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Estimation of the temperature band characterizing the liquid–glass transition interval for chalcogenide glasses

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The temperature dependence of the viscosity of inorganic glasses in the glass transition region is successfully described by the Williams–Landel–Ferry (WLF) equation. For the studied glasses, the value of $f_g = 1/C_1$ weakly depends on the nature of the glasses. There is a linear correlation between delta δT_g and T_g. From the data on the parameters of the WLF equation C_1 and C_2, we calculated delta δT_g, as well as the relaxation time of the structure τ_g at the glass transition temperature of the glasses under study.

Keywords: Viscosity in the glass transition region, Williams–Landel–Ferry equation, kinetic glass transition criterion, chalcogenide glasses, fluctuation volume fraction, liquid–glass transition.

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1. Introduction

In different classes of amorphous substances in the field of glass transition, the mobility of various kinetic units associated with the different nature of the interaction between particles is frozen. However, it is noteworthy that the basic laws of the liquid–glass transition are qualitatively the same for different glazing systems, regardless of their nature, which is confirmed by the presence of universal rules and equations in the field of glass transition [1,2].

The viscosity of glassy substances increases sharply in the glass transition region when the melts are cooled. They glaze when the same maximum viscosity reaches $\eta_g = \eta(T_g)$

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

This ratio is an approximate rule of viscosity constancy at the glass transition temperature of T_g. From Mazurin's review [3] it follows that in most of the glasses studied so far, the value of T_g corresponds to the temperatures at which the viscosity values η_g are in the range from 10^{11} to 10^{12} Pa · s, i.e. they fluctuate in the region of the approximate value (1) with a noticeable spread. The constancy of $\eta_g = \text{const}$ is better performed in glassy systems of the same class.

The temperature dependence of the viscosity of simple low-viscosity liquids is described by the Frenkel equation [1,4]:

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

with a constant activation energy $U = \text{const}$ (η_0 — high-temperature viscosity limit). In glass-forming melts, the activation energy of viscous flow in the glass transition region is quite dependent on the temperature of $U = U(T)$. In this regard, the Williams–Landel–Ferry ratio (WLF equation) [5] has become widespread:

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

where τ — the time of structural relaxation. The justification of this equation for various flowing liquids is shown in many works [1,5]. Table 1 shows the values of the parameters of this equation C_1 and C_2 and the characteristics of the glass transition process calculated on their basis for various chalcogenide glasses [6].

This paper is devoted to the study of the kinetic criterion of glass transition in glasses As−S, Se−Ge, As−Se.

2. Applicability of the WLF equation to glass under study

Let's imagine the WLF ratio (3) in the form of a straight line equation

$$\ln a_T = -C_1\,\frac{T - T_g}{T - T_g + C_2},$$

and check the linearity of the $y = -(T - T_g)/\ln a_T$ from $x = (T - T_g)$. Experimental data on the temperature dependence of the viscosity of chalcogenide glasses were used from the electronic reference book SciGlass [7] (Table 2).

From Fig. 1 it can be seen that this dependence of $y(x)$ in the glass transition region is linear, which confirms the applicability of the WLF equation. Similar graphs are built for all compositions of the studied glasses. From these

Table 1. The parameters of the WLF equation (3) C_1 and C_2 for glasses As–S, Se–Ge, As–Se and glass transition process characteristics [7]

№	Glass, mol.%		C_1	C_2, K	T_g, K	δT_g, K	f_g	$C_g \cdot 10^3$	τ_g, s
	As	S							
1	12.5	87.5	12.0	81.20	318.5	6.7	0.083	33.3	134.8
2	15.0	85.0	13.0	101.5	326.0	7.8	0.077	30.0	156.3
3	17.5	82.5	12.3	86.50	337.5	7.0	0.081	32.2	140.1
4	20.0	80.0	13.9	112.8	351.5	8.1	0.072	27.4	162.5
5	25.0	75.0	14.5	120.7	379.1	8.3	0.069	25.8	166.6
6	27.0	73.0	17.2	174.8	386.7	10.1	0.058	20.4	202.8
7	28.6	71.4	19.2	216.7	391.6	11.3	0.052	17.6	225.4
8	30.0	70.0	18.9	210.6	396.4	11.2	0.053	18.0	223.2
9	32.5	67.5	18.2	210.4	403.5	11.6	0.055	19.0	231.4
10	35.0	65.0	22.2	286.9	418.8	12.9	0.045	14.5	258.2
11	36.7	63.3	22.7	303.9	423.4	13.4	0.044	14.1	267.4
12	37.6	62.4	26.3	364.2	432.2	13.8	0.038	11.6	276.8
13	39.0	61.0	25.6	350.5	441.3	13.7	0.039	12.0	273.4
14	40.0	60.0	27.0	355.7	449.6	13.2	0.037	11.2	263.2
15	40.6	59.4	27.8	379.2	446.1	13.7	0.036	10.8	273.0
16	41.1	58.9	26.3	359.7	444.2	13.7	0.038	11.6	273.4
17	42.1	57.9	27.0	360.5	440.4	13.3	0.037	11.2	266.8
18	42.7	57.3	27.0	359.7	433.5	13.3	0.037	11.2	266.2
	Se	Ge							
1	97	3	12.8	63.7	317	5.0	0.078	30.6	99.3
2	95	5	11.8	41.8	330	3.5	0.085	34.5	71.0
3	92	8	12.7	64.0	352	5.1	0.079	31.1	101.2
4	90	10	19.6	183.9	356	9.4	0.051	17.1	187.6
5	85	15	19.2	225.4	396	11.7	0.052	17.6	234.4
6	83	17	18.5	243.9	411	13.2	0.054	18.5	263.4
7	80	20	21.7	354.1	430	16.3	0.046	14.9	325.8
8	75	25	13.5	200.4	487	14.8	0.074	28.4	296.6
	As	Se							
1	3	97	11.8	41.8	316	3.5	0.085	34.5	71.0
2	5	95	12.7	48.8	320	3.9	0.079	31.1	77.2
3	10	90	17.5	108.4	331	6.2	0.057	19.9	123.5
4	14.9	85.1	16.7	110.6	344	6.6	0.060	21.3	132.7
5	25	75	23.3	238.6	364	10.3	0.043	13.7	205.2
6	26.5	73.5	25.0	299.5	365	12.0	0.040	12.4	239.6
7	28.6	71.4	29.4	368.2	370.5	12.5	0.034	10.1	250.4
8	40	60	18.5	169.9	443	9.2	0.054	18.5	183.5
9	42.2	57.8	21.7	245.0	437	11.3	0.046	14.9	225.4
10	43.3	56.7	21.3	247.9	435	11.7	0.047	15.4	233.0
11	45	55	20.4	244.3	433	12.0	0.049	16.2	239.4
12	48.5	51.5	20.0	245.0	425.5	12.3	0.050	16.7	245.0
13	49	51	22.7	278.0	431	12.2	0.044	14.1	244.6
14	50	50	15.6	138.9	440	8.9	0.064	23.3	177.8
15	50.6	49.4	17.2	185.3	426	10.8	0.058	20.4	215.0
16	51	49	16.1	165.8	425	10.3	0.062	22.3	205.6
17	52.7	47.3	16.4	153.4	422	9.4	0.061	21.8	187.2
18	53.7	46.3	15.2	135.5	415	8.9	0.066	24.3	178.9

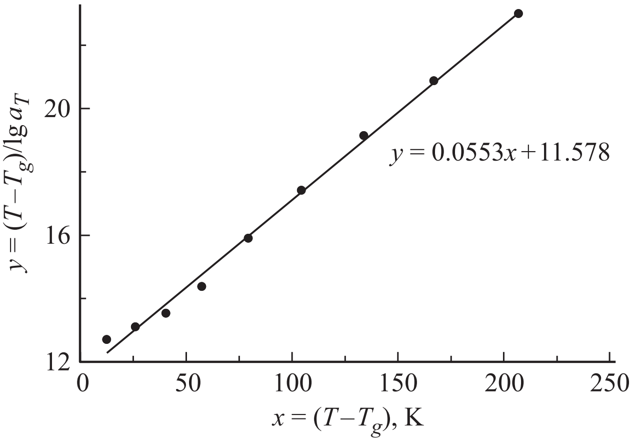

Figure 1. The temperature dependence of the viscosity of As–S glasses in coordinates corresponding to the Williams–Landel–Ferry equation. The data from [7] was used. Contents As — 32.5 mol. %.; S — 67.5 mol.%.

lines $y-x$ the values of the parameters of the WLF equation C_1 and C_2 (Table 1) are determined.

From the interpretation of the WLF equation in the framework of the model of delocalized atoms [6,8,9] it follows that the parameter C_1 is the inverse of the fraction of the fluctuation volume f_g, frozen at the glass transition temperature,

$$C_1 = \frac{1}{f_g}. \tag{4}$$

The fluctuation volume of the amorphous substance ΔV_e is due to the thermal displacements of atoms (kinetic units) [8,9]:

$$\Delta V_e = N_e \Delta V_e,$$

where N_e — the number of delocalized atoms, ΔV_e — the elementary fluctuation volume required for the delocalization of the atom — its marginal displacement from the local equilibrium position. The volume fraction of the fluctuation volume f_g, obtained from the data on the parameter C_1, naturally weakly depends on the nature of amorphous substances [6,8] (Table 1)

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

3. Relaxation aspects of the transition of liquid–glass

In the glass transition region, molecular rearrangements become so slow that the change in the structure of the melt during cooling does not have time to follow the change in temperature. At the same time, like viscosity, the relaxation time of the structure $\tau(T)$, which is closely related to the cooling rate of the liquid $q = (dT/dt)$, increases dramatically. Bartenev [10] proposed a relationship between

Table 2. Temperature dependence of viscosity $\eta(T)$ of As$-$S glasses [7]

№	Glass, mol.%		$\lg(\eta, P)$, at temperature T, K									
	As	S	13	12	11	10	9	8	7	6	5	4
1	12.5	87.5	318.5	324.7	333.0	345.3	362.0	384.0	410.5	440.5	476.5	531.0
2	15.0	85.0	326.0	333.3	344.0	357.6	373.9	392.5	418.0	450.0	489.5	539.0
3	17.5	82.5	337.5	344.0	353.0	365.3	381.3	403.5	429.4	458.7	496.0	546.0
4	20.0	80.0	351.5	360.8	370.6	380.9	395.5	415.2	439.0	467.5	504.5	561.5
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
6	27.0	73.0	386.7	398.3	410.7	424.0	438.5	454.5	473.0	500.0	537.5	593.0
7	28.6	71.4	391.6	404.3	417.8	432.2	447.6	464.3	484.0	511.5	547.5	599.0
8	30.0	70.0	396.4	409.0	422.4	436.6	451.9	468.3	489.0	516.5	552.0	603.0
9	32.5	67.5	403.5	416.2	429.7	444.1	461.0	483.0	508.0	537.5	570.5	610.5
10	35.0	65.0	418.8	432.7	447.6	463.6	480.8	500.6	524.9	552.0	583.0	620.0
11	36.7	63.3	423.4	437.4	453.1	469.6	487.4	507.0	531.0	557.8	588.8	626.5
12	37.6	62.4	432.2	446.8	462.6	479.4	497.6	516.9	538.4	562.7	591.0	630.0
13	39.0	61.0	441.3	455.8	471.3	487.9	506.0	525.6	546.2	569.7	598.0	639.0
14	40.0	60.0	449.6	463.7	478.7	494.1	510.6	528.5	548.7	571.0	599.3	636.5
15	40.6	59.4	446.1	460.5	475.8	492.3	510.6	528.5	548.7	571.0	599.3	636.5
16	41.1	58.9	444.2	458.7	474.3	490.9	508.7	527.5	549.0	573.0	601.5	641.0
17	42.1	57.9	440.4	454.5	469.6	485.7	503.0	521.4	542.0	565.2	592.0	629.0
18	42.7	57.3	433.5	447.7	462.7	478.8	496.0	514.5	533.7	555.5	583.0	624.5

these quantities (kinetic criterion of glass transition)

$$q\tau_g = C, \tag{5}$$

where τ_g — the time of structural relaxation at the glass transition temperature T_g, C — an empirical parameter with temperature dimension. Under q should be understood as the absolute value of the rate of change of temperature $|q|$ when cooling a melt or when heating glass.

Wolkenstein and Ptitsyn [11] have developed a rigorous physical theory, where the behavior of kinetic units that can be in two states with different energies separated by an energy barrier, is investigated. The solution of the kinetic equation shows that at some temperature of T_g, a fraction of the particles freezes in the excited state, which means glassy of the system. Temperature T_g meets the condition

$$\left(\frac{d\tau}{dT}\right)_{T=T_g} = -\frac{1}{q}. \tag{6}$$

In this theory, the kinetic criterion for the liquid–glass transition is the glass transition equation [9]

$$q\tau_g = \delta T_g. \tag{7}$$

The designation of the right side of this equation via δT_g was proposed by Nemilov [12]. The value δT_g characterizes the temperature interval of the transition from liquid to glass under cooling.

Let us dwell on the evaluation of the parameter of the glass transition equation δT_g for the glasses under study.

Substituting the dependence $\tau(T)$ from the WLF equation (3) into the ratio (6) results in equality

$$q\tau_g = \frac{C_2}{C_1}, \tag{8}$$

comparison of which with the glass transition equation (7) allows you to obtain a formula for calculating the temperature band δT_g according to data on the parameters of the WLF equation

$$\delta T_g = \frac{C_2}{C_1}. \tag{9}$$

For the examined glasses (Table 1), the value of δT_g is As$-$S: $\delta T_g = 6.7-13.8$ K; Se$-$Ge: $\delta T_g = 3.5-16.3$ K; As$-$Se: $\delta T_g = 3.5-13.4$ K.

The second parameter of the WLF equation C_2 is equal to the ratio f_g to the coefficient of thermal expansion of the fluctuation volume at the glass transition temperature β_f [8]:

$$C_2 = \frac{f_g}{\beta_f}, \tag{10}$$

wherein the product $\beta_f T_g$ is a one-to-one function f_g

$$\beta_f T_g = f_g \ln(1/f_g). \tag{11}$$

From the equations (4), (9) and (10) taking into account (11) it follows that the parameter of the glass transition equation (7) δT_g is determined by the glass transition temperature and the fraction of the fluctuation volume f_g

$$\delta T_g = \frac{f_g}{\ln(1/f_g)} T_g. \tag{12}$$

Since glasses of the same class have $f_g \approx \text{const}$, we can expect a linear correlation between the values of δT_g and T_g. In fact, as can be seen from Figs. 2 and 3, the glass As$-$S, Se$-$Ge temperature band δT_g, within which the transition from liquid to glass occurs, linearly depends on the glass transition temperature T_g. For the glassy As$-$Se system, there is practically no linear dependence (Fig. 4).

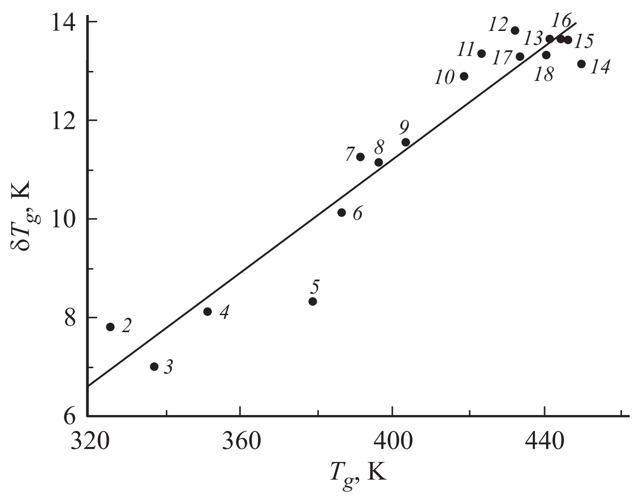

Figure 2. Linear correlation between the temperature band δT_g, which characterizes the glass transition interval, and the glass transition temperature T_g of the glasses of the As–S system. Numbers at points correspond to the numbers of glasses in Table 1.

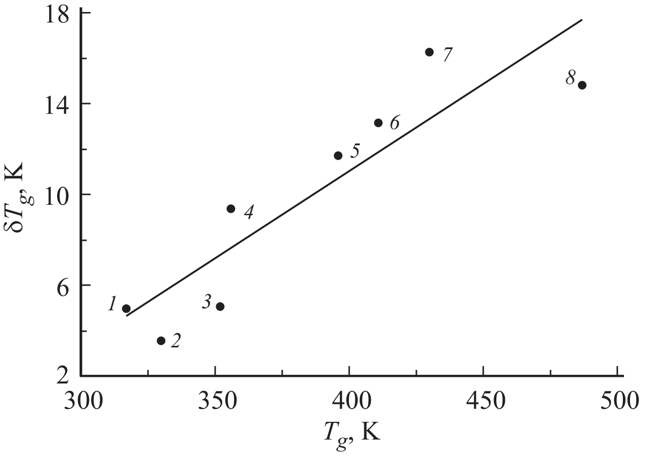

Figure 3. Linear correlation between δT_g and T_g for Se–Ge glasses. Numbers at points correspond to the numbers of glasses in Table 1.

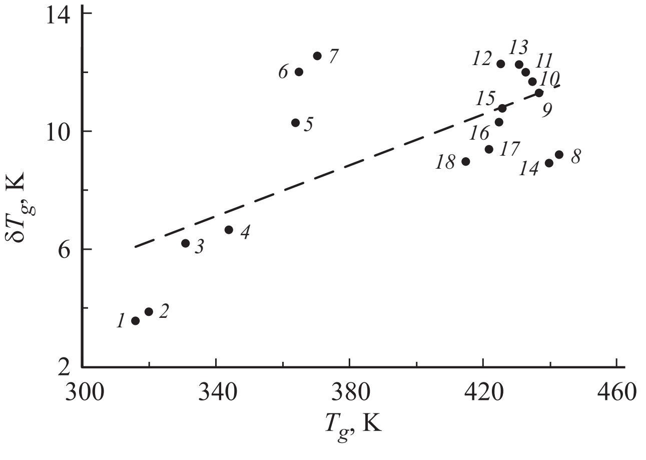

Figure 4. Linear correlation between δT_g and T_g for As–Se glasses. Numbers at points correspond to the numbers of glasses in Table 1.

4. Calculation of the relaxation time of the structure at glass transition temperature

The glass transition temperature, although weak, depends on the cooling rate of the melt q. The temperature at which the maximum viscosity of $\eta_g \approx 10^{12}\,\text{Pa}\cdot\text{s}$ is reached is called the standard glass transition temperature T_g, and the corresponding cooling rate

$$q = 3\,\text{K/min} = 0.05\,\text{K/s} \tag{13}$$

is taken as the standard cooling rate [1,3,13,14]. In dilatometry of glasses and polymers, almost all countries of the world use, as a rule, approximately the same rate of cooling (13). In view of the weak (logarithmic) dependence T_g, from q small fluctuations q about standard value (13) are not particularly at the value of T_g. Therefore, it is generally assumed that the vast majority of the available data on T_g actually refers to the standard cooling rate. For other rates q, there is little data.

According to the formula (8) at the standard cooling rate $q = 0.05\,\text{K/s}$ according to the parameters of the WLF equation C_1 and C_2, we calculated the time of structural relaxation τ_g at the glass transition temperature (Table 1) of As–S: $\tau_g = 135{-}277\,\text{s}$; Se–Ge: $\tau_g = 71{-}325\,\text{s}$; As–Se: $\tau_g = 71{-}267\,\text{s}$.

Approximately the same results are obtained by Maxwell's well-known formula: $\tau = \eta/G$, where G — shear modulus. For most oxide inorganic glasses, the instantaneous shear modulus G_∞ is about $G_\infty = (20{-}25)\cdot 10^9\,\text{Pa}$ and changes little with temperature. For a large aggregate of inorganic oxide glasses at a standard cooling rate $q = 0.05\,\text{K/s}$ the logarithm of viscosity at the glass transition temperature is $\lg(\eta_g,\ \text{Pa}\cdot\text{s}) = 12.76 \pm 0.26$. Apparently, at the standard cooling rate, the approximate viscosity constancy at the glass transition temperature can be represented as $\eta_g \approx 10^{12}{-}10^{13}\,\text{Pa}\cdot\text{s}$. Of this data on the values of G_∞ and η_g at the level of qualitative estimates we have [3,12,13,15,16]:

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

which, in order of magnitude, coincides with the results of the calculation according to the formula (8) according to the data on the parameters of the WLF equation C_1 and C_2.

5. Conclusion

The glass transition of a liquid is a pronounced relaxation process and obeys kinetic laws. As we approach the liquid–glass transition region, the molecular rearrangements in the glass-forming melts become so slow that the change in structure does not have time to follow the decrease in temperature. From the point of view of the relaxation approach in the process of glass transition of the liquid, the ratio between the time of structural relaxation τ and the cooling rate of the melt $q = dT/dt$ plays a decisive role. The relationship of these values is expressed by the glass transition equation: $q\tau_g = \delta T_g$, where τ_g — relaxation time at $T = T_g$, δT_g — temperature band.

According to the parameters of the Williams–Landel–Ferry equation, at the standard cooling rate, a temperature band of δT_g was calculated, within which the liquid passes into glass. For the studied chalcogenide glasses, the value of δT_g is in the range from 3.5 to 16.3 K.

When constructing a correlation between the values δT_g and T_g, the glasses As–S, Se–Ge have a pronounced linear dependence, and As–Se does not have it.

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Conflict of interest

The authors declare that they have no conflict of interest.

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