A new approach to the criterion of the liquid-glass transition

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Annotation. A liquid transforms into a frozen glassy state when its cooling rate \( q = \frac{dT}{dt} \) reaches a certain fraction of \( C_g \) of the characteristic cooling rate \( q_g = \frac{T_g}{\tau_g} \), which is closely related to the structure relaxation time \( \tau_g \) at the glass transition temperature \( T_g \).

Key words: generalized criterion, glass transition temperature, relaxation time, cooling rate, model, atomic delocalization.

Elucidation of the nature of the glass transition of liquids is the most difficult problem in condensed matter physics (see, for example, [1-4]).

This work is devoted to the analysis and generalization of kinetic criteria for glass transition using the model of delocalized atoms [5, 6]. The characteristic cooling rate of the glass-forming melt is introduced and a generalized criterion for the liquid-glass transition is proposed.

From the point of view of the relaxation approach, in the process of glass transition of a liquid, the decisive role is played by the relationship between the relaxation time of the structure \( \tau \) and the cooling rate of the melt \( q \). In 1951, Bartenev [7], proceeding from general considerations, proposed the following relationship between these quantities (the glass transition equation)

\[
C q \tau_g = 1,
\]

where \( \tau_g \) is the relaxation time at the glass transition temperature \( T_g \), \( C \) – is an empirical parameter. Here and below, \( q \) should be understood as the absolute value of the rate of temperature change \( |q| \) when cooling the melt or when heating the glass.

Volkenshtein and Ptitsyn [8] developed a physical theory according to which particles of a glass-forming liquid can be in two states separated by an energy barrier. The solution of the constructed kinetic equation leads to the conclusion that the criterion for the liquid-glass transition is the following equation

\[
C \tau_g = \delta T_g .
\]

The \( \delta T_g \) value is interpreted as a temperature band characterizing the interval of the transition from liquid to glass upon cooling.

Schmelzer et al. [1, 9] introduce the characteristic time of temperature variation \( \tau_T = T/q \) and consider the relationship between \( \tau_T \) and the relaxation time of the structure \( \tau \). According to Schmelzer's assumption, the liquid passes into a glassy state when, upon cooling, the time of structural relaxation \( \tau \) increases and becomes equal to the characteristic time of temperature change \( \tau_T \). Proceeding from these considerations, taking into account \( q = \frac{dT}{dt} \), Schmelzer formulated the following kinetic criterion for glass transition [1, 9].

\[
\frac{\tau}{\tau_T}\approx 1, \quad \left[ \frac{1}{T} \frac{dT}{dt} \right]_{T-T_T} = C_3, \quad C_3 \approx 1 .
\]

Let us dwell on the analysis of the indicated glass transition criteria using the model of delocalized atoms [5, 6].
The temperature dependence of the structural relaxation time in the glass transition region \( \tau(T) \) is successfully described by the Williams-Landel-Ferry (WLF) equation [10]

\[
\ln \frac{\tau(T)}{\tau(T_g)} = -\frac{C_1}{T - T_g} - \frac{C_2}{T - T_g + C_2}
\]

Substitution of \( \tau(T) \) from this equation into the Volkenstein–Ptitsyn relation [8]

\[
\frac{dT}{d\tau} = C T^g
\]

leads to equality

\[
q_T = \frac{C_2}{C_1}
\]

where the parameters of the WLF equation \( C_1 \) and \( C_2 \) within the framework of the model of delocalized atoms have the following physical meaning [5]

\[
C_1 = \frac{1}{f_g}, \quad C_2 = \frac{f_g}{\beta_f}
\]

moreover, the product of \( T_g \) and the coefficient of thermal expansion of the fluctuation volume at the glass transition temperature \( \beta_f \) is a single-valued function of the fraction of the fluctuation volume \( f_g \) frozen at the glass transition temperature [5],

\[
\beta_f T_g = f_g \ln(1/f_g)
\]

From the above expressions (5) - (7) we obtain the following interpretation of the glass transition equation

\[
q_T = \frac{f_g}{\ln(1/f_g)} T_g
\]

The fluctuation volume of an amorphous substance \( \Delta V_e \) is due to thermal displacements of atoms [5]

\[
\Delta V_e = N_e \Delta V_e
\]

where \( N_e \) is the number of delocalized atoms (kinetic units), \( \Delta V_e \) is the elementary fluctuation volume required for the delocalization of an atom - its limiting displacement from the local equilibrium position. The volume fraction of the fluctuation volume \( f_g \) frozen at the glass transition temperature \( T_g \) weakly depends on the nature of amorphous substances [5, 6] (Table 1)

\[
f_g = \frac{\Delta V_e}{V_T} \approx 0.020 - 0.030
\]

For glasses of one class, the value of \( f_g \) turns out to be an almost universal constant \( f_g \approx const. \) The constancy of \( f_g \) is valid with the accuracy of the constancy of the logarithm of the ratio of the limiting values of viscosity [11]:

\[
1/f_g = \ln(\eta_0/\eta_g), \quad \eta_0 \approx const
\]

where \( \eta_0 \approx const \) is the high-temperature limit of viscosity, \( \eta_g \approx const \) is the viscosity at the glass transition temperature (the rule of constancy of viscosity at \( T = T_g \)).

Dividing both sides of equality (8) by the glass transition temperature \( T_g \), we arrive at the generalized kinetic glass transition criterion

\[
q_T = C_g, \quad C_g = \frac{f_g}{\ln(1/f_g)} \approx 7 \cdot 10^{-3},
\]

which can be written as an expression for determining the transition temperature \( T_g \)

\[
\left( \frac{1}{T} \frac{dT}{d\tau} \right)_{T=T_g} = C_g, \quad C_g \approx 7 \cdot 10^{-3}.
\]

When estimating \( C_g \), we used the averaged value \( f_g \approx 0.025 \) (Table 1).

Relation (10) can be considered as a justification and generalization of the Schmelzer glass transition criterion (3). In this case, the constant \( C_3 \) acquires a certain physical meaning

\[
C_3 = C_g = \frac{f_g}{\ln(1/f_g)} \approx const \approx 7 \cdot 10^{-3}
\]

This eliminates the drawback of criterion (3), which is reduced to equating the constant \( C_3 \) to one: \( C_3 \approx 1 \), and in fact in the form of a postulate without any special justification. It is easy to see that...
Schmelzer's criterion (3) leads to an erroneous equality: \( q \tau_g \approx T_g \), which contradicts the glass transition equation (2), which follows from the classical Volkenstein-Ptitsyn theory. For example, for silicate glasses at \( T_g \approx 800 \) K, the product \( q \tau_g \) according to criterion (3), should correspond to the value: \( q \tau_g \approx 800 \) K, while the typical values of the product \( q \tau_g \) for these glasses are about [6]: \( q \tau_g \approx (5 \times 10)^3 \) K.

### Table 1

Parameters of the Williams – Landel – Ferry equation \( C_1, C_2 \) and glass transition characteristics of amorphous substances (data from [6] were used)

| Amorphous substance | \( T_g \) K | \( C_1 \) | \( C_2 \) K | \( \delta T_s = \frac{C_2}{C_1} \) K | \( f_s = \frac{1}{C_1} \) | \( C_s \) \( \cdot 10^3 \) |
|---------------------|----------|-------|--------|----------------|----------------|---------|
| Sodium silicate glass Na\(_2\)O-SiO\(_2\) | | | | | | |
| Na\(_2\)O, mol.\% | 15 | 782 | 36 | 430 | 12 | 0.028 | 7.8 |
| 20 | 759 | 36 | 390 | 11 | 0.028 | 7.8 |
| 25 | 739 | 35 | 355 | 10 | 0.028 | 7.8 |
| 30 | 721 | 35 | 322 | 9 | 0.028 | 7.8 |
| 33 | 712 | 35 | 304 | 9 | 0.028 | 7.8 |
| 35 | 705 | 35 | 291 | 8 | 0.028 | 7.8 |
| Polyisobutylene | 202 | 38 | 104 | 2.7 | 0.026 | 7.1 |
| Polyvinyl acetate | 305 | 36 | 47 | 1.3 | 0.028 | 7.8 |
| Polyvinylchloroacetate | 296 | 40 | 40 | 1.0 | 0.025 | 6.8 |
| Polymethyl acrylate | 276 | 42 | 45 | 1.1 | 0.024 | 6.4 |
| Polyurethane | 238 | 36 | 33 | 0.9 | 0.028 | 7.8 |
| Natural rubber | 300 | 38 | 54 | 1.4 | 0.026 | 7.1 |
| Methacrylate polymers | | | | | | |
| ethyl | 335 | 40 | 65 | 1.6 | 0.025 | 6.8 |
| n-butyl | 300 | 39 | 97 | 2.5 | 0.026 | 7.1 |
| n-butyl | 253 | 37 | 107 | 2.9 | 0.027 | 7.5 |
| Mg\(_6\)Cu\(_{17}\)Sn\(_{16}\).5 | 653 | 38 | 100 | 2.6 | 0.026 | 7.1 |
| Fe\(_{0.7}\)P\(_{3.2}\)C\(_7\) | 736 | 38 | 120 | 3.2 | 0.026 | 7.1 |
| Metallic glass | | | | | | |
| Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) | 602 | 39 | 93 | 2.4 | 0.026 | 7.1 |
| Pt\(_{40}\)Ni\(_{15}\)P\(_{25}\) | 500 | 37 | 95 | 5 | 0.027 | 7.5 |
| Pd\(_{77}\)Cu\(_{23}\)Sn\(_{16}\).5 | 653 | 38 | 100 | 2.6 | 0.026 | 7.1 |
| Fe\(_{0.7}\)P\(_{3.2}\)C\(_7\) | 736 | 38 | 120 | 3.2 | 0.026 | 7.1 |
| Low molecular weight organic glasses | | | | | | |
| Propanol | 98 | 41 | 25 | 0.6 | 0.024 | 6.4 |
| Propylene glycol | 160 | 44 | 40 | 0.9 | 0.023 | 6.1 |
| Glycerol | 185 | 42 | 53 | 1.3 | 0.024 | 6.4 |
| Rosin | 303 | 36 | 29 | 0.8 | 0.028 | 7.8 |
| Isobutyl alcohol | 118 | 38 | 38 | 1.0 | 0.026 | 7.1 |

The generalized kinetic criterion for glass transition (10) as applied to silicate glasses for the product \( q \tau_g \) gives the values (\( T_g \approx 700\text{+}800 \) K)

\[
q \tau_g = C_s T_g = 5 \times 6 \text{ K},
\]

which are in agreement with the typical data for the indicated glasses.

The generalized criterion for the liquid-glass transition (9) proposed by us can be formulated as follows: a liquid passes into a frozen glassy state when its cooling rate \( q \) reaches a certain fraction of \( C_g \) of the characteristic cooling rate \( q_0 = (T_g/\tau_g) \), which is closely related to the relaxation time of the structure \( \tau_g \) at glass transition temperature \( T_g \):

\[
\frac{q}{q_0} = \left( \frac{T_g}{\tau_g} \right) = C_g \quad (11)
\]

A similar, but slightly different formulation is possible: the liquid glassy when the relaxation time of the structure \( \tau_g \) reaches a fraction of \( C_g \) of the characteristic time of temperature change \( \tau_q = (T_q/q) : \)
\[
\frac{\tau_g}{\tau_f} \left( \frac{T_g}{q} \right) = C_g.
\] (12)

Thus, a generalization of the kinetic criteria for glass transition of Bartenev (1), Volkenstein - Ptitsyn (2), Schmelzer (3) has been proposed. The generalized kinetic criterion for glass transition (9) includes the relaxation time \( \tau_g \), the cooling rate \( q \), the transition temperature \( T_g \), and the almost universal value of \( C_g \), which is determined by the volume fraction of the fluctuation volume \( f_g \) frozen at the glass transition temperature \( T_g \).

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