

THEORY  
AND SIMULATION

## On the Temperature Dependence of the Glass Transition Activation Energy

D. S. Sanditov<sup>a,b,\*</sup>, I. V. Razumovskaya<sup>c</sup>, and A. A. Mashanov<sup>a</sup>

<sup>a</sup> Buryat State University, Ulan-Ude, 670000 Buryatia, Russia

<sup>b</sup> Institute of Physical Materials Science, Siberian Branch, Russian Academy of Sciences,  
Ulan-Ude, 670047 Buryatia, Russia

<sup>c</sup> Moscow State Pedagogical University, Moscow, 119435 Russia

\*e-mail: Sanditov@bsu.ru

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**Abstract**—The temperature dependence of the glass transition activation energy for amorphous organic polymers and inorganic glasses is calculated using the Williams–Landel–Ferry equation for the relaxation time (viscosity). The results obtained are in satisfactory agreement with the experiment. The nature of the dependence of the glass transition activation energy on the temperature is discussed.

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### INTRODUCTION

The nature of the transition of an amorphous substance from a liquid (highly elastic) to a glassy state is still not fully understood. The glass transition of a liquid is closely associated with an increase in viscosity during cooling of the melt, and the activation energy of glass transition, as a rule, coincides with the activation energy of a viscous flow (relaxation) in the liquid–glass transition region.

The temperature dependence of the viscosity of simple low-viscosity liquids, such as acetone, is well described by the Frenkel equation [1]

$$\eta = \eta_0 \exp\left(\frac{U}{RT}\right) \quad (1)$$

with activation energy  $U = \text{const}$ . Here  $\eta_0$  is the pre-exponential factor and  $R$  is the gas constant. However, for glass-forming melts, the activation energy in formula (1) in the glass transition region is quite strongly dependent on temperature:  $U = U(T)$ . In connection with this, the empirical equations of viscosity are proposed that implicitly take into account the dependence  $U(T)$ . Among them, the Williams–Landel–Ferry ratio [2, 3] became widespread:

$$\ln a_T = -C_1 \frac{T - T_g}{T - T_g + C_2}, \quad (2)$$

$$a_T = \frac{\tau(T)}{\tau(T_g)} \equiv \frac{\eta(T)}{\eta(T_g)},$$

where  $C_1$  and  $C_2$  are the empirical constants,  $T_g$  is the glass transition temperature, and  $\tau$  is the relaxation time. The validity of this equation was proved in many

works for various glassy systems [2–6], including amorphous polymers.

For example, in [7, 8], the derivation of expression (2) was proposed without specifying functions  $\tau(T)$  and  $\eta(T)$ :

$$\ln a_T = -\left(\frac{A^2}{B}\right) \frac{T - T_g}{T - T_g + \left(\frac{A}{B} T_g\right)}, \quad (3)$$

$$A = -\left. \frac{\partial \ln \eta}{\partial (T/T_g)} \right|_{T=T_g}, \quad (4)$$

$$B = \left. \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial (T/T_g)^2} \right|_{T=T_g}. \quad (5)$$

The expansion of the function  $\ln \eta(T)$  near  $T_g$  in terms of small dimensionless parameter  $\lambda = (T - T_g)/T_g$  was used ([8]).

Thus, constant equations (2) acquire physical meaning—they can be expressed through derivatives  $A$  and  $B$  as

$$C_1 = \frac{A^2}{B}, \quad (6)$$

$$C_2 = \frac{A}{B} T_g. \quad (7)$$

The present work is devoted to the assessment of the temperature dependence of the glass transition activation energy  $U(T)$  using the data on the parameters of the Williams–Landel–Ferry equation  $C_1$  and

**Table 1.** Parameters of the Williams–Landel–Ferry equation and the glass transition activation energy at  $T = T_g$  for amorphous organic polymers and inorganic glasses (according to [2, 4, 30])

Amorphous substances	$T_g$ , K	$C_1$ , K	$C_2$ , K	$U_g$ , kJ/mol
PbO–SiO <sub>2</sub> (42.07 mol % PbO)	711	36	250	212
Na <sub>2</sub> O–B <sub>2</sub> O <sub>3</sub> (2.8 mol % Na <sub>2</sub> O)	544	29	130	131
Sheet glass	807	36	305	241
Polyisobutylene	202	38	104	64
Poly(vinyl acetate)	305	38	104	96
Polyurethane	238	36	33	71
Natural rubber	300	38	54	95

$U_g$  was calculated by formula (13).

$C_2$ . The calculation option  $U(T)$  is discussed without specifying the type of function  $U(T)$ . Since the main laws governing the transition of an amorphous substance from a highly elastic to a glassy state are qualitatively identical for many glass-forming systems, including amorphous organic polymers and inorganic glasses (e.g., [4, 9]), the objects of our research are inorganic polymers along with amorphous polymers.

#### CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE GLASS TRANSITION ACTIVATION ENERGY USING THE WILLIAMS-LANDELA-FERRI EQUATION

It is easy to verify that Eq. (2) is algebraically derived from the Vogel–Fulcher–Tammann relation ([4]):

$$\eta = \eta_0 \exp\left(\frac{B_0}{T - T_0}\right), \quad (8)$$

where the empirical constant  $B_0$  has a temperature dimension and is measured in kelvins. The parameters of Eqs. (2) and (8) are related by equalities

$$B_0 = C_1 C_2, \quad (9)$$

$$T_0 = T_g - C_2. \quad (10)$$

Assuming the pre-exponential factors in the formulas for viscosity (1) and (8) to be equal, we obtain the following temperature dependence of the activation energy of a viscous flow:

$$U = \frac{B_0 RT}{T - T_0}. \quad (11)$$

Since for many amorphous polymers and inorganic glasses the parameters of the Williams–Landel–Ferry equation  $C_1$  and  $C_2$  are known [2–11], using expres-

sions (9) and (10) it is advisable to go from dependence (11) to the value  $U(T)$  as functions of these parameters:

$$U = \frac{C_1 C_2 RT}{T - T_g + C_2}. \quad (12)$$

This equality implies a simple relation for calculating the glass transition activation energy  $U_g = U(T_g)$  at the glass transition temperature  $T = T_g$  is

$$U_g = C_1 RT_g. \quad (13)$$

For sheet (window) silicate glass, for example,  $C_1 = 36$  and  $T_g = 807$  K [10], whence we have  $U_g = 241$  kJ/mol. The methods of relaxation spectrometry [4, 10, 11] for this glass lead to almost the same value of  $U_g = 242$  kJ/mol. For polyisobutylene ( $T_g = 202$  K and  $C_1 = 38$ ) and natural rubber ( $T_g = 300$  K and  $C_1 = 38$ ) the values of  $U_g$ , which are 64 and 95 kJ/mol, respectively, are also consistent with the data of relaxation spectrometry [11].

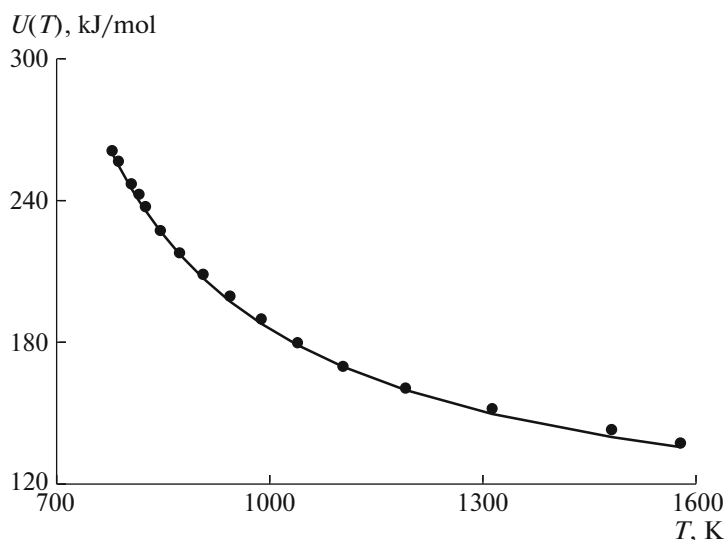
It is known that many glassy systems pass from a liquid to a glassy state at almost the same viscosity  $\eta_g \sim 10^{12}$  Pa s (the approximate rule of constancy of viscosity at  $T_g$ ). High temperature viscosity limit  $\eta_0 \sim \eta(T \rightarrow \infty)$  also turns out to be approximately constant,  $\eta_0 \sim 10^{-3.5}$  Pa s. Therefore, the activation energy at the glass transition temperature  $U_g = U(T_g)$  can be estimated by formula (1) at  $T = T_g$ ,  $\eta_g \sim \eta(T_g) \sim 10^{12}$  Pa s, and  $\eta_0 \sim 10^{-3.5}$  Pa s [4]:

$$U_g = \left(\ln \frac{\eta_g}{\eta_0}\right) RT_g \approx 36 RT_g, \quad (14)$$

which practically coincides with relation (13).

Consequently, the weak dependence of the parameter  $C_1$  on the nature of glasses  $C_1 \sim \text{const} \sim 35\text{--}40$  (Table 1) [2, 4] is explained by the approximate constancy of viscosities  $\eta_g$  and  $\eta_0$ :

$$C_1 = \ln\left(\frac{\eta_g}{\eta_0}\right).$$



**Fig. 1.** Temperature dependence of glass transition activation energy  $U(T - T_g)$  for sheet silicate glass: the symbols refer to experiment and the curve refers to calculations by formula (12).

It should be noted here that the rule of constancy of viscosity at  $T_g$ , according to modern research, is not always justified ([12]). Nevertheless, for most of the glasses studied, the values of  $T_g$  correspond to temperatures at which viscosity is in the range from  $10^{11}$  to  $10^{12}$  Pa s. The constancy of the high temperature viscosity limit  $\eta_0 \sim \text{const}$  also turns out to be very approximate. Therefore, relation (14) gives only the first rough approximation. The assessment of  $U_g$  by formula (13) is preferred.

Thus, to calculate  $U(T)$  in the glass transition region according to formula (12) it is necessary to know three quantities:  $C_1$ ,  $C_2$ , and  $T_g$ . The data on parameters  $C_1$ ,  $C_2$ , and the glass transition temperature  $T_g$  for many amorphous organic polymers are available in the book [2]; for inorganic glasses, in the monograph [4], which also describes one of the methods for determining  $C_1$  and  $C_2$ .

Figure 1 shows the temperature dependence of the glass transition activation energy for sheet silicate glass. The curve refers to the calculation by formula (12), and the symbols refer to the experimental data. The latter are obtained from the data on the viscosity log  $\eta(T)$  using Eq. (1), from which it follows

$$U = 2.3RT [\log \eta(T) - \log \eta_0]. \quad (15)$$

As you can see, the points lie on the calculated curve, which confirms the good applicability of the Williams–Landel–Ferry formula. Similar plots  $U(T)$  are constructed for a number of organic amorphous polymers (e.g., Fig. 2 for poly(vinyl acetate)). For some glasses and polymers Table 1 lists the values of parameters  $C_1$ ,  $C_2$  and  $T_g$  included in relation (12), as well as the value of  $U_g$  calculated by formula (13).

#### ON THE POSSIBILITY OF USING THE TAYLOR SERIES EXPANSION OF FUNCTION $U(T)$

It is of some interest to estimate the temperature dependence of the glass transition activation energy without specifying the function  $U(T)$ . One of these methods of calculating  $U(T)$  is presented below.

Let expand function  $U(T)$  near  $T_g$  in terms of a small increment of temperature  $(T - T_g)$  and restrict ourselves to the first three members of the series

$$U = U_g - D_1(T - T_g) + D_2(T - T_g)^2, \quad (16)$$

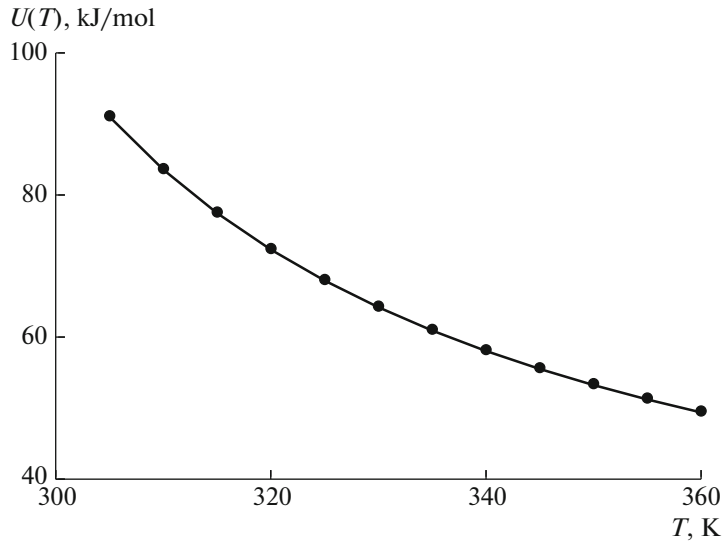
$$D_1 = -\left(\frac{\partial U}{\partial T}\right)_{T_g}, \quad (17)$$

$$D_2 = \frac{1}{2}\left(\frac{\partial^2 U}{\partial T^2}\right)_{T_g}. \quad (18)$$

In fact, the parameter of smallness in expansion (16) is still the dimensionless quantity  $\lambda = (T - T_g)/T_g$ , but  $T_g$  in the first and second degree is hidden in the coefficients  $D_1$  and  $D_2$ . Considering the viscosity in dependence (1) as a complex function of temperature, including derivatives (4) and (5), and using formulas (6) and (7), we express  $D_1$  and  $D_2$  through parameters  $C_1$ ,  $C_2$ , and the glass transition temperature  $T_g$  (Appendix):

$$D_1 = C_1 R \left( \frac{T_g}{C_2} - 1 \right), \quad (19)$$

$$D_2 = \frac{C_1}{C_2} R \left( \frac{T_g}{C_2} - 1 \right). \quad (20)$$



**Fig. 2.** Temperature dependence of glass transition activation energy  $U(T - T_g)$  for poly(vinyl acetate): the symbols refer to experiment and the curve refers to calculations by Eq. (12).

Coefficient  $D_2$  differs by  $C_2$  times from  $D_1$ . According to  $C_1$ ,  $C_2$ , and  $T_g$  and using formulas (16), (19), and (20) the temperature dependence of the glass transition activation energy can be calculated.

Coefficients  $D_1$  and  $D_2$  calculated by formulas (19) and (20) for sheet silicate glass and polyurethane were compared with the characteristics of curves  $U(T - T_g)$  obtained from the experimental data on the temperature dependence of viscosity (Table 2). The coefficients of curve  $U(T - T_g)$  as polynomials of the second degree were calculated by the fitting method at the fixed values of  $C_1$  and  $C_2$  (17.48 and 276.75, respectively) and using the Origin program (Fig. 3). In the

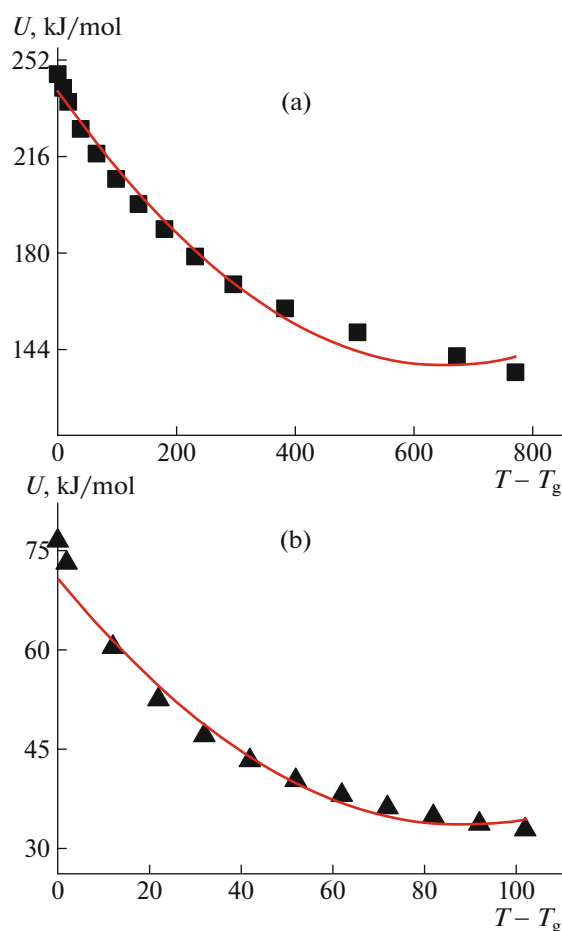
second case, the temperature dependence of the activation energy was described by a polynomial of the second degree, which allowed us to obtain the values of  $D_1$  and  $D_2$ . It was further taken into account that in a wide temperature range, the role of the cubic term in the Taylor series expansion of  $U$  may begin to manifest itself. Therefore, the temperature dependence of the activation energy was also interpreted as a polynomial of the third degree (Fig. 4), which somewhat changed the coefficient  $D_2$  (Table 2).

In general, within the framework of the approximation under consideration, a satisfactory agreement between the theoretical and experimental values of the coefficients is observed. The coincidence in all calcu-

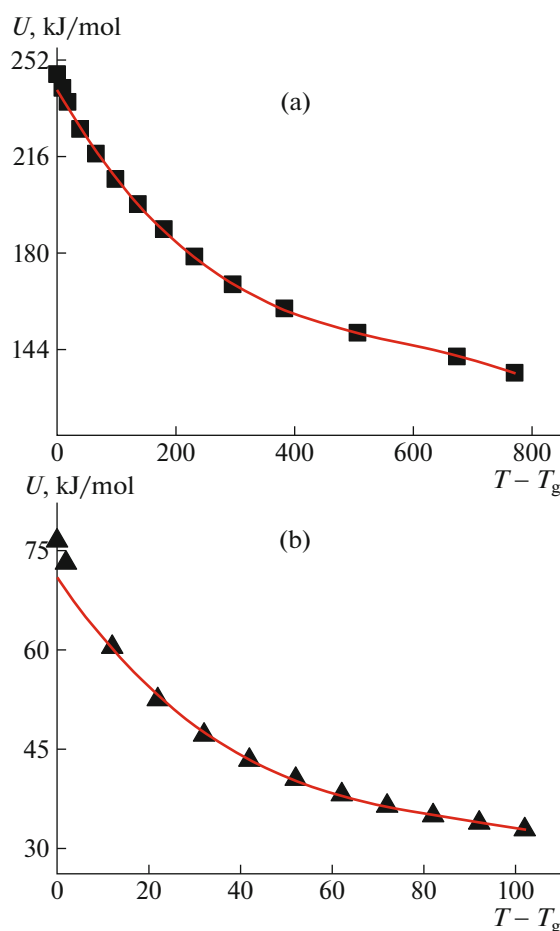
**Table 2.** Coefficients  $D_1$  and  $D_2$  calculated in different ways

Calculation method	$D_1$ , kJ/(mol K)	$D_2$ , kJ/(mol K <sup>2</sup> )
Sheet glass		
Using formulas (19) and (20) at $C_1 = 17.48$ and $C_2 = 276.75$	0.278	$10^{-5}$
Fitting of $U(T - T_g)$ at $C_1 = 17.48$ and $C_2 = 276.75$	0.325	$2.1 \times 10^{-4}$
Description of $U(T - T_g)$ by the second-degree polynomial	$0.314 \pm 0.012$	$2.400 \times 10^{-4} \pm 0.182 \times 10^{-4}$
Description of $U(T - T_g)$ by the third-degree polynomial*	$0.384 \pm 0.013$	$5.675 \times 10^{-4} \pm 0.538 \times 10^{-4}$
Polyurethane		
Using formulas (19) and (20) at $C_1 = 15.60$ and $C_2 = 32.60$	0.815	$25 \times 10^{-3}$
Fitting of $U(T - T_g)$ at $C_1 = 15.60$ and $C_2 = 32.60$	0.750	$4 \times 10^{-3}$
Description of $U(T - T_g)$ by the second-degree polynomial	$0.851 \pm 0.050$	$4.83 \times 10^{-3} \pm 0.60 \times 10^{-3}$
Description of $U(T - T_g)$ by the third-degree polynomial**	$1.022 \pm 0.117$	$1.018 \times 10^{-2} \pm 0.343 \times 10^{-2}$

\*  $D_3 = -3.198 \times 10^{-7} \pm 0.518 \times 10^{-7}$ ; \*\*  $D_3 = -3.773 \times 10^{-5} \pm 2.385 \times 10^{-5}$ .



**Fig. 3.** Description of the temperature dependence of the glass transition activation energy by the second degree polynomial for (a) sheet glass and (b) polyurethane: the symbols refer to experiment and the curves refer to calculations using the Origin program.



**Fig. 4.** Description of the temperature dependence of the glass transition activation energy by the third-degree polynomial for (a) sheet glass and (b) polyurethane: the symbols refer to experiment and the curves refer to calculations using the Origin program.

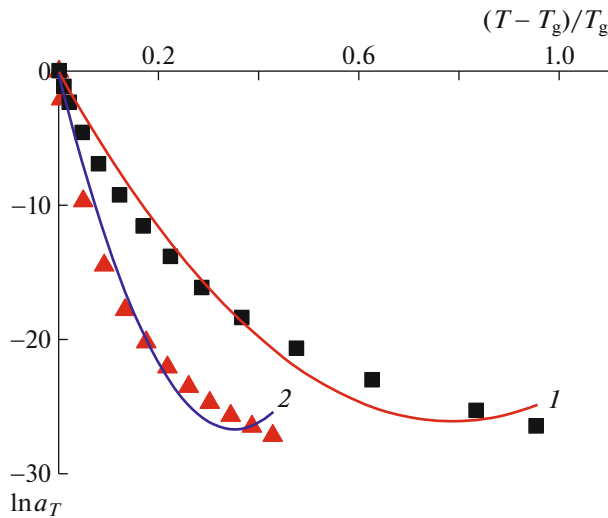
lations is better for  $D_1$  and worse for  $D_2$  (Table 2). This is because the calculations were carried out for a wide temperature range, where the approximations cease to be performed. Thus, the temperature dependence of the activation energy in a fairly wide temperature range is well described by the polynomial of the second degree.

#### ASSESSMENT OF THE TEMPERATURE AREA OF APPLICABILITY OF THE THEORETICAL DERIVATION OF THE WILLIAMS–LANDEL–FERRY FORMULA

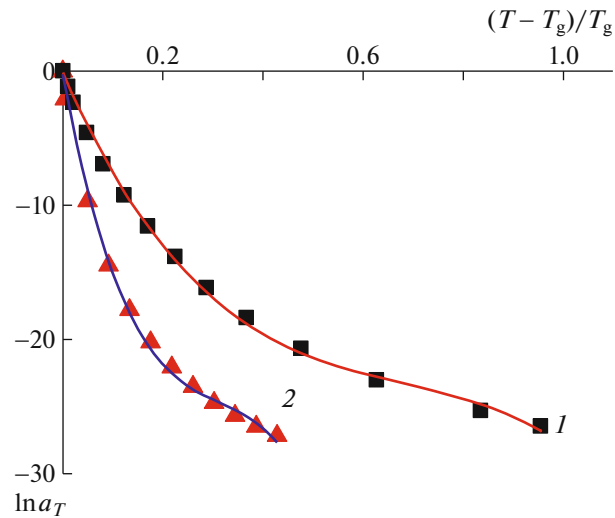
Obtaining the Williams–Landel–Ferry formula in the form of expression (3) suggested that such values of the smallness parameter  $\lambda = (T - T_g)/T_g$ , at which the modulus of the quadratic term in the Taylor series is at least an order of magnitude smaller than the modulus of the linear term were taken into account [8]. Then we

will estimate the values of  $\lambda$  for inorganic glass and polyurethane, for which the quadratic term is an order of magnitude smaller than the linear one.

Figure 5 shows the experimental dependences of  $\ln a_T$  on  $\lambda$  for the inorganic glass and polyurethane interpreted as the polynomial of the second degree. The same dependences are described by the polynomial of the third degree in Fig. 6. The coefficients of polynomial  $B_1$  and  $B_2$  are related to  $A$  and  $B$  defined by formulas (4) and (5) as  $B_1 = -A$  and  $B_2 = B$ . This expansion for the two materials under consideration has common features. The coefficients at  $\lambda$  in the first and second degree in both cases have the same order of magnitude with respect to modulus. The coefficient at  $\lambda^3$  is negative (like the coefficient at  $\lambda$  in the first degree). For the inorganic glass, its modulus is approximately the same in order of magnitude as the first coefficients of the series. For polyurethane, it is an order of magnitude smaller.



**Fig. 5.** Experimental dependences of  $\ln a_T$  on parameter  $\lambda = (T - T_g)/T_g$  for (1) inorganic glass and (2) polyurethane and their description by the polynomial  $y(x) = B_0 + B_1x + B_2x^2$ : the symbols refer to experiment and the curves refer to calculations. For glass  $B_0 = 0$ ,  $B_1 = -66.4 \pm 2.8$ , and  $B_2 = 42.2 \pm 3.6$ ; for polyurethane  $B_0 = 0$ ,  $B_1 = -151.6 \pm 7.2$ , and  $B_2 = 215.2 \pm 20.7$ .



**Fig. 6.** Dependences of  $\ln a_T$  on  $\lambda$  for (1) inorganic glass and (2) polyurethane and their description by the polynomial  $y(x) = B_0 + B_1x + B_2x^2 + B_3x^3$ : the symbols refer to experiment and the curves refer to calculations. For glass  $B_0 = 0$ ,  $B_1 = -84.7 \pm 2.1$ ,  $B_2 = 111.4 \pm 7.3$ , and  $B_3 = -54.5 \pm 5.7$ ; for polyurethane  $B_0 = 0$ ,  $B_1 = -201.7 \pm 5.9$ ,  $B_2 = 588.8 \pm 40.9$ , and  $B_3 = -626.6 \pm 67.7$ .

The obtained values of the expansion coefficients showed that the method of deriving the Williams–Landel–Ferry equation for inorganic glass presented in this work is valid at  $\lambda < 0.1$ , that is, at temperatures above  $T_g$  by approximately 80–90 K. In this temperature range, the derived relations between the coefficients and the Williams–Landel–Ferry formula itself should work quite well.

#### ON THE NATURE OF THE DEPENDENCE OF GLASS TRANSITION ACTIVATION ENERGY ON THE TEMPERATURE

The main 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, metal amorphous alloys, aqueous solutions, and chalcogenides, as is confirmed by the presence of universal equations and rules in the glass transition region [4, 9–11, 13–16].

However, for different classes of glasses the mobility of various kinetic units at  $T_g$  is frozen. The glass transition of linear amorphous organic polymers is a physical relaxation process associated with the loss of segmental mobility at the glass transition temperature, and the glass transition of inorganic glasses with a network structure is a chemical relaxation process and is related to the freezing of the process of switching

valence bonds of the silicon–oxygen–silicon type. The glass transition of densely crosslinked crosslinked polymers (e.g., epoxides) also has its own specifics.

The existence of universal laws of the liquid–glass transition means that the glass transition processes of different systems can be described by a general theory capable of predicting, for example, the nature of the evolution of the macroscopic properties of a system.

The creation of such a general theory of glass transition is an extremely difficult task, which is unlikely to be solved in the next few decades. The discussion on the nature of glass transition has a century-long history (reviews [13–16]). The outlined picture is clearly reflected in the existence of a large number of phenomenological approaches. Let us briefly consider one of them.

We come down from the idea that the physical cause of the sharp increase in the glass transition activation energy with decreasing temperature is the configurational change in the structure of the glass-forming melt [15, 17, 18]. Moreover, the microscopic nature of the configurational structural change is not disclosed. In the developed model of delocalized atoms [19–22], microscopic concepts (“energy of delocalization of an atom,” “elementary volume necessary for the ultimate displacement of an atom”) appear formally. However, the model as a whole is

phenomenological in nature and is applicable to various amorphous systems.

In the framework of this model, for glass-forming liquids, the glass transition activation energy (viscous flow) in Eq. (1) is the sum of two terms [14, 23]:

$$U = U_{\infty} + U_s(T), \quad (21)$$

where  $U_{\infty}$  is the potential of transition of the kinetic unit (atom, molecule) to a new local position and  $U_s(T)$  is the potential of the configurational change in the structure, which is a function of temperature:

$$U_s(T) = RT \left[ \exp\left(\frac{\Delta\epsilon_e}{RT}\right) - 1 \right], \quad (22)$$

where  $\Delta\epsilon_e$  is the energy of delocalization of the atom (its maximum displacement from the local equilibrium position). Atomic delocalization is related to the rearrangement of neighboring particles (short-range fluctuation) and reflects a local configurational change in the structure.

At elevated temperatures  $RT \gg \Delta\epsilon_e$  configurational structural change potential  $U_s(T) = 0$  and viscosity equation (1) taking into account expressions (21) and (22) describes the dependence with a constant activation energy  $U = U_{\infty}$ :

$$\eta = \eta_0 \exp\left(\frac{U_{\infty}}{RT}\right). \quad (23)$$

Thus, the value of  $U_{\infty}$  turns out to be the high-temperature limit of the activation energy of a viscous flow.

At low temperatures in the glass transition region, the atomic delocalization energy  $\Delta\epsilon_e$  is comparable with the energy of thermal vibrations of the lattice ( $\sim 3RT$ ), and the relative number  $N_e/N$  of delocalized atoms responsible for fluidity above  $T_g$  decreases according to law  $\exp(-\Delta\epsilon_e/kT)$  [14]. The structure of the melt becomes denser, and an activation jump of an atom to a new position requires a preliminary local configurational change (loosening) of the structure near it: the potential of configurational structural change  $U_s(T)$  increases dramatically. This explains the almost exponential increase in the activation energy of fluidity in the glass transition region.

The idea of separating the activation energy of fluidity into two components was expressed by Ya.I. Frenkel [24]. It was further developed by V.N. Filipovich and S.V. Nemilov [17, 18], as well as by the scientific school of the University of Sheffield [25–27], in which the two-exponential viscosity equation was obtained. With a more rigorous approach under  $U(T)$  one should understand the free activation energy [17, 18, 28, 29], as in the classic Eyring studies.

Thus, the configurational change in the structure described within the framework of the model of delocalized atoms is responsible for the temperature dependence of the glass transition activation energy (viscous flow) in the region of transition from a highly elastic state to a glassy one.

## CONCLUSIONS

For amorphous organic polymers and inorganic glasses, methods for calculating the temperature dependence of the glass transition activation energy are considered  $U(T)$ . This dependence is satisfactorily described near the values of  $T_g$  using the Williams–Landel–Ferry equation for viscosity (relaxation time). It is shown that there is a way to evaluate  $U(T)$  using the Taylor series expansion of function  $U(T)$  near the glass transition temperature. In a first approximation, it is enough to restrict ourselves to the linear and quadratic terms of the series. 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 of configurational structural change upon cooling of the glass-forming melt.

## APPENDIX

Let represent Eq. (1) as

$$\ln \eta = \ln \eta_0 + \frac{1}{RT} U, \quad (1.1)$$

$$U = U(T),$$

and take the derivative

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

According to equality (4), for parameter  $A$  we arrive at the relation

$$A = -\frac{\partial \ln \eta}{\partial(T/T_g)} \Big|_{T=T_g} \quad (1.2)$$

$$= -\frac{1}{R} \left[ \left( \frac{\partial U}{\partial T} \right)_{T_g} - \frac{U_g}{T_g} \right] = \frac{D_1}{R} + \frac{U_g}{RT_g},$$

which takes into account that the quantity  $D_1$  defined by derivative (17):

$$D_1 = -(\partial U / \partial T)_{T_g}.$$

From expressions (6) and (7) we obtain the following formula for parameter  $A$ :

$$A = \frac{C_1}{C_2} T_g. \quad (1.3)$$

Equating the right-hand sides of equalities (1.2) and (1.3), we arrive at the relation

$$D_1 = \frac{C_1 R T_g}{C_2} - \frac{U_g}{T_g}, \quad (1.4)$$

which given  $U_g = C_1 R T_g$  (expression (13)) is converted to Eq. (19) or

$$D_1 = U_g \left( \frac{1}{C_2} - \frac{1}{T_g} \right). \quad (19.1)$$

Formula (20) for the coefficient  $D_2$  we will find from the following calculations:

$$\begin{aligned} \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial (T/T_g)} &= \frac{T_g^2}{2} \frac{\partial}{\partial T} \left( \frac{\partial \ln \eta}{\partial T} \right) = \frac{T_g^2}{2R} \frac{\partial}{\partial T} \left[ \frac{1}{T} \frac{\partial U}{\partial T} - \frac{U}{T^2} \right] \\ &= \frac{T_g^2}{2R} \left\{ \frac{1}{T} \left( \frac{\partial^2 U}{\partial T^2} \right) - \frac{1}{T^2} \left( \frac{\partial U}{\partial T} \right) - \frac{1}{T^2} \left( \frac{\partial U}{\partial T} \right) + \frac{2U}{T^3} \right\}, \quad (1.5) \\ B &= \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial (T/T_g)} \Big|_{T=T_g} = \frac{T_g}{R} \left\{ D_2 + \frac{D_1}{T_g} + \frac{U_g}{T_g^2} \right\}. \end{aligned}$$

Here  $D_1$  and  $D_2$  are determined by derivatives (17) and (18). Further, in this relation for  $D_1$  we take into account expression (1.4). Then,

$$\begin{aligned} B &= \frac{T_g}{R} \left\{ D_2 + \frac{1}{T_g} \left( \frac{C_1}{C_2} R T_g - \frac{U_g}{T_g} \right) + \frac{U_g}{T_g^2} \right\} \\ &= \frac{T_g}{R} \left\{ D_2 + \frac{C_1 R}{C_2} \right\}. \quad (1.6) \end{aligned}$$

From expressions (7) and (1.3) we have

$$B = \frac{C_1}{C_2} T_g^2.$$

Substituting the parameter  $B$  from this formula to equality (1.6), we finally obtain Eq. (20) for  $D_2$ .

The same result can be observed by directly substituting series (16) in the formula for viscosity (1) and calculating the derivatives  $A$  and  $B$ .

The final expansion of the activation energy in the Taylor series is as follows:

$$\begin{aligned} U &= U_g \left[ 1 - \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) \right. \\ &\quad \left. + \frac{1}{C_2} \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g)^2 \right] \\ &= U_g \left\{ 1 - \left( \frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) \left( 1 - \frac{1}{C_2} \right) (T - T_g) \right\}. \quad (1.7) \end{aligned}$$

The quadratic term of the series can be neglected, if it is substantially less than the linear, that is,

$$\frac{1}{C_2} (T - T_g) \ll 1 \quad \text{or} \quad (T - T_g) \ll C_2. \quad (1.8)$$

For sheet inorganic glass, for example, this means requirement  $(T - T_g) \ll 277$  K; i.e., coefficient  $D_1$  can be determined by drawing a tangent to the curve  $U(T)$  20–30 degrees higher than the values of  $T_g$  and measuring the tangent of its angle. For polyurethane ( $C_2 = 32.6$  K) the corresponding temperature interval is much smaller. Further, using formula (19.1) according to  $D_1$  and  $T_g$  the coefficient  $C_2$  can be calculated (the value of  $U_g$  was estimated by formula (13)).

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