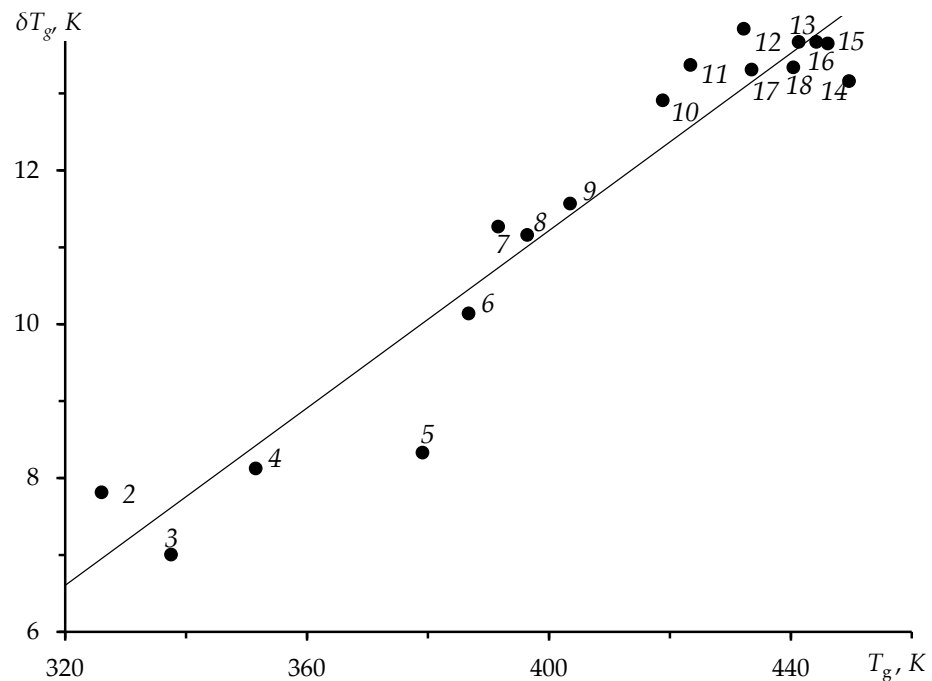

Figure 2. Linear correlation between the temperature interval δT_g characterizing the glass transition range and the glass transition temperature T_g of glasses in the As-S system. The point numbers correspond to the glass order numbers in Table 1.
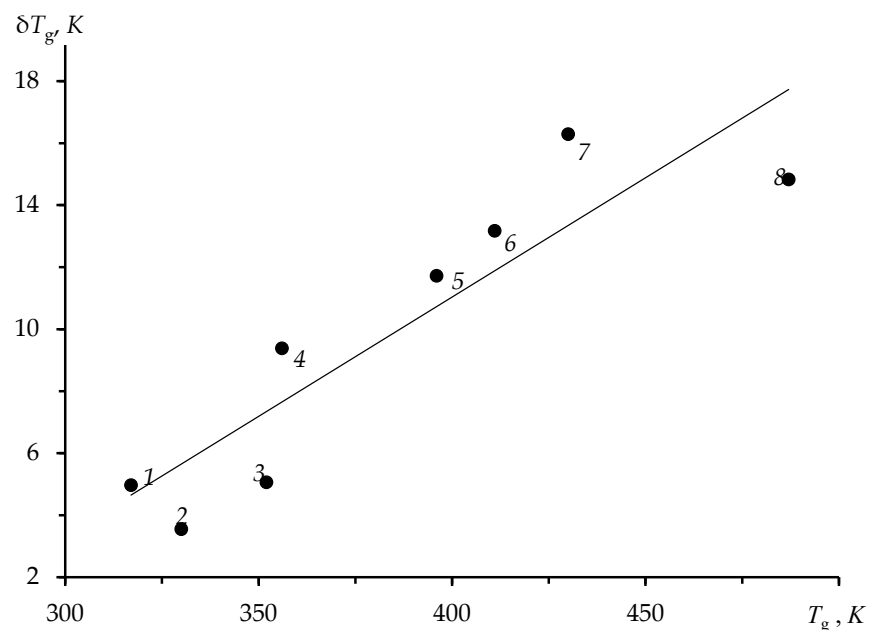
Figure 3. Linear correlation between δT_g and T_g for Se-Ge glasses. The point numbers correspond to the glass order numbers in Table 1.

For the As-Se glassy system, there is practically no linear dependence (Figure 4).
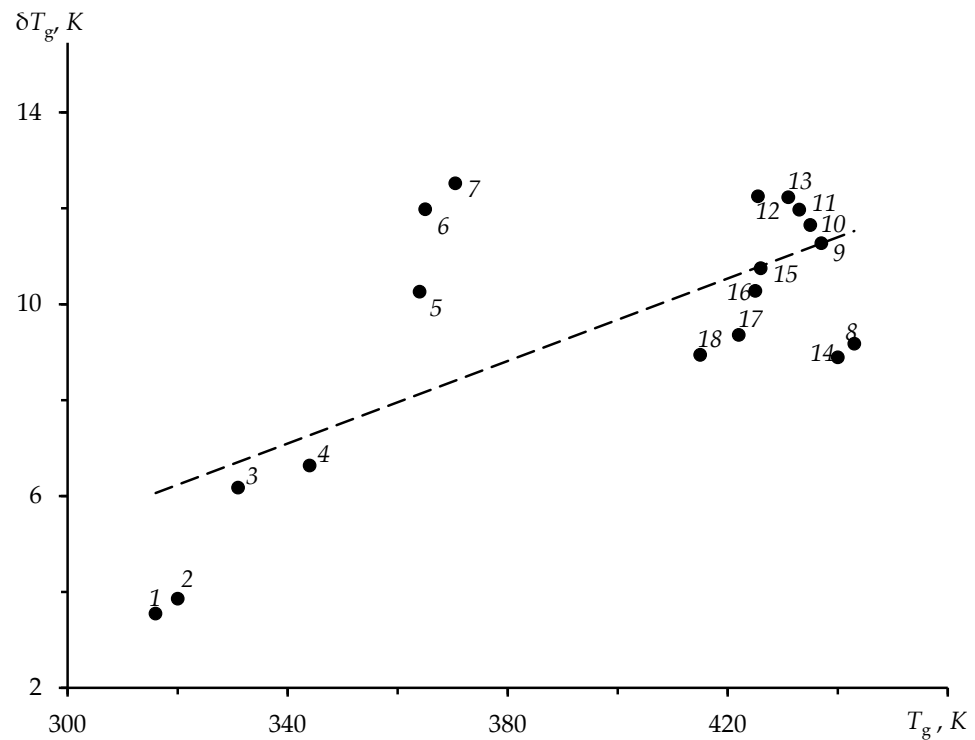
Figure 4. Correlation between δT_g and T_g for As-Se glasses. The point numbers correspond to the glass order numbers in Table 1.

A small scatter in the values of the fraction of the fluctuation volume f_g for amorphous polymers, according to the data in Table 1, which ranges from 0.024 to 0.028, also indicates the relative constancy of the factor in front of T_g in the Equation (15).

4. Calculation of the Structure Relaxation Time at the Glass Transition Temperature

The temperature at which the glass transition of the liquid occurs depends on the melt cooling rate q, although this dependence is weak. The standard glass transition temperature T_g is considered to be the temperature at which the limiting viscosity $\eta_g \approx 10^{12}$ Pa·s is reached. It corresponds to the cooling rate

$$q = 3 \text{ K/min} = 0.05 \text{ K/s}, \tag{16}$$

which is considered a standard cooling rate [3,10,32,33]. In the dilatometry of glasses and polymers, approximately the same cooling rate is almost universally used (16). In view of the weak (logarithmic) dependence of T_g on q, small fluctuations of q around the standard value (16) do not particularly affect the value of T_g. Therefore, it is generally assumed that most available data on T_g actually refer to the standard cooling rate. There are little data for other rates q.

According to Formula (11), at a standard cooling rate $q = 0.05$ K/s, according to the data on the WLF equation parameters C_1 and C_2, the structural relaxation time τ_g was calculated at the glass transition temperature (Table 1) As-S: 135–277 s; Se-Ge: 71–325 s; As-Se: 71–267 s; polyvinyl acetate: 61 s; natural rubber: 57 s; polymethyl methacrylate: 22 s; polyurethane: 18 s; polyvinyl chloroacetate: 20 s; polyisobutylene: 54 s.

For comparison, we can present the results of calculating the relaxation time of the structure for oxide systems using the well-known Maxwell formula: $\tau = \eta/G$, where G is the shear modulus. For most oxide inorganic glasses, the instantaneous shear modulus G_∞ is about $G_\infty = (20–25) \cdot 10^9$ Pa, which changes little with temperature. For a large set of oxide inorganic glasses at a standard cooling rate $q = 0.05$ K/s, the logarithm of viscosity at the glass transition temperature is $\log(\eta_g, \text{Pa·s}) = 12.76 \pm 0.26$. At a standard cooling

rate, the approximate constancy of viscosity at the glass transition temperature can be represented as $\eta_g \approx 10^{12}$–10^{13} Pa·s. From these data on the quantities G_∞ and η_g, at the level of qualitative estimates, we obtain [10,31,32,34,35]:

$$\tau_g = \frac{\eta_g}{G_\infty} \approx 10^2 \text{ s,} \tag{17}$$

which coincides in order of magnitude with the results of calculation by Formula (11), according to the data on the parameters of the WLF equation C_1 and C_2.

5. Discussion

The liquid–glass transition has a dual nature demonstrating both kinetic [36–39] and thermodynamic phase transformation features [7,38–43]. Indeed, the higher the temperature of an amorphous material, either polymer or inorganic, including metallic systems, the more chemical bonds are broken in it. Broken bonds weaken the bond lattice of material, and because of that, the viscosity of amorphous materials is lower at higher temperatures, with typical molecular building blocks of the material becoming increasingly free to move. Hence, there is a gradual change of its solid-like behavior to a more gas-like type behavior which in the kinetic approach is agreed to occur when the viscosity is getting lower than a certain value, such as the generically agreed through Equation (1) $\eta_g = 10^{12}$ Pa·s.

In the thermodynamic phase transformation approach, often labeled as configuron percolation theory (CPT) [5,9,11], the broken bonds in amorphous materials are termed configurons [6] and are analyzed as a separate phase [7,40]. The glass–liquid transition is then described on the basis of the Kantor–Webman theorem, which states that the rigidity threshold of an elastic percolating network is identical to the percolation threshold [44]. The configuron phase up to the temperatures close to T_g is a point-like set, and the mathematical set theory characterizes it as a set with a Hausdorff dimensionality equal to nil. On the further increase in temperature of the glass, exactly at T_g, the system of configurons forms for the first time a macroscopic percolation cluster. Accordingly to Kantor–Webman theorem, at this temperature and above it, the material is not anymore an elastic solid (glass), transforming into a liquid. The cluster made up of configurons is known to be a fractal characterized by the Hausdorff dimensionality 2.55 ± 0.05 within set theory [45]. Thus, the set of configurons changes its dimensionality in a stepwise manner from 0 to 2.55 ± 0.05 at T_g, which can be interpreted as a kind of symmetry change characterizing the structural difference between glasses and a molten phase of matter [34,40]. It is important that this approach (i.e., CPT) enables structurally to distinguish glasses from melts using experimental data of X-ray diffraction in amorphous materials [11,34,46,47]. Thus, the account of configuron phase formation above the T_g (in the melt) shows that the glass–liquid transition within CPT is similar in nature to the second-order phase transformations following Ehrenfest's classification of phase transformations.

From the point of view of the relaxation theory of glass transition, the liquid–glass transition process (vitrification) has a pronounced relaxation character and is subject to kinetic laws [4,5]. During the cooling of the glass-forming liquid in the glass transition region, molecular rearrangements become slower, as a result of which the change in the structure does not have time to follow the decrease in temperature. An equation similar to the Bartenev Equation (8) has been successfully used not only for the liquid–glass transition process but also for other relaxation processes [29]. When the temperature changes at a constant rate q, the condition for observing a structural relaxation transition is written as $q\tau_i = C$, where τ_i is the relaxation time of the *i*-th relaxation process. As an example, thermal stimulation of the electrical depolarization of an amorphous polymer can be cited, which refers to structural relaxation, and the condition for its observation is described by a similar relation [48]. Within the framework of this approach, the relation between the structural relaxation time τ and the melt cooling rate $q = dT/dt$ plays a decisive role in the glass transition of a liquid. The relationship between these quantities is expressed by the glass transition equation: $q\tau_g = \delta T_g$, where τ_g is the relaxation time at $T = T_g$, and δT_g

is the temperature range. In the model of delocalized atoms developed by Sanditov [8], it is considered that atom delocalization, which is an ultimate displacement of an active atom, is a necessary condition for an elementary event in the process of viscous flow of glasses and melts. For this reason, as a result of the freezing of the atom delocalization process in the glass transition region, viscous flow effectively stops at T_g, and the melt vitrifies, e.g., passes into a glassy state. This occurs when the energy of thermal vibrations of the disordered lattice per atom becomes equal to or lower than the atom delocalization enthalpy, which provides a certain glass transition criterion [11]. It was shown that the analysis of the viscosity equations allows numerical estimations of δT_g [8,17]. Moreover, it shall be noted that these are not limited to only WLF or VFT models [5,9,20].

The dependence of the glass transition equation parameter δT_g on the glass transition temperature T_g in Equation (15) is due to a small spread in the fraction of the fluctuation volume f_g. Such a dependence can also be obtained from several other considerations. If the equation for the so-called fragility of glass-forming melts, which is determined by the temperature dependence of the viscosity of the liquid $\eta(T)$ near the glass transition temperature [49]

$$m = \left. \frac{d \ln \eta(T)}{d\left(T_g/T\right)} \right|_{T=T_g} \tag{18}$$

substitute the temperature dependence of viscosity from the WLF Equation (3); then, this will lead to the expression:

$$m = \left(\frac{C_1}{C_2}\right) T_g. \tag{19}$$

Considering expression (12) at $m \approx const$, a linear correlation follows between the temperature interval δT_g and the glass transition temperature T_g:

$$\delta T_g = \left(\frac{1}{m}\right) T_g. \tag{20}$$

The fragility m serves as a characteristic of glass classification [50]. Hence, we can conclude that this linear correlation is valid for glasses of the same class with an almost constant fragility $m \approx const$. For example, silicate glasses with a network structure have a lower fragility m than glasses with a chain structure.

For most glasses, the value of δT_g, according to (15), at known values of f_g is no higher than 1% of the glass transition temperature. Thus, the narrowness of the temperature interval δT_g can be explained by the low value of the fraction of the fluctuation volume f_g frozen at the glass transition temperature, which agrees with the classical concept of a small temperature interval in which the liquid structure freezes.

Although we currently do not have the necessary data for calculations, we note that empirical parameters of the WLF equation for polystyrene polymers could be of particular interest, as it was recently shown that the architecturally-different blends of these polymers could exhibit interesting surface transitions potentially affected by the liquid–glass transition related to the evident role played by the polymer topology in it [49,51,52].

6. Conclusions

The calculation of the temperature interval δT_g, within which the liquid transforms into a glassy solid state, was carried out in this work according to the empirical parameters of the Williams–Landel–Ferry equation C_1 and C_2 at the standard cooling rate q. e.g., for the investigated chalcogenide glasses, the value of δT_g is in the range from 3.5 K to 16.3 K for amorphous organic polymers and low molecular weight organic glasses from 0.6 K to 1.6 K. It is assumed that due to the relatively small spread in the fluctuation volume fraction f_g for amorphous polymers and glassy systems of the same class, there is a linear dependence of the temperature interval δT_g on T_g, although not for all materials, which requires further research in this area.

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