On relaxation nature of glass transition in amorphous materials

Damba S. Sanditov[a,b], Michael I. Ojovan[c,d,*]

[a] *Buryat State University, Ulan-Ude 670000, Russia*
[b] *Institute of Physical Material Science, Siberian Branch, Russian Academy of Sciences, Ulan-Ude 670047, Russia*
[c] *Department of Materials, Imperial College London, SW7 2AZ, United Kingdom*
[d] *Department of Radiochemistry, Lomonosov Moscow State University, Moscow 119991, Russia*

ABSTRACT

A short review on relaxation theories of glass transition is presented. The main attention is paid to modern aspects of the glass transition equation $q\tau_g = C$, suggested by Bartenev in 1951 (q – cooling rate of the melt, τ_g – structural relaxation time at the glass transition temperature T_g). This equation represents a criterion of structural relaxation at transition from liquid to glass at $T = T_g$ (analogous to the condition of mechanical relaxation $\omega\tau = 1$, where the maximum of mechanical loss is observed). The empirical parameter $C = \delta T_g$ has the meaning of temperature range δT_g that characterizes the liquid-glass transition. Different approaches of δT_g calculation are reviewed. In the framework of the model of delocalized atoms a modified kinetic criterion of glass transition is proposed $(q/T_g)\tau_g = C_g$, where $C_g \cong 7 \cdot 10^{-3}$ is a practically universal dimensionless constant. It depends on fraction of fluctuation volume f_g, which is frozen at the glass transition temperature $C_g = f_g/ln(1/f_g)$. The value of f_g is approximately constant $f_g \cong 0.025$. At T_g the process of atom delocalization, i.e. its displacement from the equilibrium position, is frozen. In silicate glasses atom delocalization is reduced to critical displacement of bridge oxygen atom in Si-O-Si bridge necessary to switch a valence bond according to Muller and Nemilov.

An equation is derived for the temperature dependence of viscosity of glass-forming liquids in the wide temperature range, including the liquid-glass transition and the region of higher temperatures. Notion of (bridge) atom delocalization is developed, which is related to necessity of local low activation deformation of structural network for realization of elementary act of viscous flow – activated switch of a valence (bridge) bond. Without atom delocalization ("trigger mechanism") a switch of the valence bond is impossible and, consequently, the viscous flow. Thus the freezing of atom delocalization process at low temperatures, around T_g, leads to the cease of the viscous flow and transition of a melt to a glassy state. This occurs when the energy of disordered lattice thermal vibrations averaged to one atom becomes equal or less than the energy of atom delocalization.

The Bartenev equation for cooling rate dependence of glass transition temperature $T_g = T_g(q)$ is discussed. The value of f_g calculated from the data on the $T_g(q)$ dependence coincides with result of the f_g calculation using the data on viscosity near the glass transition. Derivation of the Bartenev equation with the account of temperature dependence of activation energy of glass transition process is considered. The obtained generalized relation describes the $T_g(q)$ dependence in a wider interval of the cooling rate compared Bartenev equation. Experimental data related to standard cooling rate $q = 3$ K/min were used in this work.

1. Background

Glasses are solid amorphous materials which transform into liquids upon heating through the glass transition e.g. the solid-like behavior of glasses is separated from liquid-like behavior at higher temperatures by the glass transition temperature, T_g. The glass transition has a pronounced relaxation, kinetic character [1–7] although it is similar to a second-order phase transition in the Ehrenfest sense with continuity of volume and entropy, and discontinuity of their derivatives which are used in practice to detect T_g [8–12]). Discussion of nature of glass continues [13–16] and after some lull it increases significantly, especially in the second decade of the new century as the microscopic mechanism generating the glassy state of matter is still debated. Although specified in the UIPAC definition of glass transition as a second order phase transformation [17] glasses are most often considered as just extremely viscous liquids rather than resulting from

any kind of thermodynamic phase transition thus experimental evidences of phase transition at T_g, such as the specific heat jump, large change of the thermal expansion coefficient and the absence of variation of T_g at low cooling rates are mostly ignored. Decent models treating microscopic mechanisms behind slowing down of relaxation at T_g and describing transitions in liquids and glass transition as true phase transformation have been nevertheless developed among which one can see for example [18–26]. Tournier e.g. considers the transition at T_g as due to a change of the undercooled-liquid Gibbs free energy, which is the driving force of the glass transition. The classical Gibbs free energy change for a crystal formation has been completed with an enthalpy saving which allowed a description of liquid-liquid and stable glass transitions. Most important is that both percolation-based models [22,24–26] and the Tournier model of glass transition [18–21,23] correctly predicts the specific heat jump, the large change of the thermal expansion coefficient at T_g. Moreover newer experimental evidences have been recently found revealing thermodynamic (although kinetically controlled) nature of glass transition such as direct visualisation of macroscopic percolating clusters formed by molecules at glass transition as predicted by theoretical models [27], clustering [28] and structural changes upon glass-transition revealed by in-situ studies of glass-transition by synchrotron XRD via reciprocal and real-space radial distribution functions [29,30], and high-precision measurements of third- and fifth-order nonlinear dielectric susceptibilities that strongly support theories based on thermodynamic amorphous order which is fractal by dimension [31]. The glass transition may therefore belong to a currently developed class of critical phenomena generically termed *topological phase transitions* which are amenable to the scaling approach and characterised by diverging length and time at the transition [32] operating however with fractional dimensions of the conventional space of joining bonds of matter [22,24,25,27,33,34].

The nature of glass transition remains nevertheless one of the topical non-solved problems of the condensed matter physics. Unlike crystal or liquid glassy solid state is in non-equilibrium state, which happens to be (meta)stable, since the transition into equilibrium state is restricted by activation barrier. Both ancient inorganic (silicate) glasses found in natural environments fossil and amber can be given as examples that kept the amorphous structure for tens of millions of years. During external actions, e.g. during annealing, a slow, but continuous density increase is observed – its volume relaxation, which reflects the tendency of the system to the equilibrium state. This paper is devoted to discussion of the modern aspects of relaxation theory of glass transition and viscous flow of glass-forming liquids. New results using this model were obtained, and development of this model is considered.

1.1. Bartenev's approach

1.1.1. The empirical equation of glass transition

The structure of matter freezes during the glass transition, corresponding to conditions, at which molecular rearrangements become so slow (relaxation time becomes so long), that structural changes cannot follow changes of external parameters (in this case temperature). Thus it follows naturally that the glass transition temperature T_g depends on the cooling rate of the glass-forming melt $q = dT/dt$. The lower the cooling rate, the lower the glass transition temperature (Fig. 1.1).

From these and other experimental data it follows that glass transition is a relaxation process and obeys kinetic laws. Evolution of a glass-forming system depends on the rate of changes of external parameters (temperature, pressure), as well as on the relaxation time of the system to the corresponding equilibrium state. Thus, from the point of relaxation approach in the process of liquid-glass transition a deciding role is played by the relation between relaxation time τ and cooling rate q [5–7,35–37]. In Bartenev [37] on the basis of general considerations has suggested the following kinetic criterion of glass
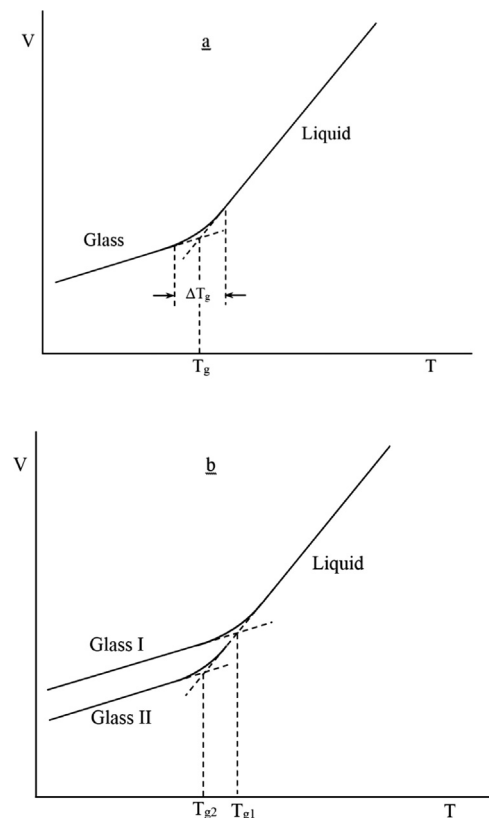

Fig. 1.1. Volume change during the liquid–glass transition in the process of cooling. ΔT_g – glass transition region, T_g – glass transition temperature. T_{g1} – corresponds to cooling rate q_1, and T_{g2} – to cooling rate q_2, $q_2 < q_1$.

transition

$$q\tau_g = C, \tag{1.1}$$

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.

Relation (1.1), which is sometimes called main equation of glass transition [38–40], is successfully applied in relaxation spectrometry of polymers and glasses [39,40] as a condition of structural relaxation transition at $T = T_g$ and is an analogous of usage of criterion $w\tau = 1$ during mechanical relaxation, at which the maximum of mechanical losses is observed. Equations like (1.1) are as well used for description of other relaxation processes, e.g. for thermosimulated electric depolarization of amorphous polymers [39] (e.g. $q\tau_i = C_i$, where τ_i is the relaxation time of i-th relaxation process).

The transition of a liquid into a glassy state upon cooling (and also under the action of high pressure) is called structural glass transition, and the transition from a viscous Newtonian fluid to an elastic glassy body under periodic mechanical action with a certain frequency v is called dynamic (sometimes mechanical) glass transition [39]. The Bartenev equation (1.1) is a condition for the realization of structural glass transition, which is analogous to the criterion of dynamic glass transition at temperature T_v [39,41]

$$2\pi v \tau_g = 1. \tag{1.2}$$

By excluding relaxation time τ_g from Relations (1.1) and (1.2), it is possible to obtain the frequency $v = v_{equiv}$, which is equivalent to a given cooling rate q [39]

$$\nu_{equiv} = \left(\frac{1}{2\pi C}\right) q. \tag{1.3}$$

At $C = q\tau_g$ this equation becomes a more convenient known formula [41]