

Научная статья

УДК 51-7

DOI: 10.18101/2304-5728-2026-3-91-99

MODELING THE TEMPERATURE BAND IN THE LIQUID-GLASS TRANSITION REGION

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Abstract. The transition from a glass-forming melt to a solid state occurs within a specific temperature range. This range encompasses the so-called temperature band, the estimates of which vary among authors. The transition phase is characterized by a discrepancy between the exponential functional dependence of the structure's relaxation time on temperature, leading to a variety of methods for calculating the temperature band with varying degrees of approximation.

This paper proposes an interpretation of the temperature band using the parameters of the delocalized atom model. Using these data, the temperature band was calculated, the results of which are consistent with those estimated using the Williams-Landel-Ferry equation.

The proposed equation, modified to take into account the delocalized atom model, coincides with the well-known formula for the temperature band. The resulting relationship allows the temperature band to be calculated directly from experimental results.

It has been established that the proposed formula is applicable regardless of the specific temperature dependence of the structural relaxation time and how the activation energy of the glass transition changes with temperature.

It has been shown that for glassy solids with approximately equal relative fluctuation volumes, the temperature band linearly correlates with the glass transition temperature in the liquid-to-glass transition region.

Keywords: glass transition equation, temperature band, structural relaxation time, relative fluctuation volume, Williams-Landel-Ferry equation, silicate glasses, amorphous polymers.

For citation

Mantatov V. V. Modeling the Temperature Band in the Liquid-Glass Transition Region. *Bulletin of Buryat State University. Mathematics, Informatics*. 2026. N. 3. P. 91–99.

Introduction

The most important result following from classical relaxation theories of the liquid-glass transition [1, 2] is the glass transition equation

$$q\tau_g = \delta T_g, \quad (1)$$

which is responsible for the transition of the glass-forming melt into a solid state upon cooling at the glass transition temperature. Where $q=dT/dt$ is the cooling rate of the melt, τ_g is the relaxation time of the structure of the substance at the glass transition temperature.

The glass transition equation ($q\tau_g = C$) was first proposed by Bartenev [3], and then it was further developed in the theory of Volkenstein and Ptitsyn [1]. Later, the author [4] found a similar equation using the Mandelstam-Leontovich theory [2]. He also proposed a form of this equation (1) replacing the right-hand side with the designation δT_g , which was called the “temperature band”.

The temperature band refers to the temperature range within which the transition from a melt to a solid occurs. A number of methods for calculating the δT_g value for the same substances yield results that vary by up to two tens of degrees ($\delta T_g \approx 20$ K) [1, 3–5]. The specific factors underlying the differences in temperature range estimates in the works of different researchers have not yet been established. This problem is the subject of further scientific research.

This article proposes the calculation of the temperature band using the theory of the following authors [1, 4]

$$\delta T_g = -\left(\frac{\partial T}{\partial \ln \tau}\right)_{T=T_g} \cong -\left(\frac{\partial T}{\partial \ln \eta}\right)_{T=T_g}. \quad (2)$$

Using experimental data on viscosity for the liquid-glass transition, the temperature band can be calculated using this equation (2).

Nemilov [4], based on the fact that the Volkenshtein-Ptitsyn theory [1] does not consider a set of values for the structural relaxation time, proposes modifying relation (2). Instead of the equal sign, a proportionality sign is used. Since the viscosity of most glassy substances changes by an order of magnitude in the liquid-to-glass transition region, the proportionality coefficient in [4] was adopted as 2.3. Temperature band calculations performed using the method [4] yield somewhat overestimated values. Nevertheless, the validity of introducing this empirical coefficient when using the T_g parameter in calculating the viscosity of glasses in the glass transition temperature range was confirmed [4]. The approach deserves attention, but the physical meaning of the empirical factor used remains to be clarified.

However, another point of view exists: the glass transition process of a liquid can often be adequately described using a single average relaxation time [6–11]. On the other hand, taking into account the entire spectrum of relaxation times is fraught with certain difficulties. Therefore, it is advisable to calculate the temperature band directly using the Volkenshteyn-Ptitsyn relation (2), omitting the empirical correction. This is provided that τ is the most probable re-

laxation time, localized at the maximum of the curve within the continuous spectrum describing the glass transition process [6].

Derivation of the equation from relaxation theory

In the work [1] the relation was derived

$$q\tau_g = \frac{kT_g^2}{U}. \quad (3)$$

It was based on the fact that under glass transition conditions

$$\left(\frac{d\tau}{dT}\right)_{T=T_g} = -\frac{1}{|q|} \quad (4)$$

the dependence of the structural relaxation time on temperature $\tau(T)$ in the first approximation is a simple exponential at $U=const$,

$$\tau = \tau_0 \exp\left(\frac{U}{kT}\right). \quad (5)$$

They also received

$$\frac{U}{kT_g^2} = -\left(\frac{\partial \ln \tau}{\partial T}\right)_{T=T_g}, \quad (6)$$

which follows from the glass transition condition (4) at $U=const$ and $T=T_g$.

Formulas (1), (3) and (6) allow us to obtain the Volkenstein-Ptitsyn equation under consideration [1] (2):

$$\delta T_g = -\left(\frac{\partial T}{\partial \ln \tau}\right)_{T=T_g}. \quad (2)$$

An alternative method for deriving equation (2)

The transition of glass-forming liquids to the glassy state is characterized by a violation of the exponential dependence $\tau(T)$ (5) at $U=const$ [5-10]. Currently, there is no universally accepted theoretical model describing the dependence of the relaxation time on temperature $\tau(T)$ in the glass transition region. Given the relevance of the problem, it is appropriate to pay attention to the equation proposed by Razumovskaya and Bartenev [12],

$$\ln a_T = -\left(\frac{A^2}{B}\right) \frac{T-T_g}{T-T_g\left(1+\frac{A}{B}\right)}, \quad a_T = \frac{\tau(T)}{\tau(T_g)} \cong \frac{\eta(T)}{\eta(T_g)}, \quad (7)$$

$$A = \left.\frac{\partial \ln \tau}{\partial (T/T_g)}\right|_{T=T_g}, \quad (8)$$

$$B = \frac{1}{2} \frac{\partial^2 \ln \tau}{\partial (T/T_g)^2} \Big|_{T=T_g}. \quad (9)$$

After replacing $\tau(T)$ in condition (3) with the expression from equation (7), we arrive at the relation

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

and we obtain equation (2), bearing in mind (8)

$$\delta T_g = \frac{T_g}{A} = - \left(\frac{\partial T}{\partial \ln \tau} \right)_{T=T_g}. \quad (10)$$

Discussion of results

1. The proposed derivation shows that the Volkenstein-Ptitsyn formula (10) is independent of both the specific functional dependence of $\tau(T)$ and variations in the activation energy (U) with temperature (i.e., whether $U(T)$ changes or $U=const$). This finding is further supported by the continuity and monotonicity of the function $\tau(T)$ in derivative (2) [13].
2. Relation (7) takes the same form as the well-known empirical equation of the Williams-Landel-Ferry (WLF) [8, 14]

$$\ln a_T = -C_1 \frac{T - T_g}{T - T_g + C_2}, \quad (11)$$

which provides a good description of the dependences $\tau(T)$ and $\eta(T)$ in the glass transition region for various amorphous substances. Here, the empirical parameters C_1 and C_2 are determined through the derivatives A (8) and B (9)

$$C_1 = \frac{A^2}{B}, \quad C_2 = \frac{A}{B} T_g. \quad (12)$$

Their ratio is equal to the temperature band δT_g (see (10))

$$\frac{C_2}{C_1} = \frac{T_g}{A} = \delta T_g. \quad (13)$$

Thus, the proposed viewpoint suggests that the WLF equation (11) is agnostic regarding the specific functional form of the temperature dependence of the relaxation time $\tau(T)$.

3. The derivative A in equality (4) is defined as the so-called “fragility” of the glass-forming melt [16]

$$m = \frac{\partial \ln \eta}{\partial (T_g/T)} \Big|_{T=T_g}$$

which remains constant for glasses of the same class ($m=const$). It follows that the value of A is also constant. It follows that, based on formula (13), a linear correlation should be expected between the temperature band δT_g

and the glass transition temperature T_g . This correlation is confirmed for some glassy systems (Fig. 1, 2).

4. Using the basic principles of the Nemilov [4] method, we will calculate the temperature range using the Volkenstein-Ptitsyn formula (2)
- 5.

$$\delta T_g = -\frac{1}{2.3} \left(\frac{\Delta T}{\Delta \lg \eta} \right)_{T_g} = -\frac{1}{2.3} \left(\frac{T_{12} - T_{13}}{\lg \eta_{12} - \lg \eta_{13}} \right) = \frac{1}{2.3} (T_{12} - T_{13}),$$

where T_{12} and T_{13} are temperatures corresponding to the logarithms of viscosity $\lg \eta_{12} = 12$ and $\lg \eta_{13} = 13$.

The evaluation result for several silicate glasses [11] was found to be consistent with predictions

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

aligns with the data for the same glasses obtained using the WLF equation (13) [11],

$$\delta T_g = \frac{C_2}{C_1} \approx (6-12) \text{ K}$$

and also with the product $q\tau_g$ – with the left side of the glass transition equation [5]: $q\tau_g \approx (5-12) \text{ K}$. The values of $\delta T_g \approx (1-3) \text{ K}$ obtained for amorphous organic polymers and low-molecular organic glasses align with the corresponding values $q\tau_g \approx (1-3) \text{ K}$ for these systems [5].

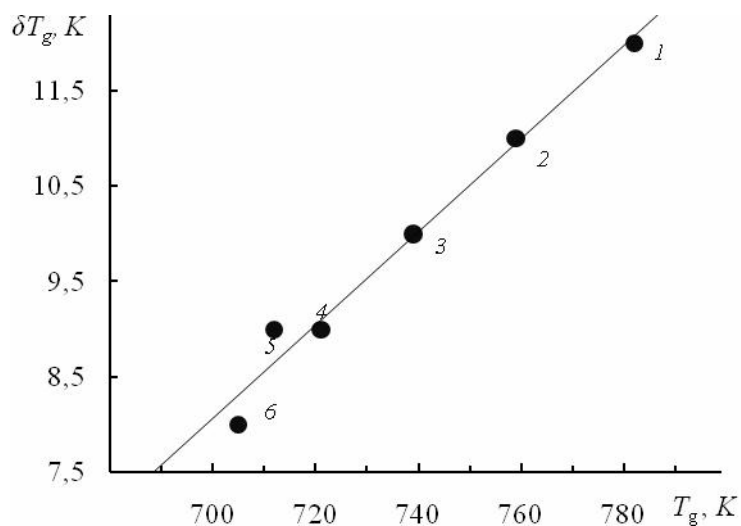


Fig. 1. Linear correlation between the δT_g temperature band, which characterizes the temperature range of the liquid-to-glass transition, and the glass transition temperature T_g of sodium silicate glasses. Na₂O content, mol.%: 15(1), 20(2), 25(3), 30(4), 33(5), and 35(6). Data from [17] were used.

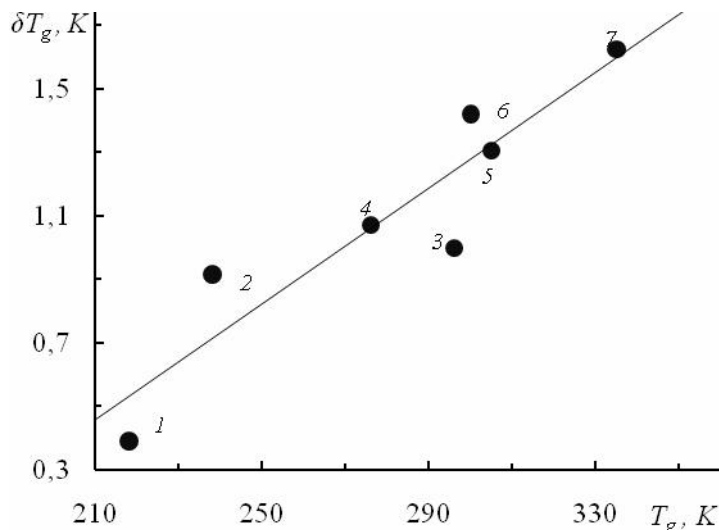


Fig. 2. Correlation between ΔT_g and T_g for amorphous organic polymers. 1 – Polyhexene-1; 2 – Polyurethane; 3 – Polyvinyl chloroacetate; 4 – Polymethyl acrylate; 5 – Polyvinyl acetate; 6 – Natural rubber; 7 – Ethyl methacrylate. Data from [12].

Conclusion

An analysis is performed on the derivation of the equation for the temperature dependence of the structural relaxation time $\tau(T)$ in the glass transition region. Subsequently, using this equation, a new approach is proposed for interpreting the Volkenstein-Ptitsyn relation for the glass transition equation parameter ΔT_g — the temperature band characterizing the transition interval from liquid to glass.

The results of calculations of the temperature range (ΔT_g) characterizing the freezing of the structure in glass-forming liquids — performed using the WLF equation parameters and the delocalized atom model for inorganic oxide glasses — are in satisfactory agreement with the glass transition equation $q\tau_g \approx (5-10)$ K. Similar calculations for amorphous organic polymers and low-molecular organic glasses also show satisfactory agreement with the left-hand side of the glass transition equation (1).

A linear correlation is shown between the temperature band ΔT_g , which is included in the temperature range of the transition from liquid to glass, and the glass transition temperature T_g for sodium silicate glasses and low-molecular organic glasses.

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The article was submitted 28.08.2026; approved after reviewing 10.09.2026; accepted for publication 17.09.2026.

МОДЕЛИРОВАНИЕ ПОЛОСЫ ТЕМПЕРАТУР В ОБЛАСТИ ПЕРЕХОДА ЖИДКОСТЬ — СТЕКЛО

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Аннотация. Переход от стеклообразующего расплава к твердому состоянию реализуется в определенном диапазоне температуры. Этот диапазон охватывает так называемую полосу температур, оценки которой расходятся у разных авторов. Переходная фаза характерна несоответствием функциональной зависимости времени релаксации структуры от температуры по экспоненте, что приводит к разнообразию способов расчета полосы температур с различной степенью приближения.

В данной работе предлагается интерпретация полосы температур с использованием параметров модели делокализованных атомов. По этим данным проведен расчет полосы температур, результаты которого не отличаются от оценки, проведенной по уравнению Вильямса — Ландела — Ферри.

Предлагаемое уравнение, модифицированное с учетом модели делокализованных атомов, совпадает с известной формулой для полосы температур. Полученное соотношение позволяет вычислять полосу температур непосредственно по результатам эксперимента.

Установлено, что предлагаемая формула применима вне зависимости от конкретного вида температурной зависимости времени структурной релаксации и от того, как меняется энергия активации процесса стеклования с температурой.

Показано, что для стеклообразных твердых тел, имеющих приблизительно равный относительный флуктуационный объем, полоса температур линейно коррелирует с температурой стеклования в области перехода жидкость — стекло.

Ключевые слова: уравнение стеклования, полоса температур, время структурной релаксации, относительный флуктуационный объем, уравнение Вильямса — Ландела — Ферри, силикатные стекла, аморфные полимеры.

Для цитирования

Мантатов В. В. Моделирование полосы температур в области перехода жидкость — стекло // Вестник Бурятского государственного университета. Математика, информатика. 2026. № 3. С. 91–99.

Статья поступила в редакцию 28.08.2026; одобрена после рецензирования 10.09.2026; принята к публикации 17.09.2026.