REVIEWS OF TOPICAL PROBLEMS

Relaxation aspects of the liquid–glass transition

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Contents

Abstract. Relaxation theories of the glass transition and viscous flow of glass-forming melts are presented. The focus is on modern representations of the glass transition equation $q\tau_g = \delta T_g$ that describes the appearance of a glassy state during cooling. Here, $q = dT/dt$ is the temperature change rate during melt cooling and τ_g is the relaxation time at the glass transition temperature T_g. Various methods for calculating the characteristic temperature band δT_g during the liquid–glass transition are considered. The generalized equation for the dependence of T_g on the melt cooling rate is derived. Based on the model of delocalized atoms, a modified kinetic glass transition criterion is discussed. A generalized viscosity equation for glass-forming liquids is derived.

Keywords: glass transition, amorphous polymers, inorganic glasses, metal amorphous melts, glass transition equation, viscosity, glass transition criterion, relaxation theories

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1. Introduction

The nature of the liquid–glass transition remains an urgent unsolved problem of the physics of condensed matter. On the one hand, the transition of an amorphous substance from a liquid state to a glassy solid has a pronounced relaxational, kinetic character [1–7], and on the other hand, the liquid–glass transition resembles a second-order phase transition in a number of fundamental features (see, e.g., [8–12]). This problem has been discussed beginning from the first half of the 20th century. After some quieting down, the discussion was revitilized, especially in the second decade of the 21st century [13–16].

The International Union of Pure and Applied Chemistry (UPAC) defines the glass transition as a second-order phase transition [17]. Molecular models have been proposed that consider the microscopic mechanisms slowing down the

structure relaxation at temperatures close to the glass transition temperature T_g and describe the liquid–liquid and liquid–glass transitions as phase transitions [18–26]. For example, Tournier discusses the transition at T_g using a change in the Gibbs free energy of a supercooled liquid as the driver of the liquid–glass transition. The classical change in the Gibbs free energy during crystallization was supplemented by a change in the enthalpy. This allowed Tournier to describe both the liquid–liquid and liquid–glass transitions. The Tournier model [18–21, 23] and models based on the percolation theory [22, 24–26] describe the jumps in the heat capacity and thermal expansion coefficient at T_g quite successfully. Experiments [29–31] showed that the glass transition has a thermodynamic nature, although it is kinetically controllable. The authors of [22, 24, 25, 27, 32–34] assume that the glass transition can belong to a class of critical phenomena generally called topological phase transitions. Nevertheless, in numerous theoretical and experimental studies [1–7, 38–48], the liquid–glass transition is regarded as a purely relaxational, kinetic process.

Unlike a crystal or liquid, a glassy solid is in the non-equilibrium state, which proves to be quite stable because its transition to the equilibrium state is restricted by a potential barrier. An example is fossil resins such as amber, retaining the amorphous structure for a few dozen million years. The density of glasses exposed to external action, in particular, annealing very slowly but continuously, increases due to the relaxation of the system volume to equilibrium.

This review is devoted to the discussion of modern aspects of the relaxation nature of the glass transition and the viscous flow of glass-forming liquids. New results obtained in the model of delocalized atoms are presented. The further development of this model is considered.

2. Bartenev approach

2.1 Empirical glass transition equation
Molecular rearrangements in the glass transition region become so slow (the structural relaxation time is so long) that the change in the structure has no time to follow the change in external parameters (temperature in the case under discussion). Therefore, it is natural that the glass transition temperature T_g depends on the cooling rate $q = \mathrm{d}T/\mathrm{d}t$ of the glass-forming melt. The smaller the cooling rate, the lower is the glass transition temperature.

These and other experimental data show that the glass transition is a relaxation process and obeys kinetic laws. The evolution of a glass-forming system depends on the rate of change of external parameters such as temperature and pressure and the time of system relaxation to the corresponding equilibrium state.

Thus, from the standpoint of the relaxation approach, the liquid–glass transition process critically depends on the relation between the structural relaxation time τ and the cooling rate q [5–7, 35–37].

In 1951, based on general considerations, Bartenev [37] proposed the kinetic glass transition criterion

$$q\tau_g = C, \tag{2.1}$$

where τ_g is the relaxation time at the glass transition temperature T_g and C is an empirical parameter with the dimension of temperature. Hereafter, we let q denote the absolute value $|q|$ of the temperature change rate during melt cooling or glass heating.

Relation (2.1), which is sometimes called the basic glass transition equation [38–40], is successfully used in the relaxation spectroscopy of polymers and glasses [39, 40] as the condition for realizing the structural relaxation transition at $T = T_g$, similarly to the criterion $\omega\tau = 1$ used in the case of mechanical relaxation, where ω is the circular frequency at which maximum mechanical losses are observed. Equation (2.1) is also used to describe other relaxation processes, for example, the thermally stimulated electric depolarization of amorphous polymers [39] ($q\tau_i = C_i$, where τ_i is the relaxation time of the ith process).

The transition of a liquid to the glassy state under cooling (and under the action of high pressure) is called the structural glass transition, while the transition from a viscous Newtonian liquid to an elastic glassy body under the action of a periodic mechanical force at a certain frequency v is called the dynamic (sometimes, mechanical) glass transition [39]. Bartenev equation (2.1) is the condition for realizing the structural glass transition, similar to the dynamic glass transition criterion at a temperature T_v [39, 41]

$$2\pi v\tau_g = 1. \tag{2.2}$$

Eliminating the relaxation time τ_g from (2.1) and (2.2), we can obtain the frequency $v = v_{equiv}$ equivalent to a given cooling rate q [39],

$$v_{equiv} = \frac{1}{2\pi C}\, q. \tag{2.3}$$

For $C = q\tau_g$, this equality transforms into the more convenient known relation [41]

$$v_{equiv} = \frac{1}{2\pi\tau_g}. \tag{2.4}$$

The structural relaxation time τ_g at the glass transition temperature of inorganic glasses is of the order of [38–40, 42]

$$\tau_g \approx (1-2) \times 10^2 \text{ s}. \tag{2.5}$$

In particular, for sodium–silicate glasses [36] (see also Table 4 in Section 9),

$$\tau_g = (160-240) \text{ s}. \tag{2.6}$$

From (2.4), we then have the equivalent frequency

$$v_{equiv} \approx 10^{-3} \text{ Hz}$$

for these glasses.

The last result means that the dynamic glass transition temperature T_v coincides with the structural glass transition temperature T_g only at low frequencies of the order of 10^{-3} Hz: the structural and dynamic glass transitions occur simultaneously and the structural (topological) and viscous deformation components are frozen simultaneously [39].

2.2 Dependence of the glass transition temperature on the melt cooling rate
The dependence of the glass transition temperature on the melt cooling rate is the most important problem in the glassy state theory. This problem is also important for practical

Table 1. Parameters of Bartenev–Ritland* equation (2.8) and the fraction f_g of the fluctuation volume at the glass transition temperature [44, 45].

Glass	T_g, K	$a_1 \times 10^3$, K^{-1}	$a_2 \times 10^5$, K^{-1}	a_2/a_1	$a_1/a_2 + 2.9$	f_g [see Eqn (11.4)]
Rosin	313	3.098	8.3	0.027	40	0.025
Polystyrene	345	2.78	9.0	0.032	34	0.029
PMMA**	349	2.75	8.9	0.032	34	0.029
SKS rubber	208	4.62	15.0	0.032	34	0.029
SKN-18 rubber	218	4.41	13.2	0.030	36	0.028
SKN-40 rubber	246	3.90	12.0	0.031	35	0.028
Ebonite	349	2.72	9.6	0.035	31	0.032
Boric anhydride	534	1.81	5.6	0.031	35	0.028
Silicate glasses***						
No. 1	714	1.34	4.28	0.032	34	0.029
No. 2	744	1.29	4.24	0.033	33	0.030
No. 3	809	1.19	3.60	0.030	36	0.028
No. 4	885	1.086	3.33	0.031	35	0.028
No. 5	1025	0.94	2.67	0.028	39	0.026

  * Values of a_1 and a_2 correspond to the case of the decimal logarithm ($\log q$) in Bartenev equation (2.8).
  ** Polymethyl methacrylate.
*** Composition of silicate glasses (mass.%). No. 1: SiO_2 — 55.3, Na_2O — 3.8, K_2O — 9.2, PbO — 30, Al_2O_3 — 1.7;
No. 2: SiO_2 — 38.1, Na_2O — 1.3, K_2O — 2.5, PbO — 52, Al_2O_3 — 3.4, B_2O_3 — 1.8, CaO — 0.5, MgO — 0.4;
No. 3: SiO_2 — 70.9, Na_2O — 16.1, K_2O — 0.6, CaO — 8.1, MgO — 2.9, other oxides — 1.4;
No. 4: SiO_2 — 56, Na_2O — 10.1, CaO — 17, MgO — 4, Al_2O_3 — 11, B_2O_3 — 2;
No. 5: SiO_2 — 57.6, CaO — 7.4, MgO — 8, K_2O — 2, Al_2O_3 — 25.

applications, for example, for the development of the optimal glass-annealing regime.

Substituting the relaxation time τ_g from the known expression

$$\tau = \tau_0 \exp\left(\frac{U}{RT}\right) \qquad (2.7)$$

in the glass transition equation with $T = T_g$ and $\tau = \tau_g$, Bartenev [37] obtained the dependence of the glass transition temperature on the cooling rate:

$$\frac{1}{T_g} = a_1 - a_2 \ln q, \qquad (2.8)$$

$$a_1 = \frac{R}{U} \ln\left(\frac{C}{\tau_0}\right), \qquad (2.9)$$

$$a_2 = \frac{R}{U}, \qquad (2.10)$$

where a_1 and a_2 are empirical constants, τ_0 is the vibrational period of a molecule, U is the activation energy of the glass transition process, R is the universal gas constant, and C is the parameter of glass transition equation (2.1). Equation (2.8) was derived assuming that U is a constant independent of temperature,

$$U = \text{const}.$$

In 1954, three years later, based on different initial assumptions, Ritland [43] proposed the same relation (2.8). Relation (2.8) is often called the Bartenev–Ritland equation [1, 2].

The glass transition temperature is measured both in the heating regime during glass softening and in the glass-forming melt cooling regime. It has been found that although the values of T_g obtained in these regimes are somewhat different, the dependence of the glass transition temperature on the heating rate is approximately the same

as the dependence of T_g on the cooling rate. Bartenev verified dependence (2.8) using a thermal expansion curve in the course the heating of a silicate glass and also a hardening curve in the course of cooling this glass [37]. Experimental points in both regimes lie on a straight line in coordinates $(1/T_g, \lg q)$, which agrees with Eqn (2.8). The linear dependence of $1/T_g$ on $\lg q$ is observed for a variety of glasses [38, 44–47], including metal glasses [48].

At the same time, some glasses revealed a deviation from Bartenev–Ritland equation (2.8) at sufficiently high heating (cooling) rates [45].

The dependence $T_g(q)$ was systematically investigated in a broad heating rate range from 0.2 to 50 K min^{-1} in [44, 45]. The authors of these papers studied various amorphous materials: rosin, ebonite, organic amorphous polymers, and silicate glasses with glass transition temperatures in the range 208–1025 K (Table 1). The validity of Bartenev equation (2.8) was confirmed with rare exceptions.

The ratio of parameters a_1 and a_2 was found to be practically constant ($a_2/a_1 \approx 0.03$) for various amorphous materials (see Table 1):

$$\frac{a_2}{a_1} \approx \text{const} \approx 0.027 - 0.035. \qquad (2.11)$$

Table 2 presents the results of our study of oxygen-free $Se-Ga$, $Se-Bi$, $In-Se$, and $As-Sb-Se$ glasses. Data from the SciGlass database were used [49]. The dependence of $1/T_g$ on $\ln q$ proved to be linear (Fig. 1), confirming the applicability of Eqn (2.8) to these systems. Oxygen-free glasses reveal the same properties as oxide glasses do: $a_2/a_1 \approx 0.028 - 0.034$. Only $In-Se$ glass deviates in its properties from the general picture.

Bartenev and Luk'yanov studied the dependence of the glass transition temperature of amorphous materials on the heating rate using the method of thermal linear expansion [45]. Circular rod samples 4 mm in diameter and 50 mm in length were placed into the middle part of a tubular electric oven 500 mm in length. The temperature along the sample was constant to within a degree. The temperature

Table 2. Parameters of Bartenev–Ritland equation (2.8) and the fraction f_g of the fluctuation volume for oxygen-free and oxide glasses [49].

Glass	T_g, K	$a_1 \times 10^3$, K^{-1}	$a_2 \times 10^5$, K^{-1}	a_2/a_1	f_g [see (11.4)]
Se – Bi	309	3.12	10.45	0.034	0.031
Se – Ga	315	3.09	9.29	0.030	0.027
In – Se	316.7	3.09	5.54	0.018	0.017
As – Sb – Se	444.8	2.15	6.74	0.031	0.028
GeO$_2$	762	1.23	3.45	0.028	0.026
P$_2$O$_5$ – TeO$_2$	578	1.67	4.99	0.030	0.027
SiO$_2$ – Al$_2$O$_3$ – B$_2$O$_3$ – P$_2$O$_5$ – MgO – Na$_2$O – K$_2$O	1064	0.89	3.20	0.036	0.032
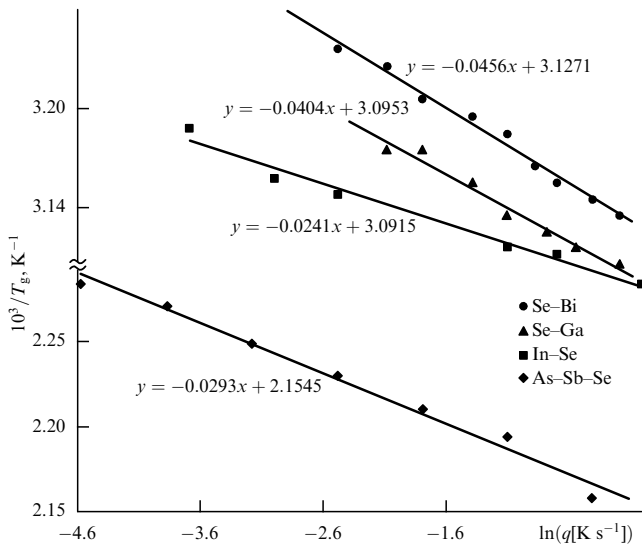
Figure 1. Dependences of the glass transition temperature on the heating rate for oxygen-free glasses in coordinates $(1/T_g, \ln q)$. The content of Se/Be (mol.%): 77.28/22.72; Se/Ga (mol.%): 95.56/4.44p In/Se (mol.%): 7.11/92.89; As/Sb/Se (mol.%): 32.91/7.64/59.45 [49].

measurement error was 0.5 K for polymers and 1 K for silicate glasses. The accuracy of the sample elongation measurement during its expansion was 1–2 μm. To exclude the influence of the thermal prehistory, carefully annealed samples were used. Bartenev and Gorbatkina [44] studied the dependence of the glass transition temperature of rubbers on the cooling rate. The sample length was measured with an accuracy of 1.5–2.0 μm. The cooling rate was varied from 0.3 to 30 K min^{-1}.

3. Mandelstam–Leontovich theory

In the approach based on nonequilibrium thermodynamics [50, 51], along with parameters characterizing the state of a system in classical equilibrium thermodynamics, the non-equilibrium states are described by introducing additional internal (structural) order parameters. The analysis of the liquid–glass transition from these positions is the development of concepts formulated by Bragg and Williams [52] in 1934 and Mandelstam and Leontovich [41] in 1937.

To describe the liquid–glass transition or, conversely, glass softening, at least one additional internal parameter ξ is introduced, describing the system transition to nonequilibrium [41]. If the system state in the equilibrium is completely determined by two independent variables, the pressure p and the temperature T, the equilibrium value of the parameter $\xi = \xi^e$ has the form

$$\xi = \xi^e(p, T).$$

But if p and T change, then ξ reaches a new equilibrium value not instantly but at some finite rate, and hence $\xi \neq \xi^e$. In such a nonequilibrium process, the parameter ξ is a new independent variable determining the system state. For example, a change in ξ can result in a change in the system volume V. Then the state equation takes the form

$$V = V(p, T, \xi).\qquad(3.1)$$

If the parameter ξ is expressed in terms of the 'internal' entropy increment corresponding to the irreversible process of establishing equilibrium,

$$T \, dS_{\text{int}} = \varphi \, d\xi,$$

then, for example, the differential of the thermodynamic Gibbs potential takes the form

$$d\Phi = S \, dT + V \, dp - \varphi \, d\xi, \quad \varphi = -\left.\frac{d\Phi}{d\xi}\right|_{p,T}.$$

Furthermore, to make the thermodynamic equations closed, it is necessary to introduce the relaxation equation for ξ, which has the form [41]

$$\frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi^e),\qquad(3.2)$$

for small deviations from equilibrium, where τ is the system relaxation time.

Thus, the description of the relaxation process involves the proper choice of the parameter ξ characterizing the nonequilibrium structure of matter in the glass transition region and the formulation of system relaxation equations.

The best known theories are those in which the internal parameter ξ is the fraction n_2 of particles in the excited state (Volkenstein–Ptitsyn [6, 7] and Gotlib–Ptitsyn [53] theories), a fictitious temperature T^* [54], and the free volume fraction f [55].

A periodic (sinusoidal) mechanical action on an equilibrium liquid by a sound wave with a circular frequency ω was considered in [41]. This action produces local overdense and rarefied regions characterized by the density deviation $\Delta\rho$ from its mean value in the system, and deviations of the temperature ΔT and the structural parameter $\Delta\xi$ from their equilibrium values.

The Mandelstam–Leontovich theory [41] has a rigorous physical basis and is mathematically clearly formulated in terms of the response of the system properties to an external action. In addition, systems of equations of nonequilibrium thermodynamics are derived from this theory (see review [56]).

Following [35], we consider how, based on the Mandelstam–Leontovich theory, a relation can be derived between

the melt cooling rate q and the structure relaxation time τ_g at the temperature T_g [in the form of an expression similar to Bartenev equation (2.1)].

A relation from the Mandelstam–Leontovich theory describing the appearance of the solid-like state of a liquid can be written in the form [41]

$$P = P_\infty \pm \frac{\Delta P}{1 + \omega\tau} \ . \tag{3.3}$$

Here, P_∞ is the value of a property P corresponding to the solid state of the liquid, ω is the circular frequency of the external action (in the general case, the operator $\partial/\partial t$ determining the time dependence of the external action), and ΔP is the contribution to the property due to structural relaxation changes (the relaxation contribution).

Because the solid-like behavior of a liquid, according to modern concepts, corresponds to the glassy state, this theory is also applicable to describing this state. The condition of the liquid–glass transition in this version of the kinetic glass transition theory [35] is equality (2.2),

$$\omega\tau_g = 1 \ . \tag{3.4}$$

According to relation (3.3), the transition from the equilibrium liquid to glass occurs not at the point T_g but within some temperature interval. We assume that temperature changes by the sinusoidal law

$$T = \Delta T_0 \sin(\omega t) \ . \tag{3.5}$$

A part of the sinusoid can be regarded as a linear dependence of T on t in a wide enough time interval. The temperature change in this time interval is approximately ΔT_0 [35].

The temperature change rate can be found by differentiating relation (3.5) with $\omega = \mathrm{const}$,

$$\frac{dT}{dt} = \Delta T_0 \omega \cos(\omega t) \ .$$

Then, for ωt equal to an integer multiple of π (within the specified range of ωt), we have $|\cos(\omega t)| \equiv 1$. This gives

$$\omega = (\Delta T_0)^{-1} \frac{dT}{dt} = \frac{q}{\Delta T_0} \tag{3.6}$$

with $q = dT/dt$. This equality coincides with relation (2.3) for $C = \Delta T_0$, where C is the empirical parameter of Bartenev equation (2.1) with the dimension of temperature.

Substituting ω from (3.6) in glass transition condition (3.4), we obtain a relation between the melt cooling rate q and the structural relaxation time τ_g at the temperature T_g [35],

$$|q|\tau_g = \Delta T_0 \ , \tag{3.7}$$

which can be regarded as a substantiation of glass transition equation (2.1). Here, ΔT_0 is a scale factor that allows the linear temperature change in the interval ΔT_0 to be approximately considered as a part of a stretched periodic process with the frequency ω. Because the external action with the frequency ω produces no changes in the system outside the glass transition interval ΔT_g, ΔT_0 is the temperature interval where the glass transition occurs.

Indeed, at high temperatures, when the relaxation time is small and periodic variations ΔT_0 do not satisfy condition (3.6), the liquid is in the metastable state and no local variations in T are manifested in its properties; because the state is not frozen, all regions of the system return to equilibrium: the condition $\tau\omega < 1$ holds. The structure relaxation time τ is smaller than the period $1/\omega$ of the mechanical action ($\tau < 1/\omega$) and the liquid has the time $1/\omega$ to return to the equilibrium state. At low temperatures, the condition $\tau\omega > 1$ is satisfied because of a large relaxation time, and periodic variations ΔT_0 do not return the system to the metastable liquid state. During the time $1/\omega$ of mechanical action, the liquid structure has no time to relax to equilibrium. In the intermediate temperature interval, when the system temperature decreases and corresponds to the condition $\omega\tau_g = 1$, the system is in the frozen state, which does not pass into the metastable liquid state upon decreasing the thermodynamic temperature.

4. Volkenstein–Ptitsyn relaxation theory

Volkenstein and Ptitsyn [6, 7] developed a rigorous physical theory for studying the behavior of kinetic units that can exist in two states with different energies separated by an energy barrier. The energy of excited state 2, populated with a fraction of particles n_2, exceeds the energy of ground state 1 with the fraction of particles n_1 by $\Delta E = U_1 - U_2$, where U_1 and U_2 are kinetic barriers for the respective $1 \to 2$ and $2 \to 1$ transitions.

The kinetic equation for such a system has a form similar to Eqn (3.2),

$$\frac{dn_2}{dT} = -\frac{1}{q\tau}(n_2 - n_{20}) \ , \tag{4.1}$$

where n_{20} is the equilibrium value of n_2 and τ is the relaxation time. The solution of Eqn (4.1) and rather time-consuming mathematical analysis show that the value of n_2 is frozen at some temperature T_g, which means that the glass transition occurs.

The glass transition temperature T_g satisfies the equation

$$\left.\frac{d\tau}{dT}\right|_{T=T_g} = -\frac{1}{|q|} \ . \tag{4.2}$$

It follows from the theory that the equilibrium balance of particles changes considerably only in a very narrow temperature interval. This is manifested in the fact that the annihilation rate of active particles passes through a maximum upon cooling within this interval and decreases with time to zero.

The criterion for glass transition during cooling is obtained by solving for the maximum of the function describing the structure freezing rate,

$$|q|\tau_g = \frac{1}{\Psi(T_g)} \ . \tag{4.3}$$

Here, $[\Psi(T_g)]^{-1}$ is defined in [35] as the temperature interval of the liquid–glass transition under cooling.

The Volkenstein–Ptitsyn theory [6, 7] describes the known experimental properties of the glass transition process: the dependence of T_g on q and breaks in the curves of the temperature dependences of the volume and enthalpy at $T = T_g$. The theory describes hysteresis phenomena during the glass transition.

We note that relation (4.3) coincides with glass transition equations (2.1) and (3.7).

5. Configuron percolation theory

Structural rearrangements appearing in an amorphous material during the glass transition result in characteristic jumps in the derivatives of thermodynamic quantities such as the thermal expansion coefficient. This is why the glass transition was considered a second-order phase transition. In experiments, these jumps (bends) allow finding T_g for typical heating (cooling) rates. Figure 2 illustrates this with an example of the temperature dependence of the linear expansion coefficient of glass. The thermal expansion coefficient (TEC) strongly increases as the temperature approaches T_g, reaches a maximum at T_g, and then rapidly decreases; a sharp peak is thus formed, as is demonstrated in Fig. 2 by the temperature dependence of the TEC deviation from its value in the glassy state. In the configuron percolation theory (CPT), the glass–liquid transition is regarded as a threshold effect in which percolation occurs through broken chemical bonds called configurons. The glass transition temperature is [24, 25, 32–34]

$$T_g = \frac{H_d}{S_d + R \ln\left[(1 - f_c)/f_c\right]} , \qquad (5.1)$$

where H_d and S_d are the quasi-equilibrium configuron (broken bonds) formation enthalpy and entropy and f_c is the critical fraction of space occupied by configurons under percolation (the percolation threshold). Melts like SiO_2 have a percolation threshold equal to the universal Sher–Zallen threshold $f_c = \vartheta_c$, where $\vartheta_c = 0.15 \pm 0.01$, whereas complex materials are characterized by different thresholds $f_c \ll \vartheta_c$ [32–34]. However, the glass–liquid transition is kinetically controlled and has a certain temperature range. This is illustrated in Fig. 3 according to the CPT, explaining the dependence of T_g on the cooling rate by the relaxation of configurons (the involvement of a large volume of matter during bond breaking). A larger radius of a configuron efficiently reduces the percolation threshold because the time of relaxation processes in the system
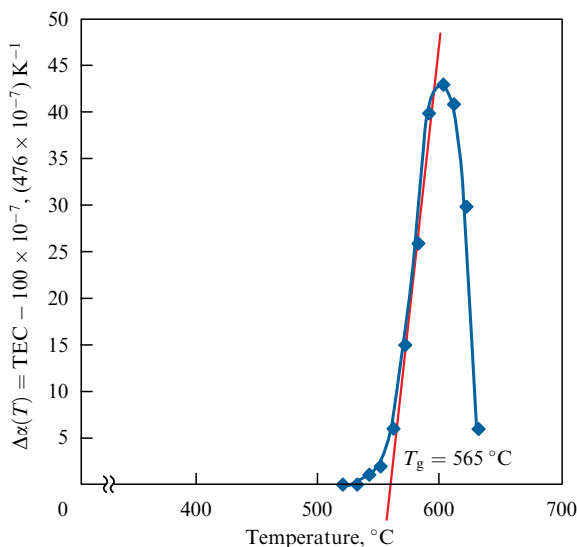

Figure 2. Temperature dependence of the deviation $\Delta\alpha(T)$ of the thermal expansion coefficient (TEC) from its value in the glassy state for a high-alkaline silicate $60\,SiO_2 - 10\,B_2O_3 - 3\,Al_2O_3 - 20.5\,ZrO_2 - 20\,Na_2O$ glass used for nuclear waste immobilization. $T_g = 565\,°C$.
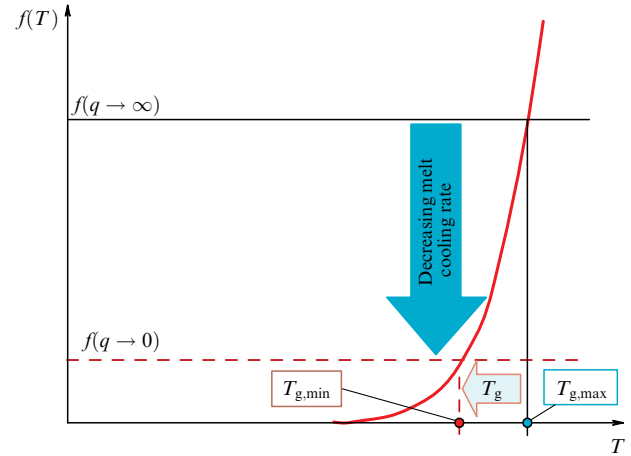

Figure 3. Effective decrease in the confuguron percolation threshold as the melt cooling (glass heating) rate decreases and T_g decreases accordingly [32].

increases as the cooling rate is decreased [32]. Thus, the percolation threshold is maximal when the temperature change rate is maximal and decreases as the cooling rate decreases.

Indeed, the dissociation of bonds is always caused by local rearrangements of the atomic-vibration centers when an instant bond break leads to the formation of a non-equilibrium configuron with a small initial volume V_d, which then gradually evolves into the relaxed volume V_c. This results in the dependence of the glass transition temperature on the cooling rate of the form

$$\frac{1}{T_g} = \frac{S_d}{H_d} + \frac{\left[\ln\left(1/\vartheta_c\right) + \ln\left((V_c - V_d)/V_d\right)\right] R}{H_d} - \frac{mR}{H_d} \ln \frac{q}{q_0} , \qquad (5.2)$$

where q_0 is a standard cooling rate introduced for obtaining a dimensionless quantity in the logarithm. The index $m < 1$ is the exponent in the Rayleigh–Plesset equation for the bubble dynamics in liquid ($m = 2/3$ for B_2O_3) [32]. Equation (5.2) coincides with Bartenev–Ritland equation (2.8), demonstrating their agreement. In the CPT framework, the coefficients a_1 and a_2 in the Bartenev–Ritland equation become

$$a_1 = \frac{S_d}{H_d} + \frac{R}{H_d}\left(\ln \frac{1}{\vartheta_c} + \ln \frac{V_c - V_d}{V_d}\right), \qquad (5.3)$$

$$a_2 = \frac{mR}{H_d} . \qquad (5.4)$$

A comparison of (2.10) and (5.4) shows that the activation energy of the glass transition process is determined by the ratio of the chemical-bond dissociation enthalpy and the exponent m:

$$U = \frac{H_d}{m} . \qquad (5.5)$$

Therefore, the relaxation activation energy is higher than H_d, because the Raylegh–Plasset exponent is smaller than unity. We note that a_1 and a_2 are inversely proportional to H_d. Thus, there is a linear correlation between a_1 and a_2, which corresponds to experimental data (see Table 1).

6. Glass transition equation.
The value of the product $q\tau_g$ of the cooling rate and the structural relaxation time

Given the coincidence of relations (3.7) and (4.3) obtained in classical glass transition theories [6, 7, 41], Nemilov [35] introduced the common notation

$$\Delta T_0 \equiv \frac{1}{\Psi(T_g)} = \delta T_g$$

for the right-hand sides of these equalities. Then the relation between the cooling rate q and the structural relaxation time τ_g is described by the general glass transition equation [35]

$$q\tau_g = \delta T_g, \tag{6.1}$$

which determines the appearance of a glassy state at the temperature T_g under cooling. According to [35], "the right-hand side of Eqn (6.1) is a scale factor introducing the temperature change value corresponding to a certain change in the relaxation time required for obtaining glass."

This equation is the most important result following from the Mandelstam–Leontovich [41] and Volkenstein–Ptitsyn [6, 7] relaxation theories. The detailed investigation of this relation in the future is of interest.

First of all, it is necessary to find methods for calculating "the temperature range δT_g characterizing the liquid–glass transition interval during cooling" [35]. We note that δT_g is not the 'macroscopic' glass transition interval ΔT_g itself, which is defined as the temperature region in the vicinity of T_g where physical properties (volume, enthalpy, heat capacity, etc.) drastically change. It can be expected from general considerations that δT_g is within ΔT_g, but their equality follows from nowhere.

The glass transition temperature T_g is experimentally found as the coordinate of the intersection point of extrapolated temperature dependences of the glass and glass-forming melt properties. However, the problem of accurately determining the beginning and end (boundaries) of the glass transition interval ΔT_g remains unsolved (see review [1]).

Because the glass transition temperature depends on the cooling rate q, some researchers [38–40, 45] proposed the concept of a standard cooling rate,

$$q = 3 \text{ K min}^{-1} = 0.05 \text{ K s}^{-1}, \tag{6.2}$$

used in glass technology. In glass and polymer dilatometry, in fact, in all countries, cooling rate (6.2) is typically used. Because of the weak (semi-logarithmic) dependence of T_g on q, small deviations of q from the standard value do not strongly affect the value of T_g, with rare exceptions. When q is changed by a factor of 10, the glass transition temperature shifts only slightly by $\Delta T = 0.03T_g$ [38, 45]. Therefore, it is usually assumed that most of the data on T_g are related to the standard cooling rate. In this review, we use experimental data obtained for the standard cooling (heating) rate. The data for other values of q are scarce.

The structural relaxation time values in (2.5) and (2.6) for inorganic glasses, $\tau_g \approx 100-240$ s, correspond to the standard melt cooling rate [36–40, 42]. Hence, for the standard cooling rate $q = 0.05$ K s^{-1} and relaxation time $\tau_g \approx 100-250$ s, the product $q\tau_g$ in the left-hand side of glass transition equation (6.1) for inorganic (in particular, silicate)

glasses is approximately

$$q\tau_g \approx 5-12 \text{ K}. \tag{6.3}$$

Therefore, for the temperature range δT_g in the right-hand side of glass transition equation (6.1) under standard conditions, we should expect approximately the same values $\delta T_g \approx 5-12$ K.

7. Estimate of the glass transition temperature band δT_g

7.1 Bartenev calculation method

Because the commonly accepted theoretical expression describing the peculiar temperature dependence of the structural relaxation time $\tau(T)$ in the glass transition region is absent, Volkenstein and Ptitsyn [6, 7] considered only the simplest case, assuming that in the first approximation this dependence is described by a usual exponential: Frenkel equation (2.7).

By substituting $\tau(T)$ from Eqn (2.7) in glass transition condition (4.2) for $U = $ const, Volkenstein and Ptitsyn obtained the relation [6, 7]

$$q\tau_g = \frac{RT_g^2}{U}, \tag{7.1}$$

coinciding with glass transition equation (6.1). In this approximation, the parameter in Eqn (6.1) acquires the physical sense

$$\delta T_g = \frac{RT_g}{U}T_g. \tag{7.2}$$

Bartenev [38, 45] used relation (7.2) to calculate the parameter C of his Eqn (2.1). We now replace C by δT_g because $C = \delta T_g$. The ratio RT_g/U was determined from the relaxation time equation (2.7) for $T = T_g$,

$$\frac{RT_g}{U} = \frac{1}{\ln(\tau_0/\tau_g)} \approx \text{const} \approx 0.03,$$

where $\tau_0 \approx 10^{-12}$ s and $\tau_g \approx 10^2$ s. Taking (7.2) into account, we obtain the relation

$$\delta T_g \approx 0.03T_g \tag{7.3}$$

for calculating δT_g from the glass transition temperature data. The estimate for inorganic silicate glasses ($T_g \approx 800$ K) using this expression gives the approximate value

$$\delta T_g \approx 20 \text{ K}, \tag{7.4}$$

which considerably exceeds the product $q\tau_g \approx 5-10$ K [see (6.3)].

In our opinion, the overstated value in (7.4) is caused by the assumption made in the derivation of (7.1) that the glass transition activation energy is constant ($U = $ const). It is known that U drastically increases at temperatures close to T_g [3–5]. It is easy to see that by repeating the procedure presented above with the temperature dependence of the activation energy $U(T)$ taken into account, we can obtain, instead of (7.1), the glass transition equation in which the parameter δT_g is [15]

$$\delta T_g = \frac{RT_g^2}{U_g}\left[1 - \frac{T_g}{U_g}\left(\frac{dU}{dT}\right)_{T=T_g}\right]^{-1}. \tag{7.5}$$

Table 3. Calculations of the temperature band δT_g for silicate glasses and amorphous polymers using various methods*.

Glass (glass composition, mol.%)	T_{12}, K	T_{13}, K	δT_g, K (7.15)	δT_g, K (7.17)	$\delta T_g = C_2/C_1$, K (7.8)	C_1	C_2, K	τ_g, s
Sodium-silicate $Na_2O - SiO_2$ glasses [49]								
15 $Na_2O - 85$ SiO_2	819	790	29	13	12	36	430	239
20 $Na_2O - 80$ SiO_2	792	766	26	11	11	36	390	217
25 $Na_2O - 75$ SiO_2	769	745	24	10	10	35	355	202
30 $Na_2O - 70$ SiO_2	749	727	22	10	9	35	322	184
33 $Na_2O - 67$ SiO_2	738	717	21	9	9	35	304	174
35 $Na_2O - 65$ SiO_2	726	705	21	9	8	35	291	166
Window glass** [40]	846	825	21	9	8	36	305	160
Polyalkali silicate glasses [62]								
69.04 $SiO_2 - 30.96$ Na_2O	736	718	18	8	7	46	340	147
79.29 $SiO_2 - 12.97$ $Na_2O - 7.75$ Li_2O	700	683	17	7	7	45	315	140
43.22 $SiO_2 - 9.55$ $Na_2O - 47.23$ CsO	721	704	17	7	6	31	200	129
71.59 $SiO_2 - 24.4$ $Na_2O - 4.01$ Li_2O	695	681	14	6	6	36	231	128
Amorphous polymers [58]								
Polyisobutylene	—	202	6	—	2.7	38	104	54
Polyvinyl acetate	—	305	9	—	1.3	36	47	26
Polyvinyl chloroacetate	—	296	9	—	1.0	40	40	20
Polymethyl methacrylate	—	276	8	—	1.1	42	45	22
Polyurethane	—	238	7	—	0.9	36	33	18
Natural rubber	—	300	9	—	1.4	38	54	57
Methacrylate polymers:								
ethyl	—	335	10	—	1.6	40	65	32
n-butyl	—	300	9	—	2.5	39	97	50
n-octyl	—	253	8	—	2.9	37	107	58

* $\tau_g = C_2/(qC_1)$, C_1 and C_2 are parameters of the Williams–Landel–Ferry equation, $q = 0.05$ K s^{-1}.
** Window glass composition (weight %) [40]: SiO_2 — 72.7, CaO — 8.6, MgO — 3.4, Al_2O_3 — 1.3, Na_2O — 13.6, K_2O — 0.4.

Here, U_g is the activation energy of the glass transition process at the glass transition temperature. The derivative $(dU/dT)_{T_g}$ is negative because the activation energy increases $(dU > 0)$ under cooling $(dT < 0)$. Therefore, the expression in square brackets in the right-hand side of (7.5) is greater than unity and hence the estimate using expression (7.2) is overstated.

7.2 Calculation of δT_g from the Williams–Landel–Ferry equation
As mentioned above, simple exponential dependence (2.7) for $U = $ const does not work in the glass transition region. Therefore, empirical equations were proposed to implicitly take the temperature dependence of the glass transition activation energy $U(T)$ into account. Among them, the Williams–Landel–Ferry (WLF) equation [57, 58],

$$\ln a_T = -C_1 \frac{T - T_g}{T - T_g + C_2}, \qquad a_T = \frac{\tau(T)}{\tau(T_g)} \cong \frac{\eta(T)}{\eta(T_g)}, \quad (7.6)$$

for the relaxation time $\tau(T)$ and viscosity $\eta(T)$ became quite popular. The validity of Eqn (7.6) is confirmed in many papers for various amorphous materials [5, 57–61].

Substituting $\tau(T)$ from Eqn (7.6) in glass transition condition (4.2), we obtain the glass transition equation in the form [36]

$$q\tau_g = \frac{C_2}{C_1}, \qquad (7.7)$$

whence the expression

$$\delta T_g = \frac{C_2}{C_1} \qquad (7.8)$$

is obtained for calculating δT_g from empirical parameters C_1 and C_2 of the WLF equation.

The estimate using (7.8) for silicate glasses (Table 3),

$$\delta T_g \approx 8-12 \text{ K}, \qquad (7.9)$$

is consistent with the product $q\tau_g$ in (6.3).

7.3 Nemilov calculation method
Taking the logarithm of relaxation time equation (2.7) and taking the temperature derivative $(d \ln \tau/dT)$ at $U = $ const and $T = T_g$, we obtain

$$-\frac{\partial T}{\partial \ln \tau}\bigg|_{T=T_g} = \frac{RT_g^2}{U}. \qquad (7.10)$$

Relations (7.2) and (7.10) give the Volkenstein–Ptitsyn formula [6, 7] for δT_g:

$$\delta T_g = -\frac{\partial T}{\partial \ln \tau}\bigg|_{T=T_g}. \qquad (7.11)$$

In [35], Nemilov proposed to replace the equality sign in this formula by the proportionality sign, because the Volkenstein–Ptitsyn theory deals with not the relaxation time spectrum but only the single time τ. It is further assumed that the proportionality coefficient should be universal, and it is somewhat arbitrarily set equal to $\ln 10 = 2.3$:

$$\delta T_g = -2.3 \frac{\partial T}{\partial \ln \tau}\bigg|_{T=T_g}. \qquad (7.12)$$

In passing from the natural logarithm to the decimal one, this proportionality coefficient is canceled and, with the relation between the relaxation time $\tau(T)$ and viscosity $\eta(T)$ taken into account, relation (7.12) is transformed into the following one [35]:

$$\delta T_g = -\frac{\partial T}{\partial \lg \tau}\bigg|_{T=T_g} \cong -\frac{\partial T}{\partial \lg \eta}\bigg|_{T=T_g}. \tag{7.13}$$

If the temperature interval is assumed to be such that the viscosity $\eta(T)$ changes by an order of magnitude from 10^{13} to 10^{12} Pa s, equality (7.13) reduces to a form convenient for calculations:

$$\delta T_g = -\frac{\partial T}{\partial \lg \eta}\bigg|_{T=T_g} \approx -\frac{\Delta T}{\Delta \lg \eta} = \frac{T_{12} - T_{13}}{\lg \eta_{12} - \lg \eta_{13}}, \tag{7.14}$$

where T_{12} and T_{13} are temperatures corresponding to the viscosity logarithms $\lg \eta_{12} = 12$ and $\lg \eta_{13} = 13$, which finally gives the Nemilov relation [35]

$$\delta T_g = T_{12} - T_{13}. \tag{7.15}$$

Formula (7.15) was used to calculate 13 silicate glasses [35]. For most of them, the value of δT_g is close to 20 K. The average of 13 values is

$$\delta T_g = T_{12} - T_{13} \approx 20 \text{ K}, \tag{7.16}$$

which coincides with Bartenev's estimate in (7.4) and is approximately twice the typical value of the product $q\tau_g \approx 5-10$ K and the value of δT_g in (7.9) obtained from the WLF equation. For sodium–silicate glasses, Nemilov's formula (7.15) gives values $\delta T_g = 21-29$ K (see Table 3).

Because Nemilov used Volkenstein–Ptitsyn formula (7.11) derived for $U = \text{const}$, we could assume that the overstated values of δT_g in (7.16) were explained using the same reason as in Bartenev's work, namely, the assumption that the glass transition activation energy was constant in the derivation of formula (7.11). However, Nemilov used not expression (7.2) but derivative (7.13), which is independent of whether the glass transition activation energy changes with temperature, because the dependence $\eta(T)$ [or $\tau(T)$] in derivative (7.13) is a continuous monotonic function in the interval ΔT [35].

In this connection, the question arises of what causes the discrepancy between Nemilov's estimate of δT_g and the product $q\tau_g$. We consider one of the possible explanations.

7.4 Calculation using the Volkenstein–Ptitsyn formula without an empirical factor

It is known that the liquid–glass transition process can often be quite well described by using one averaged relaxation time equal to the most probable relaxation time τ_α corresponding to the maximum of the continuous relaxation time spectrum of glass transitions in liquids and polymers [1–7, 39]. In relaxation spectrometry, this discrete relaxation time τ_α characterizes the α-relaxation process (glass transition) [39, 40].

In this connection, it is interesting to calculate δT_g directly from Volkenstein–Ptitsyn formula (7.11) with τ equal to the α-relaxation time. In other words, we propose to repeat the Nemilov calculation procedure without introducing the empirical proportionality coefficient 2.3.

It is easy to see that such an approach gives the values

$$\delta T_g = \frac{1}{2.3}(T_{12} - T_{13}) = 6-13 \text{ K} \tag{7.17}$$

for silicate glasses (see Table 3), which are consistent with the product $q\tau_g$ in (6.3) and with δT_g obtained for these glasses using the WLF equation (7.9) (see Table 3).

This suggests that overstated values (7.16) can be due to the empirical factor 2.3 introduced into Volkenstein–Ptitsyn formula (7.13).

The search for correct methods for calculating δT_g is in fact at the initial stage [35, 36]. Further studies of glass transition equation (6.1) will probably elucidate the real reasons for discrepancies in the estimates of δT_g by various authors. According to the estimate by Volkenstein and Ptitsyn [6, 7], the temperature band width δT_g is a few degrees, which is consistent with the classical concept [63] that the structure of glass-forming melts is frozen in a very narrow temperature region including T_g. The Volkenstein–Ptitsyn theory [6, 7] leads to the same conclusion.

Because of the importance of Volkenstein–Ptitsyn formula (7.11), we consider a new approach to explaining it. The equation obtained by Razumovskaya and Bartenev [64] without specifying the temperature dependence $\tau(T)$ has the form

$$\ln a_T = -\frac{A^2}{B} \frac{T - T_g}{T - T_g(1 - A/B)}, \quad a_T = \frac{\eta(T)}{\eta(T_g)} \cong \frac{\tau(T)}{\tau(T_g)}, \tag{7.18}$$

$$A = -\frac{\partial \ln \tau}{\partial (T/T_g)}\bigg|_{T=T_g}, \tag{7.19}$$

$$B = \frac{1}{2}\frac{\partial^2 \ln \tau}{\partial (T/T_g)^2}\bigg|_{T=T_g}. \tag{7.20}$$

The parameter A is positive because $\partial \ln \tau > 0$ for $\partial(T/T_g) < 0$. The substitution of $\tau(T)$ from (7.18) in the general glass transition equation (4.2) [6, 7]

$$\frac{d\tau}{dT}\bigg|_{T=T_g} = -\frac{1}{|q|}$$

yields

$$q\tau_g = \frac{T_g}{A},$$

whence, taking expression (7.19) for the derivative A into account, we obtain Volkenstein–Ptitsyn formula (7.11)

$$\delta T_g = \frac{T_g}{A} = -\frac{\partial T}{\partial \ln \tau}\bigg|_{T=T_g}. \tag{7.21}$$

We note the important fact that expression (7.21) in this derivation is independent of the form of the dependence $\tau(T)$. Thus, relation (7.11) has a more general character than in the Volkenstein–Ptitsyn interpretation [6, 7].

It is also important that Razumovskaya–Bartenev equation (7.18) coincides with empirical WLF relation (7.6), which, as we see, follows from a simple series expansion of $\ln \tau(T)$ [64]. This explains why the calculations of δT_g by Volkenstein–Ptitsyn formula (7.17) and WLF relation (7.9) are in good agreement (see Table 3).

8. Fragility and the glass transition temperature interval δT_g

In the last decades, the concept of fragility has gained acceptance, which is determined by the temperature dependence of the viscosity at temperatures close to the glass transition temperature [65]:

$$m = \frac{\mathrm{d} \ln \eta(T)}{\mathrm{d}(T_g/T)} \bigg|_{T=T_g} . \tag{8.1}$$

It is easy to see that substituting the dependence $\eta(T)$ from WLF equation (7.6) in expression (8.1) gives the relation [66]

$$m = \frac{C_1}{C_2} T_g . $$

Taking into account that $\delta T_g = C_2/C_1$, for $m \approx$ const, we obtain a linear correlation between δT_g and the temperature T_g for glasses of the same class,

$$\delta T_g = \frac{1}{m} T_g , \tag{8.2}$$

which is confirmed in experiments with some glasses [36]. The value of m is used to classify glasses.

9. Glass transition equation in the model of delocalized atoms

We consider the model of delocalized atoms [67], in which an important parameter is the fluctuation volume ΔV_e of the amorphous system appearing due to thermal displacements of particles from equilibrium positions,

$$\Delta V_e = N_e \Delta v_e . $$

Here, N_e is the number of delocalized atoms and Δv_e is the elementary fluctuation volume required for delocalization of an active atom (its displacement from the equilibrium position). The mobility of delocalized atoms in the glass transition region is mainly determined by the fraction of the fluctuation volume

$$f = \frac{\Delta V_e}{V} . $$

From the standpoint of this model, the parameters of WLF equation (7.6) acquire the following physical interpretation [67]:

$$C_1 = \frac{1}{f_g} , \qquad C_2 = \frac{f_g}{\beta_f} , \tag{9.1}$$

where $f_g = (\Delta V_e/V)_{T=T_g}$ is the fraction of the fluctuation volume frozen at the glass transition temperature and β_f is the thermal expansion coefficient of the fluctuation volume at $T = T_g$ ($\beta_f = (\mathrm{d}f/\mathrm{d}T)_{T=T_g}$). The product $\beta_f T_g$ depends on f_g [67, 68]:

$$\beta_f T_g = f_g \ln \frac{1}{f_g} . \tag{9.2}$$

It follows from expressions (7.8), (9.1), and (9.2) that the relative temperature interval $\delta T_g/T_g$ is a single-valued function of the fraction f_g of the fluctuation volume frozen at the glass transition temperature,

$$\frac{\delta T_g}{T_g} \cong \frac{f_g}{\ln (1/f_g)} . \tag{9.3}$$

Thus, in the framework of the model under study, the parameter δT_g of the glass transition equation is determined by the temperature T_g and the fraction f_g of the fluctuation volume frozen at $T = T_g$ [36, 69]:

$$q\tau_g = \frac{f_g}{\ln (1/f_g)} T_g . $$

We note that the parameter C_1 of the WLF equation is in fact a universal constant, at least for glasses of the same class (Table 4). This means that the fraction $f_g = 1/C_1$ of the fluctuation volume is constant [see (9.1)] (see Table 4):

$$f_g = \frac{\Delta V_e}{V} \bigg|_{T=T_g} = \frac{1}{C_1} \approx \text{const} \approx 0.024 - 0.028 . \tag{9.4}$$

For $f_g \approx$ const, equality (9.3) gives a linear correlation between δT_g and T_g. Indeed, as mentioned above, some glasses exhibit a linear correlation between the glass transition temperature T_g and the temperature interval δT_g [determined by expression (7.8)] [36].

If f_g and T_g are known, the temperature interval δT_g characterizing the liquid–glass transition can be estimated by expression (9.3). For sodium–silicate glasses, $\delta T_g = 5-6$ K, and for amorphous organic polymers, $\delta T_g \approx 2$ K. Glassy selenium ($\delta T_g = 1.8$ K) is an inorganic amorphous polymer with the transverse linear structure $-\mathrm{Se}-\mathrm{Se}-\mathrm{Se}-$. For low-molecular organic glasses, $\delta T_g \approx 1$ K (see Table 4).

Thus, the values $\delta T_g \approx 5-6$ K calculated in the model of delocalized atoms for sodium–silicate glasses are in good agreement with the product $q\tau_g \approx 5-10$ K for silicate glasses in Eqn (6.3) and with calculations of δT_g using the parameters of WLF equation (7.9).

For most glassy systems, the value of δT_g, according to (9.3) for $f_g \approx 0.025$, is about 0.7% of the glass transition temperature, and the relative temperature interval $\delta T_g/T_g$ is virtually universal for the amorphous materials studied (see Table 4):

$$\frac{\delta T_g}{T_g} \approx \text{const} \approx 0.006 - 0.008 . \tag{9.5}$$

The fact that the interval δT_g is very narrow is explained be the small fraction f_g of the fluctuation volume frozen at the glass transition temperature, in other words, by the small scale of the local structural fluctuation near T_g.

Among the methods for calculating δT_g presented above, the estimate using the parameters of the WLF equation with the help of expression (7.8) is preferable in our opinion.

The calculation of δT_g for amorphous organic polymers and low-molecular organic glasses from the data on C_1 and C_2 within the model of delocalized atoms (9.3) gives low values (see Table 4)

$$\delta T_g \approx 1-3 \text{ K} , $$

which are consistent with the product $q\tau_g \approx 1-3$ K at the standard cooling rate. Metal glasses with $\delta T_g \approx 3-5$ K occupy the intermediate position between inorganic and organic glasses (see Table 4).

Table 4. Parameters C_1 and C_2 of the WLF equation and glass transition characteristics of amorphous materials* [36].

Amorphous material	T_g, K	C_1	C_2, K	$\delta T_g = \dfrac{C_2}{C_1}$, K	f_g	$\dfrac{\delta T_g}{T_g} \times 10^3$	τ_g, s	C_0	$\dfrac{N_e}{N}\Big\|_{T=T_g}$, %
Sodium–silicate $Na_2O - SiO_2$ glasses [49]									
Na_2O, mol. %									
15	782	36	430	12	0.028	7.8	240	0.5	3.5
20	759	36	390	11	0.028	7.8	220	0.5	3.4
25	739	35	355	10	0.028	7.8	200	0.5	3.5
30	721	35	322	9	0.028	7.8	180	0.5	3.5
33	712	35	304	9	0.028	7.8	180	0.6	3.5
35	705	35	291	8	0.028	7.8	160	0.6	3.5
Metal glasses (amorphous alloys) [70, 71]									
$Pd_{40}Ni_{40}P_{20}$	602	39	93	2.4	0.026	7.1	48	0.8	3.6
$Pt_{60}Ni_{15}P_{25}$	500	37	95	2.6	0.027	7.5	52	0.8	3.6
$Pd_{77.5}Cu_6Si_{16.5}$	653	38	100	2.6	0.026	7.1	52	0.8	3.7
$Fe_{80}P_{13}C_7$	736	38	120	3.2	0.026	7.1	64	0.8	3.6
Amorphous organic polymers [58] and selenium [5]									
Polyvinyl acetate	305	36	47	1.3	0.028	7.8	61	0.8	3.5
Natural rubber	300	38	54	1.4	0.026	7.1	57	0.8	3.6
Ethyl methacrylate	335	40	65	1.6	0.025	6.8	50	0.8	3.6
Selenium	303	32	58	1.8	0.031	8.9	44	0.8	3.6
Low-molecular organic glasses [61]									
Propanol	98	41	25	0.6	0.024	6.4	12	0.7	3.6
Propylene alcohol	160	44	40	0.9	0.023	6.1	18	0.7	3.7
Glycerin	185	42	53	1.3	0.024	6.4	26	0.7	3.9

* $f_g = 1/C_1$, $\tau_g = C_2/C_1 q$.

Because $C_1 \approx$ const for glasses of the same structural type (see Table 4), it follows from (7.8) and (9.3) that C_2 and T_g are linearly related. As a result, WLF equation (7.6) can be written in the modified form

$$\ln \frac{\tau(T)}{\tau(T_g)} = -C_1 \frac{T - T_g}{T - C_0 T_g},$$

where the dimensionless quantity

$$C_0 = 1 - \frac{C_2}{T_g},$$

unlike C_2, weakly depends on the glass nature: $C_0 \approx$ const (see Table 4). Thus, the WLF equation can be written in the modified form containing two dimensionless virtually 'universal' constants C_1 and C_0.

As mentioned above, in the Volkenstein–Ptitsyn relaxation glass transition theory [6, 7], liquid molecules can be in two energy states, the ground and excited states, but the physical meaning of particle excitation from the ground to excited state is not explained. It seems that the delocalization of an active atom can be considered one of the possible variants of particle excitation in the Volkenstein–Ptitsyn theory. Then the number of delocalized atoms corresponds to the number of excited (active) particles in this theory. The delocalization of an atom, for example, in silicate glasses is then represented by a critical transverse displacement of an oxygen atom in the $Si-O-Si$ bridge [67].

The concentration N_e/N of delocalized (bridge) atoms responsible for the viscous flow of glass-forming melts at temperatures above T_g decreases to a very small value of 3–4% in the glass transition interval, which is equivalent to 'freezing' (see Table 4),

$$\frac{N_e}{N}\bigg|_{T=T_g} \cong \exp\left(-\frac{\Delta\varepsilon_e}{k_B T_g}\right) \approx \text{const} \approx 0.03 \,,$$

where k_B is the Boltzmann constant and $\Delta\varepsilon_e = p_i \Delta v_e$ is the localization energy of an atom, equal to the atom displacement work performed against the internal pressure p_i caused by interatomic (intermolecular) attraction forces. At the glass transition temperature, the atom delocalization process (the transition from the ground to excited state) is frozen. During glass softening under heating, the atom delocalization process is gradually frozen out, and the number of delocalized atoms increases from small values in the frozen state to their concentration corresponding to liquid.

In the model of delocalized atoms, in our opinion, an internal (structural) parameter such as ξ is the fraction f of the fluctuation volume, which is mainly determined by the concentration of delocalized atoms. From this standpoint, the relative temperature interval $\delta T_g/T_g$ in equality (9.3) is a single-valued function of the internal parameter f_g characterizing the system structure near the glass transition temperature.

10. Kinetic glass transition criterion

The glass transition criterion

$$\left(\frac{1}{T}\left|\frac{dT}{dt}\right|\tau\right)\bigg|_{T=T_g} = C_3, \quad C_3 \approx 1 \tag{10.1}$$

was formulated in a number of studies [1, 2, 72]. As pointed out in [35], according to (10.1), the product $q\tau_g$ for oxide (for example, silicate) glasses at $T = T_g$ should correspond to

$T_g \approx 800 \text{ K}$,

$$q\tau_g \approx 800 \text{ K}, \tag{10.2}$$

which contradicts classical relaxation glass transition theories [6, 7, 41, 63] and typical values $q\tau_g \approx 5-10 \text{ K}$ [see (6.3)].

Taking the results of the study performed in Sections 6–9 into account, we consider one of the variants of refining the glass transition criterion (10.1). Dividing both sides of glass transition equation (6.1) by the glass transition temperature T_g, we obtain the relation

$$\frac{q\tau_g}{T_g} = C_g, \tag{10.3}$$

in which C_g is in fact a universal constant [see Eqns (9.3) and (9.5)],

$$C_g = \frac{\delta T_g}{T_g} = \frac{f_g}{\ln(1/f_g)} \approx \text{const} \approx 0.007. \tag{10.4}$$

Relation (10.3) can be considered a new variant of the kinetic glass transition criterion, written in the generalized form

$$\left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g} = C_g, \quad C_g \approx 7 \times 10^{-3}. \tag{10.5}$$

Glass transition condition (10.5) does not contradict classical relaxation theories [7, 63] and the values of $q\tau_g$. For oxide glasses ($T_g \approx 700-800 \text{ K}$), this condition gives the value

$$q\tau_g = C_g T_g \approx 5-6 \text{ K},$$

in agreement with typical values of $q\tau_g$.

11. Estimate of the fluctuation volume fraction f_g

As mentioned above, the basic features of the glass transition process are qualitatively the same for all amorphous materials, irrespective of their nature: amorphous organic polymers, inorganic glasses, metal amorphous melts, aqueous solutions, chalcogenides, etc. The dependence of the glass transition temperature T_g on the cooling rate q of glass-forming solutions is then described by the same Bartenev–Ritland equation (2.8), in which the ratio of empirical parameters a_2/a_1 is virtually constant for various amorphous materials, including organic amorphous polymers and silicate glasses (see Tables 1 and 2).

We note that the values of a_2/a_1 and f_g in equalities (2.11) and (9.4) coincide. We see below that this is not accidental. Taking expression (2.10) into account, we represent the Bartenev–Ritland relation (2.8) in the form

$$\frac{U}{RT_g} = \frac{a_1}{a_2} - \ln q. \tag{11.1}$$

A comparison of the expression for viscosity [67]

$$\eta_g = \eta_0 \exp\left(\frac{1}{f_g} \right) \tag{11.2}$$

with the known Frenkel equation [73]

$$\eta_g = \eta_0 \exp\left(\frac{U}{RT_g} \right)$$

written for $T = T_g$ shows the connection between the activation energy of the viscous flow and the fluctuation volume fraction f_g:

$$\frac{U}{RT_g} \approx \frac{1}{f_g}.$$

As a rule, the glass transition activation and viscous flow energies coincide. Relation (11.1) then takes the form

$$\frac{1}{f_g} = \frac{a_1}{a_2} - \ln q. \tag{11.3}$$

Thus, the fluctuation volume fraction f_g frozen at the glass transition temperature is dependent on the melt cooling rate, which is quite natural. For the specified cooling rate $q = \text{const}$, the value of f_g is constant.

Substituting the standard value of q from equality (6.2) and a_1 and a_2 from Table 1 in (11.3), we see that the fluctuation volume fraction f_g calculated from the temperature dependence of the glass transition on the cooling rate (see Table 1)

$$f_g = \left(\frac{a_1}{a_2} + 2.9 \right)^{-1} \approx \text{const} \approx 0.025-0.030 \tag{11.4}$$

is consistent with the values of f_g derived from the viscosity in the glass transition region (9.4) (see Table 4). The values of f_g in equalities (9.4) and (11.4) are related to the standard cooling rate. We can see that the constant $C_1 = 1/f_g$ of the WLF equation is closely related to the ratio a_2/a_1 of the Bartenev equation parameters. As a rule, the ratio $a_1/a_2 \approx 40$ in equality (11.3) greatly exceeds $\ln q$ (for $q = 0.05 \text{ K s}^{-1}$): $a_1/a_2 \gg \lg q$; therefore, C_1 and a_1/a_2 almost coincide.

At the same time, the question arises: Why does the dependence of the glass transition temperature on cooling rate (2.8), which was derived by ignoring the temperature dependence $U = U(T)$ of the glass transition activation energy, prove to be quite correct?

To elucidate this question, we consider the derivation of Bartenev–Ritland equation (2.8) taking the temperature dependence $U(T)$ of the activation energy into account.

12. Generalized Bartenev–Ritland equation

In the model of delocalized atoms [67, 68], the fraction f_g of the fluctuation volume frozen at the glass transition temperature is described by the expression

$$f_g = \frac{\Delta v_e}{v} \exp\left(-\frac{\Delta \varepsilon_e}{RT_g} \right), \tag{12.1}$$

where $v = V/N$ is the atomic volume, Δv_e is the elementary volume required for atom delocalization, and $\Delta \varepsilon_e$ is the atom delocalization energy.

Substituting f_g from relation (12.1) in viscosity equation (11.2), we obtain the expression

$$\eta_g = \eta_0 \exp\left[\frac{v}{\Delta v_e} \exp\left(\frac{\Delta \varepsilon_e}{RT_g} \right) \right],$$

which coincides with the empirical viscosity equations proposed independently by Bredbury [74], Shishkin [75], and Waterton [76].

Taking the known relation between the relaxation time $\tau(T)$ and viscosity $\eta(T)$ into account, we can write the temperature dependence $\tau(T)$ similarly:

$$\tau_g = \tau_0 \exp\left[\exp\left(\frac{\Delta\varepsilon_e}{RT_g}\right)\right]. \tag{12.2}$$

Here, we assume that the atom delocalization volume is close to the atomic volume ($v/\Delta v_e \approx 1$) [77].

Substituting the relaxation time τ_g from (12.2) in glass transition equation (2.1) and making some transformations, we obtain the generalized Bartenev–Ritland equation

$$\frac{1}{T_g} = a_1 + b_1 \ln\left(1 - \frac{\ln q}{b_2}\right), \tag{12.3}$$

where $b_1 = R/\Delta\varepsilon_e$, $b_2 = \ln(C/\tau_0)$, and $a_1 = b_1 \ln b_2$. We note that the first and second terms in the right-hand side of (12.3) contain logarithms of dimensional quantities, $\ln q$ and $\ln(C/\tau_0)$, where q and C/τ_0 have the same dimension [K s^{-1}]. This dimension (or another common dimension) should be used in all calculations.

Setting $\tau_0 \approx 10^{-12}$ s and $C \approx 10$ K [36] for the standard cooling rate, we can estimate $b_2 = \ln(C/\tau_0) \approx 30$. For relatively small cooling rates, $\ln q \ll b_2$, the logarithm in the right-hand side of (12.3) can be expanded in a series, with only the first term kept:

$$\ln\left(1 - \frac{\ln q}{b_2}\right) \approx -\frac{\ln q}{b_2}.$$

Then equality (12.3) transforms into Bartenev–Ritland equation (2.8):

$$\frac{1}{T_g} = a_1 - \frac{b_1}{b_2} \ln q,$$

where $a_2 = b_1/b_2$. Therefore, Bartenev–Ritland equation (2.8) is valid at not very large rates. Indeed, as the cooling rate is increased, a deviation from dependence (2.8) is observed for a number of glasses, for example, lead–silicate ones [45]. We note that the parameter C in the glass transition equation weakly depends on the cooling rate q via $T_g(q)$. However, T_g depends on q logarithmically and, in addition, C enters the logarithm. Therefore, the parameter C can be considered virtually constant, which is confirmed by the validity of the Bartenev–Ritland equation at moderate cooling rates.

To verify relation (12.3), we constructed plots in the coordinates $(1/T_g, \ln[1 - (\ln q/30)])$ for various amorphous materials [78]. Experimental data [38, 45, 49] in these coordinates lie on straight lines, in particular, for lead–silicate glasses exhibiting a deviation from Bartenev equation (2.8).

Thus, the obtained generalized equation (12.3) is consistent with experimental data in a broader cooling rate range than Bartenev–Ritland equation (2.8).

13. Temperature dependence of the viscosity of glass-forming melts

13.1 Empirical viscosity equations for glass-forming liquids

It is known that unlike simple acetone-type liquids, the temperature dependence $\eta(T)$ of the viscosity of glass-

forming melts is not described by the usual Arrhenius exponential formula. Because of the absence of any explicit generally accepted theoretical dependence $\eta(T)$ for glass-forming melts, numerous attempts have been made to find which of the known empirical relations provides the best description of the temperature dependence of the viscosity.

In [79], the Waterton [76], Vogel–Fulcher–Tamman [80–82], and Avramov–Milchev [83] equations containing three fitting parameters were compared and the Waterton formula ('double exponential') was chosen:

$$\eta = A \exp\left[\frac{B_1}{T} \exp\left(\frac{D_1}{T}\right)\right]. \tag{13.1}$$

A similar equation

$$\eta = A \exp\left[B_2 \exp\left(\frac{D_2}{T}\right)\right]. \tag{13.2}$$

was proposed in [74] and [75]. A number of viscosity equations were analyzed in [84], and a 'double exponential' like (13.1) was also preferred. Because the exponential in square brackets in Waterton relation (13.1) depends on the temperature much more strongly than on the preexponential factor B_1/T, the latter can be considered virtually constant. Therefore, Waterton (13.1) and Bredbury–Shishkin (13.2) formulas in fact coincide.

Five most popular empirical viscosity equations, including (13.1) and (13.2), were compared in [85], with the conclusion that among them the Jenckel equation [86] most accurately describes experimental data in a broad temperature range if it is slightly modified and represented in the generalized form [85]

$$\eta = A \exp\left[\frac{B}{T} + \frac{C}{T} \exp\left(\frac{D}{T}\right)\right]. \tag{13.3}$$

At low temperatures in the glass transition region, the first term B/T in the square brackets can be disregarded due to its smallness compared to the exponential. Then (13.3) transforms into Waterton relation (13.1). In turn, the 'double exponential' like (13.1) and (13.2) allows algebraically deriving the known Williams–Landel–Ferry equation (7.6) [57, 58], which is equivalent to the Vogel–Fulcher–Tamman relation (see [5, pp. 90, 91]).

Thus, Jenckel equation (13.3) represents one of the generalized variants of basic empirical relations for the viscosity of glass-forming melts, and therefore a study of its nature is of interest.

According to Jenckel [65], the temperature dependence of the viscosity of glass-forming liquids is related to the dissociation and association of molecules. It was assumed that the degree of association of particles in these systems changes with changing the temperature, which is accompanied by the dissociation and restoration of interatomic and intermolecular bonds in the environment of a given kinetic unit. Based on these concepts, Jenckel obtained the viscosity equation presented here in its original form [86]:

$$\eta = A \exp\left\{\frac{Q}{RT}\left[1 + \alpha \exp\left(\frac{Q}{RT}\right)\right]\right\}, \tag{13.4}$$

where the expression in square brackets characterizes changes in the association degree of molecules under cooling and heating.
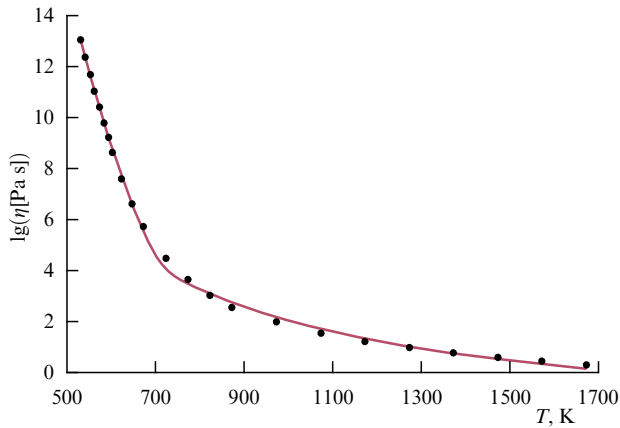
Figure 4. Temperature dependence of the melt viscosity of boric anhydride B_2O_3. Dots are experimental data; the curve is calculated from (13.5).

We see that the Jenckel theory involves only one energy quantity Q related to the decay energy of molecular associates. The value of Q for glucose or spirit liquids is close to the hydrogen bond energy.

Unlike the original, the generalized variant of Jenckel equation (13.3) proposed in [85] contains two energy quantities: B and D. The physical meaning of activation parameters RB and RD was not discussed in [85]. The author only showed that the generalized Jenckel equation better agrees with experimental data.

Possible variants of the substantiation of this equation [5, 87–89] outside the Jenckel approach [86] have been considered. A new derivation of the Jenckel equation was proposed in [77], showing that formula (13.3) contains, in fact, not four but three fitting parameters: A, B, and D.

Finally, we note that the confuguron percolation theory gives a universal equation for the temperature dependence of the shear viscosity coefficient, which is applicable to both glasses and melts [11, 24, 25, 90–96]:

$$\eta(T) = A_1 T \left[1 + A_2 \exp\left(\frac{H_m}{RT}\right) \right] \left[1 + C \exp\left(\frac{H_d}{RT}\right) \right], \quad (13.5)$$

where A_1, A_2, and C are constants, H_d is the configuron formation enthalpy, and H_m is its motion enthalpy. A comparison with other viscosity models and numerical calculations using the fitting method confirmed the validity of Eqn (13.5) for various glass-forming systems (both simple and complex organic and inorganic compositions) [93, 97]. Figure 4 illustrates this for the viscosity of glassy and melted boric acid anhydride. The curve is calculated using Eqn (13.5). Experimental data are shown by dots [12, 24]. The thermodynamic parameters of Eqn (13.5) can be determined from experimental data on the viscosity [24].

13.2 Derivation of the viscosity equation

Using the concept of a two-stage elementary viscosity event of glasses and their melts [98–100], we assume that the probability W of a transition of a kinetic unit from one equilibrium position to another is determined by the probability W_1 of the local structural change in the given kinetic unit and by the probability W_2 that this unit has the energy ΔF_∞ sufficient for hopping over to a new position (to a structurally changed

microregion),

$$W = W_1 W_2 \, .$$

In this case, the local configurational change in the structure of the kinetic unit precedes its transition and is considered a necessary condition for realizing that transition (similarly to the case of the transition of an atom to a neighboring position requiring a preliminary production of a hole into which the atom can jump [98, 99]).

According to [100], a necessary condition for the switching of a valence bond — the basic molecular mechanism of the viscous flow of inorganic glasses and their melts — is the preliminary local low-activation deformation of the structural network of atomic bonds. This can be assumed to be one of the variants of the local configurational change in the structure of the kinetic unit responsible for viscosity.

The molecular mobility at elevated temperatures is determined by the probability of the kinetic-unit transition to one of the 'ready-loosened microregions,' which typically exist at high temperatures ($W_1 = 1$):

$$W_2 = \exp\left(-\frac{\Delta F_\infty}{kT}\right). \quad (13.6)$$

As the temperature is lowered, the melt structure in the glass transition region thickens and the molecular mobility becomes strongly dependent on the probability W_1 of a local change in the structure. We discuss this concept using the model of delocalized atoms [67, 101].

The delocalization of a bound atom, i.e., its displacement from the equilibrium position in amorphous materials, is accompanied by a regrouping of neighboring particles and, in fact, reflects a local configurational structural change. Taking this into account, we consider W_1 to be the delocalization probability of an atom, written in the form [67]

$$W_1 = \exp\left(-\frac{\Delta v_e}{v_f}\right), \quad (13.7)$$

where Δv_e is the elementary fluctuation volume required for atom delocalization and $v_f = \Delta V_e / N$ is the average fluctuation volume per kinetic unit. The fluctuation volume ΔV_e of an amorphous material appears due to the delocalization of atoms — their thermal displacements from the equilibrium position (N_e is the number of delocalized atoms): $\Delta V_e = N_e \Delta v_e$ (see Section 9).

Using the quasi-lattice model [102], we find the explicit form of the temperature dependence $v_f(T)$ of the fluctuation volume. We assume that under delocalization of a bound atom due to local deformation of the lattice (the network of bonds), the corresponding lattice point is displaced from its initial position. We call such a displaced defect an excited lattice point. The number of excited lattice points is equal to the number N_e of delocalized atoms. The total number of lattice points, both unexcited N and excited N_e, is $N + N_e$. We can then write the free energy of the system related to lattice defects in the form

$$\Delta F = N_e \Delta \varepsilon_e - k_B T \ln \frac{(N + N_e)!}{N! N_e!} \, ,$$

where the expression under the logarithm gives the number of ways of arranging delocalized atoms among possible lattice points, and $\Delta \varepsilon_e$ is the atom delocalization energy.

We can show that the number of delocalized atoms corresponding to the minimum of ΔF is

$$\frac{N_e}{N} = \left[\exp\left(\frac{\Delta\varepsilon_e}{k_B T}\right) - 1 \right]^{-1}. \tag{13.8}$$

The fraction of the fluctuation volume

$$f = \frac{\Delta V_e}{V} = \frac{\Delta v_e}{v}\frac{N_e}{N},$$

taking (13.8) into account, is given by $(v = V/N)$

$$f = \frac{\Delta v_e}{v}\left[\exp\left(\frac{\Delta\varepsilon_e}{k_B T}\right) - 1 \right]^{-1}. \tag{13.9}$$

Substituting this dependence $f(T)$ in the exponent in the right-hand side of (13.7),

$$\frac{\Delta v_e}{v_f} = \frac{\Delta v_e/v}{v_f/v} = \frac{\Delta v_e}{v}\frac{1}{f},$$

we obtain the expression for the probability $W_1(T)$ of the local change in the structure in the form of a 'double exponential'

$$W_1 = \exp\left\{ -\left[\exp\left(\frac{\Delta\varepsilon_e}{k_B T}\right) - 1 \right] \right\}. \tag{13.10}$$

Now, using relations (13.6) and (13.10) and the known relation between the viscosity η and the quantity W in accordance with the Stokes–Einstein theory (see, e.g., [5])

$$\eta \sim \frac{1}{W} = \frac{1}{W_1 W_2},$$

we finally obtain the viscosity equation

$$\eta = \eta_0 \exp\left\{ \frac{\Delta F_\infty}{k_B T} + \left[\exp\left(\frac{\Delta\varepsilon_e}{k_B T}\right) - 1 \right] \right\}, \tag{13.11}$$

which coincides, in fact, with empirical Jenckel equation (13.3). Here, η_0 is the proportionality coefficient (the viscosity η as $T \to \infty$). We can probably assume from [7] that η_0 coincides with the preexponential factor in the known Eyring equation: $\eta_0 = h/v_\eta$, where v_η is the particle volume and h is Planck's constant.

13.3 Comparison with experiments

Equation (13.11) contains three parameters: η_0, ΔF_∞, and $\Delta\varepsilon_e$. The preexponential factor η_0 corresponding to the viscosity at high temperatures is found by extrapolation (using Lagrange polynomials [103]) of the viscosity curve $\lg\eta - 1/T$ to the temperature $T \to \infty$ [104]. If the value η_0 is known, then we can calculate the viscosity η by fitting the two remaining parameters ΔF_∞ and $\Delta\varepsilon_e$ in Eqn (13.11).

Experimental data on the temperature dependence $\eta(T)$ of the viscosity of glass-forming melts required for making comparisons with calculation results were taken from the SciGlass database [49]. Two-component silicate, germinate, and borate glasses were studied. The experimental data in Fig. 5 in coordinates $(\lg\eta, 1/T)$ are shown by symbols and calculations using Eqn (13.11) are shown by curves. We can see that theoretical curves agree well with experimental
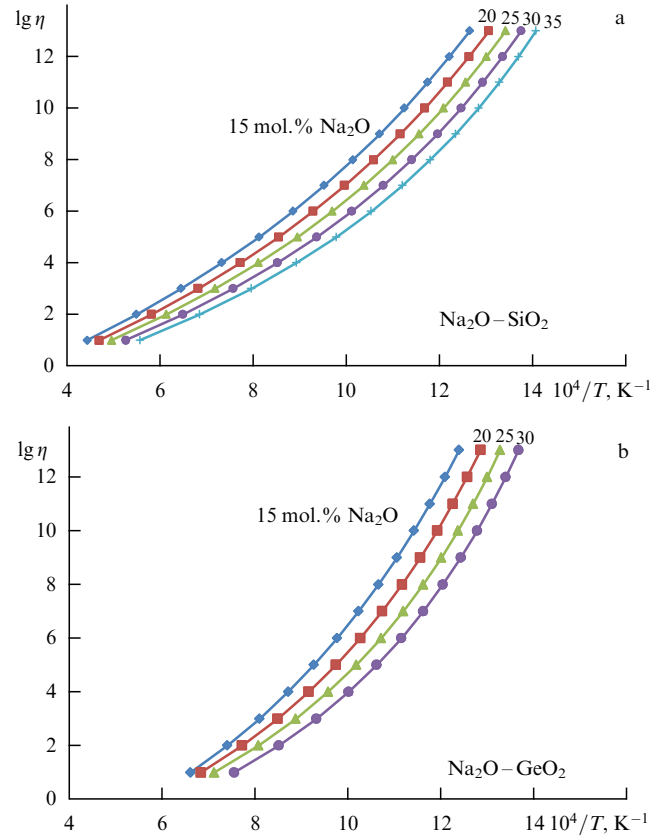

Figure 5. Temperature dependences of the viscosity of (a) sodium–silicate and (b) sodium–germanate glasses. Experimental data are shown by different symbols; the curves are calculated from (13.11).

points. Table 5 presents the values of η_0, ΔF_∞, and $\Delta\varepsilon_e$ for which calculations agree with experimental data.

Thus, viscosity equation (13.11) derived from the refined model [88, 89] is in good agreement with experimental data for glass-forming melts [77].

14. Mechanism of the viscous flow and liquid–glass transition

14.1 Role of atomic delocalization in the fluidity and glass transition processes

The viscosity of glasses is a fundamentally important property characteristic of a glassy state. It is the increased viscosity that slows the crystallization process, facilitating the melt–glass transition.

The atomic mechanism of the viscous flow in inorganic glasses is described in [105] and [56, 106–108]. A mechanism based on the activated switching of bridge bonds, i.e., on the exchange of positions of bridge bonds, was first proposed in [107].

In [106], the viscous flow model for a silicate glass was developed, considering the possibility of the dissociation of the $Si-O$ bond and switching of $Si-O$ bonds to unsaturated bonds of silicon and oxygen (Fig. 6). If bridge oxygen ion *2* approaches unsaturated silicon ion *1* due to transverse thermal vibrations, the *2–3* valence bond can be switched to the *2–1* bond with a change of partners, resulting in the formation of a new configuration of the glass network. The authors of [106] assume that the viscous flow is mainly

Table 5. Characteristics of the viscous flow of R_2O-SiO_2 ($R =$ Li, Na, K), $PbO-SiO_2$, Na_2O-GeO_2, and $Na_2O-B_2O_3$ inorganic glasses* [49].

R_2O, PbO, mol.%	$-\lg(\eta_0[\Pi])$	$\Delta\varepsilon_e$, kJ mol^{-1}	ΔF_∞, kJ mol^{-1}	T_g, K	$\Delta F_\eta(T_g)$, kJ mol^{-1}	f_g	$\Delta\varepsilon_e$, kJ mol^{-1} (14.8)
Li$_2$O				Li_2O-SiO_2			
10	2.55	20	127	814	245	0.028	24
14	2.57	20	120	788	237	0.028	23
25	2.41	19	91	738	219	0.028	22
30	2.25	19	78	721	212	0.028	21
33,3	2.23	19	71	708	208	0.028	21
Na$_2$O				Na_2O-SiO_2			
15	2.53	19	118	783	235	0.028	23
20	2.35	19	101	759	225	0.028	23
25	2.36	19	94	739	219	0.028	22
30	2.36	19	87	721	214	0.028	21
33	2.26	19	78	712	209	0.028	21
K$_2$O				K_2O-SiO_2			
13	2.33	19	121	795	235	0.028	24
15	2.31	19	117	793	232	0.028	24
20	2.14	19	100	759	222	0.025	23
25	2.22	19	90	739	217	0.025	23
PbO				$PbO-SiO_2$			
25	3.15	21	100	785	245	0.027	24
30	2.95	21	79	761	234	0.027	23
45	3.34	20	57	696	218	0.027	21
50	3.33	19	42	674	212	0.027	20
Na$_2$O				Na_2O-GeO_2			
15	3.81	22	79	801	259	0.026	24
20	3.21	22	58	773	241	0.027	23
25	3.10	21	49	749	232	0.027	22
30	3.12	21	40	727	225	0.027	22
Na$_2$O				$Na_2O-B_2O_3$			
10	3.45	18	47	618	194	0.026	19
15	3.93	20	44	680	221	0.026	21
20	3.41	21	26	727	229	0.026	22
25	3.77	22	19	735	237	0.026	22
30	4.45	23	3	748	250	0.025	23

* ΔF_∞ is the high-temperature limit of the viscous flow free activation energy; $\Delta F_\eta(T_g)$ is the fluidity free activation energy at T_g.
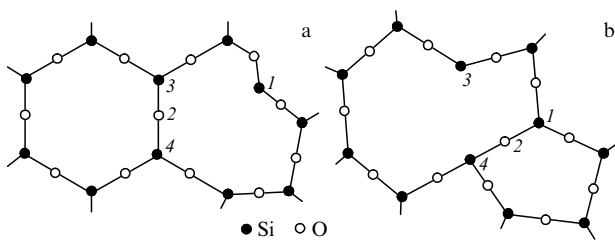
Figure 6. Bond switching in the viscous flow theory [106].
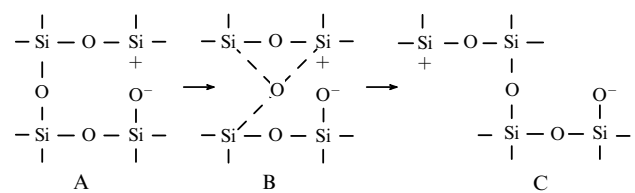
Figure 7. Valence bridge bond switching in a silicate glass [110].

determined by the switching of bonds to the unsaturated bonds of silicon rather than oxygen, as was assumed in [108] and [109].

Figure 7 presents a diagram of the switching of the valence bridge bond to an unsaturated silicon ion [110]. One of the authors of this review proposed a procedure of the motion of a bridge oxygen atom in the $Si-O-Si$ bridge during the viscous flow of silicate glasses consisting of two stages [111]. The first stage involves the delocalization (displacement) of the oxygen atom, resulting in the local low-activation stretching of the silicon–oxygen network (the A $\rightarrow$ B transition). The second stage involves the ascension of the bridge oxygen atom to the top of a potential barrier, which corresponds to the switching of the valence bridge bond (the B $\rightarrow$ C transition), i.e., a hop of the bridge atom. In this case, the A$-$B stage is considered a necessary condition for the realization of the subsequent B$-$C stage. In the viscous flow model presented above, the A$-$B and B$-$C transition probabilities are described by respective relations (13.7) and (13.6) for W_1 and W_2.

A comparison of viscosity equation (13.11) with the known Eyring equation (see [56]),

$$\eta = \eta_0 \exp\left(\frac{\Delta F_\eta(T)}{RT}\right), \tag{14.1}$$

shows that the free activation energy $\Delta F_\eta(T)$ of the viscous flow is a sum of two terms,

$$\Delta F_\eta = \Delta F_\infty + \Delta F_s(T), \tag{14.2}$$

where ΔF_∞ can be called the hopping potential of a kinetic unit (a bridge atom) and

$$\Delta F_s(T) = RT\left[\exp\left(\frac{\Delta \varepsilon_e}{RT}\right) - 1\right] \tag{14.3}$$

is the temperature-dependent potential of the local configurational change in the structure. The quantity ΔF_∞ is the high-temperature limit of the fluidity activation free energy because for $RT \gg \Delta \varepsilon_e$, the second term in the right-hand side of (13.11) vanishes and viscosity equation (13.11) reduces to the usual exponential dependence with a constant free energy activation

$$\eta = \eta_0 \exp\left(\frac{\Delta F_\infty}{RT}\right). \tag{14.4}$$

At low temperatures in the glass transition region, the delocalization energy $\Delta \varepsilon_e$ of an atom becomes comparable to the thermal vibrational energy of the lattice ($\sim 3k_B T$), and the number of delocalized atoms responsible for fluidity considerably decreases (as $\exp[-\Delta \varepsilon_e/(k_B T)]$). Therefore, the activation hop of a bridge atom (valence bond switching) requires a preliminary local deformation of the structural network (bridge atom delocalization, the A $\rightarrow$ B transition; see Fig. 7): the potential of the local configurational change in the structure $\Delta F_s(T)$ drastically increases. This explains the exponential increase in the fluidity activation free energy in the glass transition region.

The kinetic unit hopping and hence the viscous flow are impossible without the delocalization of a bridge atom (the 'trigger mechanism'). Therefore, the freezing of the active atom delocalization process at low temperatures leads to the suppression of the viscous flow and the transition of the melt to the glassy state. This moment comes when the lattice vibrational energy ($ik_B T/2 \approx 3k_B T$) per atom becomes equal to or lower than the atom delocalization energy:

$$3k_B T \leqslant \Delta \varepsilon_e. \tag{14.5}$$

We estimate the number of degrees of freedom of an atom in a solid roughly as $i \approx 6$ (similarly to the case of an ionic cubic crystal).

As expected, the energy $\Delta \varepsilon_e$ determined independently from the empirical parameter D of Jenckel equation (13.3),

$$\Delta \varepsilon_e = RD, \tag{14.6}$$

depends linearly on the temperature T_g (Fig. 8). Equality (14.6) is obtained by comparing (13.11) with empirical Jenckel equation (11.3).

The atom delocalization energy calculated for no. 15 silicate glass ($D = 2500$ K) [64],

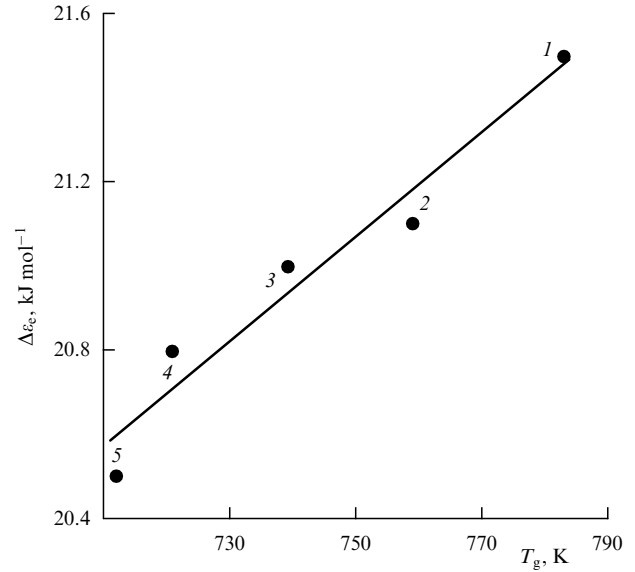$$\Delta \varepsilon_e = RD = 21 \text{ kJ mol}^{-1}, \tag{14.7}$$

Figure 8. Linear correlation between the atom delocalization energy $\Delta \varepsilon_e$ and temperature T_g in sodium-silicate $Na_2O - SiO_2$ glasses. Na_2O content (mol. %): 15 (1), 20 (2), 25 (3), 30 (4). $\Delta \varepsilon_e = RD$, where D is the empirical parameter of Jenckel equation (13.3).

is in good agreement with $\Delta \varepsilon_e$ calculated within the model of localized atoms [67] for some silicate glasses (see Table 5 and Fig. 8):

$$\Delta \varepsilon_e = RT_g \ln\frac{1}{f_g} \approx 20 - 24 \text{ kJ mol}^{-1}. \tag{14.8}$$

Formula (14.8) also demonstrates a linear correlation between $\Delta \varepsilon_e$ and T_g, because $f_g \approx \text{const} \approx 0.024 - 0.028$ (see Tables 1 and 4). According to equalities (14.5) and (14.8), the value of $\ln(1/f_g)$ must be close to 3 ($i/2 \approx 3$). Indeed, for the average value $f_g \approx 0.025 - 0.030$ (see Tables 1 and 4), we have

$$\ln\frac{1}{f_g} \approx \text{const} \approx 3.5.$$

The value of $\Delta \varepsilon_e$ calculated from (14.8) remains constant in a broad temperature range in the glass transition region [122].

Thus, the local configurational change in the structure described in the model of delocalized atoms is a necessary condition for the realization of an elementary event of the viscous flow and is responsible for the peculiar temperature dependence of the viscosity of glasses and their melts. The second terms in viscosity (13.11) and fluidity activation free energy (14.2) related to the configurational change (atom delocalization) reflect the main difference between glass-forming melts and simple melted metal liquids. These terms vanish at high temperatures ($k_B T \gg \Delta \varepsilon_e$), and the equations become the usual relations for simple liquids.

14.2 Valence–configurational theory of a viscous flow

In [56, 110], Nemilov proposed the valence–configurational theory of the fluidity of glasses and their melts, which gives the viscosity equation

$$\eta = \frac{Nh}{V_\eta} \exp\left(\frac{\Delta E_\eta^0 + \Delta E_{\eta k}(T)}{Nk_B T}\right), \tag{14.9}$$

where ΔE_η^0 is the switching potential of the bridge valence bond, $\Delta E_{\eta k}(T)$ is the potential of the configurational change in the structure, and V_η is the molar or atomic volume of particles overcoming the potential barrier, equal to the viscous flow activation free energy $\Delta E_\eta(T)$,

$$\Delta E_\eta = \Delta E_\eta^0 + \Delta E_{\eta k}(T). \tag{14.10}$$

The value of $\Delta E_{\eta k}(T)$ is determined from the experimental temperature dependence of the configurational component of the molar heat capacity $C_{p\,\text{conf}}$ [56].

In [56, 110], this theory was called valence–configurational because it deals with the valence structure of an amorphous material and its configurational changes during activation. Nemilov [56, 110] was the first to propose the decisive role of the configurational structural change in the temperature dependence of the viscous flow of glass-forming melts and glasses.

Viscosity equation (14.9) is based on a modification of Eyring equation (14.1), namely, on splitting the free activation energy $\Delta E_\eta(T)$ into two components, ΔE_η^0 and $\Delta E_{\eta k}(T)$.

15. Conclusions

The liquid–glass transition is a distinct relaxation process obeying kinetic laws. As the liquid–glass transition region is approached, molecular rearrangements in glass-forming melts become so slow that a change in the structure has no time to follow the decrease in temperature. From the standpoint of the relaxation approach, a decisive role in the glass transition process is played by the relation between the structural relaxation time τ and the melt cooling rate $q = \mathrm{d}T/\mathrm{d}t$. The relation between these quantities is expressed by the glass transition equation $q\tau_\mathrm{g} = \delta T_\mathrm{g}$, where τ_g is the relaxation time at $T = T_\mathrm{g}$ and δT_g is the temperature band characterizing the liquid–glass transition interval under cooling.

The temperature interval δT_g calculated from parameters of the WLF equation and in the model of delocalized atoms for inorganic oxide glasses is in agreement with the product $q\tau_\mathrm{g} \approx 5-10$ K, i.e., with the left-hand side of the glass transition equation. This also concerns organic glasses, where δT_g has low values $\approx 1-3$ K, consistent with the product $q\tau_\mathrm{g}$ for these systems.

In this review, as in the work of other authors, we used experimental data corresponding to the standard melt cooling rate $q = 0.05$ K s^{-1}. This is explained by the fact that the experimental data available were typically obtained for the standard cooling rate, and most of the measurements of the glass transition temperature correspond to the standard cooling rate.

We have discussed the glass transition equation in the framework of the model of delocalized atoms and the relaxation glass transition theory. Bartenev–Ritland equation (2.8) was derived taking the temperature dependence of the glass transition activation energy into account. We have shown that this equation is valid for relatively low cooling rates. The fraction f_g of the fluctuation volume calculated from the experimental dependence of the glass transition temperature on the cooling rate coincides with f_g calculated from the viscosity in the glass transition region.

We proposed a new variant of the glass transition criterion. The frequency equivalent to the standard melt cooling rate was calculated. Only at low mechanical action

frequencies about 10^{-3} Hz does the dynamic glass transition temperature T_v of inorganic glasses coincide with the structural glass transition temperature T_g, when structural and dynamic glass transitions occur simultaneously (the topological (structural) and viscous deformation components are frozen simultaneously).

We developed a concept according to which the viscous flow of glass-forming liquids is determined by excited delocalized atoms with the concentration decreasing to a very small value (about 3%) under cooling, which is equivalent to freezing. At the glass transition temperature, the atom delocalization process (atom transitions from the ground to excited state) is frozen.

In this review, we mainly considered the relaxation aspects of the liquid–glass transition and only briefly described the configuron percolation theory [24, 25, 32–34] and applications of nonequilibrium thermodynamics to the glass transition [41, 50–52, 56]. We now briefly discuss some other approaches that are of interest in our opinion.

We first mention the model of limiting configurational entropy (the 'limiting plateau' hypothesis). Based on the Adam–Gibbs theory [9], it is assumed that some intermediate metastable state exists in which the system can only be in a few configurations and cannot undergo a transition from that state to a lower state within the observation time. The limiting achievable value of the configurational entropy is then introduced. Based on such concepts, some authors proposed a glass transition model using the hypothesis about the existence of limiting configurational entropy for a system relaxing at temperatures below T_g [113–117].

One of the popular theories developed during the last decade to describe the dynamics of supercooled liquids and glass transition is the mode-coupling theory (MCT) [118–121]. In particular, the MCT explains the known empirical Colraush formula (fractional exponential) describing the temperature dependence of the relaxation time in the glass transition region.

Also of interest is the mosaic hypothesis or the theory of random first-order transitions, which are understood as the freezing of a liquid and its transformation into a mosaic structure consisting of a set of 'quasicrystals' in various amorphous states. As in the classical nucleation theory, the difference under the rearrangement caused by the interphase surface in the system is taken into account, in contrast to the Adams–Gibbs theory [122–124]. This approach, being a conglomerate of various theories, offers certain advantages and provides some interesting analytic predictions. These studies are discussed in detail in review [1].

In conclusion, we reiterate that the problem of the liquid–glass transition (glass softening) has not been solved definitively so far. The development of a rigorous theory of the supercooled liquid and glass transition process based on statistical physics faces considerable difficulties, which have not been overcome to date.

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