Glass transition criterion and plastic deformation of glass

Damba S. Sanditov¹,²,*, Michael I. Ojovan³,⁴, **, Migmar V. Darmaev¹

¹Banzarov Buryat State University, Ulan-Ude 670000, Russia
²Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences, Ulan-Ude 670047, Russia
*e-mail: sanditov@bsu.ru
³Department of Materials, Imperial College London, SW7 2AZ, United Kingdom
⁴Department of Radiochemistry, Lomonosov Moscow State University, Moscow 119991, Russia
** e-mail: m.ojovan@imperial.ac.uk, m.i.ojovan@gmail.com

Abstract

We develop the notion that amorphous substances undergo reversible configurational structural changes accompanied by local expansion and compression (atom delocalization) near the glass transition temperature. They are similar in nature to configurational changes in the structure of glasses in the case of reversible frozen (plastic) deformation and its thermally stimulated relaxation. We assume that the glass-liquid transition is associated with the process of atom delocalization caused by bond breaking and formation of elementary excitations e.g. configurons. We discuss the possibility of detection of configuron formation and atom delocalization near glass transition based on temperature dependence of X-rays or neutron first sharp diffraction (pair distribution function) minimum.

Keywords: viscosity, softening of glass, frozen deformation, atom delocalization, configuron, pair distribution function

1. Introduction

The nature of structural changes accompanying vitrification and glass-liquid transitions is not yet fully clear and discussed in many recent publications, see, for example, Refs. [1–6]. In this paper, using delocalized-atom model previously developed [2, 7, 8] we compare glass softening with reversible frozen deformation of glassy solids, which makes it possible to gain certain information about glass-liquid transition and vitrification processes. In addition, we discuss a possible scenario of liquid–glass transition based on switching off the creep triggering mechanism: atom delocalization. Our approach is based on analysis of experimental data on behavior of amorphous materials near the glass transition.

2. Glass-liquid transition as a consequence of atom delocalization

Atom delocalization in silicate glasses is an ultimate displacement of the oxygen atom in a Si–O–Si bridge due to local low-activation-energy deformation of the silicon–oxygen network of
valence bonds [7, 8]. We believe that atom delocalization as an ultimate displacement of a bridging atom is a necessary condition for an elementary event in the process of viscous flow of inorganic glass (for example, valence bond switching [5]).

During cooling of a glass-forming melt, the relative number of delocalized atoms \( \frac{N_e}{N} \) responsible for viscous flow above \( T_g \) decreases in the glass transition region falling to a negligible level which is of the order of 3% [2, 7],

\[
\left( \frac{N_e}{N} \right)_{T=T_g} \approx \text{const} \approx 0.03
\]

This is equivalent to their freezing. Here \( N_e \) is the number of delocalized atoms and \( N \) is the number of atoms. At \( T_h \), the atom delocalization process (transition of an active particle from the ground state to an excited one) becomes frozen. In the glass softening process during heating, the atom delocalization process gradually unfreezes, and the number of delocalized atoms rises from a low level in the frozen state to a concentration \( \frac{N_e}{N} \) corresponding to a liquid state.

The atom delocalization energy,

\[
\Delta \varepsilon_e = p_i \Delta v_e
\]

is closely related to elastic deformation of interatomic bonds and is equal to the work done for an ultimate atomic displacement against internal pressure \( p_i \), due to interatomic (intermolecular) attraction forces. Here \( \Delta v_e \) is the elementary fluctuation volume needed to displace an atom (atom delocalization volume) [2, 7].

Without atom delocalization (which is a creep “triggering mechanism”), viscous flow is impeded. Because of this, as a result of the freezing of the active atom delocalization process in the glass transition region, viscous flow practically stops, and the melt passes into a glassy state. This occurs when the energy of thermal vibrations of the lattice per atom becomes equal to or lower than the atom delocalization energy, \( \frac{i}{2} kT \leq \Delta \varepsilon_e \), which provides the following glass transition criterion:

\[
\frac{i}{2} kT_g \approx \Delta \varepsilon_e \tag{1}
\]

where \( i \) is the number of degrees of freedom of the kinetic unit responsible for the glass transition and \( T_g \) is the glass transition temperature.

As would be expected according to criterion (1), the energy \( \Delta \varepsilon_e \), written as

\[
\Delta \varepsilon_e = RD,
\]

where \( R \) is the gas constant and \( D \) is the empirical parameter of the Enkel equation (3), is a linear function of glass transition temperature \( T_g \) determined by an independent technique for silicate, germanate and borate glasses (Fig. 1, 2).
**Fig. 1.** Correlation between atom delocalization energy $\Delta \varepsilon_e$ and glass transition temperature $T_g$ for two-component silicate and germanate glasses at various oxide contents. $\Delta \varepsilon_e = RD$, where $R$ is the gas constant, $D$ is the empirical parameter of the Enke–El equation (3). $a$ – GeO$_2$–Na$_2$O (mol. % Na$_2$O: 1 – 30, 2 – 25, 3 – 20, 4 – 15); $b$ – SiO$_2$–PbO (mol. % PbO: 1 – 50, 2 – 45, 3 – 30, 4 – 24.6); $c$ – SiO$_2$–K$_2$O (mol. % K$_2$O: 1 – 25, 2 – 20, 3 – 15, 4 – 13); $d$ – SiO$_2$–Na$_2$O (mol. % Na$_2$O: 1 – 33, 2 – 30, 3 – 25, 4 – 20, 5 – 15); $e$ – SiO$_2$–Li$_2$O (mol. % Li$_2$O: 1 – 33, 2 – 30, 3 – 25, 4 – 14, 5 – 10). We used data from [9].
Fig. 2. Dependence of atomic delocalization energy $\Delta \varepsilon_e$ on glass transition temperature $T_g$ for Na$_2$O - B$_2$O$_3$ sodium-glass glasses. $\Delta \varepsilon_e = R D . \text{ mol. }% \text{ Na}_2\text{O}: 1 - 10, 2 - 15, 3 - 20, 4 - 25, 5 - 30$ [9].

$D$ in equation (2) is the empirical parameter in the Jenckel equation for viscosity[10, 11]

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

which successfully describes temperature dependence of viscosity $\eta(T)$ for glass-forming liquids in a wide temperature range. In the case of NaPO$_3$–MSO$_4$ (M= Li, Na, K) sulfophosphate glasses, there is also a linear correlation between the atom delocalization energy $\Delta \varepsilon_e$ and the glass transition temperature $T_g$ (Fig. 3).
Fig. 3. Correlation between the atom delocalization energy $\Delta\varepsilon_e$ and glass transition temperature $T_g$ of sulfophosphate glasses (data from [12]). $\Delta\varepsilon_e = Rc$, $c$ is the parameter of the Bradbury–Shishkin equation (5).

$\Delta\varepsilon_e$ was calculated using the formula

$$\Delta\varepsilon_e = Rc$$  \hspace{1cm} (4)

Here $c$ is an empirical constant (Table 1) in the Bradbury–Shishkin equation [13, 14]

$$\eta = \eta_0 \exp\left[a \exp\left(\frac{c}{T}\right)\right]$$  \hspace{1cm} (5)

which described the $\eta(T)$ behavior in the glass transition region.
Table 1. Properties of NaPO$_3$–MSO$_4$ (M = Li, Na, K) sulfophosphate glasses and atom delocalization model parameters (data from [12])

<table>
<thead>
<tr>
<th>No</th>
<th>Glass</th>
<th>$T_g$, K</th>
<th>$E$, MPa</th>
<th>$\mu$</th>
<th>$a$, K</th>
<th>$c$, K</th>
<th>$f_g$</th>
<th>$\Delta \varepsilon_c$, kJ/mol</th>
<th>$\Delta v_{cos}$, $\AA^3$</th>
<th>$p_i$, kg/mm$^2$</th>
<th>$H_V$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaPO$_3$</td>
<td>523</td>
<td>36100</td>
<td>0.294</td>
<td>0.99</td>
<td>2160</td>
<td>0.016</td>
<td>17.9</td>
<td>17.9</td>
<td>16</td>
<td>195</td>
</tr>
<tr>
<td>2</td>
<td>0.9 NaPO$_3$ - 0.1 Li$_2$SO$_4$</td>
<td>451</td>
<td>41400</td>
<td>0.300</td>
<td>0.97</td>
<td>1940</td>
<td>0.014</td>
<td>16.0</td>
<td>16.1</td>
<td>13</td>
<td>206</td>
</tr>
<tr>
<td>3</td>
<td>0.8 NaPO$_3$ - 0.2 Li$_2$SO$_4$</td>
<td>447</td>
<td>42100</td>
<td>0.303</td>
<td>0.95</td>
<td>1950</td>
<td>0.013</td>
<td>16.1</td>
<td>16.2</td>
<td>14</td>
<td>205</td>
</tr>
<tr>
<td>4</td>
<td>0.7 NaPO$_3$ - 0.3 Li$_2$SO$_4$</td>
<td>429</td>
<td>42300</td>
<td>0.034</td>
<td>0.95</td>
<td>1860</td>
<td>0.014</td>
<td>15.2</td>
<td>15.4</td>
<td>11</td>
<td>212</td>
</tr>
<tr>
<td>5</td>
<td>0.9 NaPO$_3$ - 0.1 Na$_2$SO$_4$</td>
<td>496</td>
<td>37300</td>
<td>0.299</td>
<td>0.97</td>
<td>2060</td>
<td>0.016</td>
<td>17.0</td>
<td>17.1</td>
<td>14</td>
<td>207</td>
</tr>
<tr>
<td>6</td>
<td>0.8 NaPO$_3$ - 0.2 Na$_2$SO$_4$</td>
<td>493</td>
<td>35500</td>
<td>0.292</td>
<td>0.96</td>
<td>2050</td>
<td>0.016</td>
<td>16.9</td>
<td>17.0</td>
<td>15</td>
<td>191</td>
</tr>
<tr>
<td>7</td>
<td>0.7 NaPO$_3$ - 0.3 Na$_2$SO$_4$</td>
<td>490</td>
<td>35400</td>
<td>0.288</td>
<td>0.95</td>
<td>2095</td>
<td>0.015</td>
<td>17.1</td>
<td>17.4</td>
<td>16</td>
<td>172</td>
</tr>
<tr>
<td>8</td>
<td>0.9 NaPO$_3$ - 0.1 K$_2$SO$_4$</td>
<td>444</td>
<td>33800</td>
<td>0.316</td>
<td>0.95</td>
<td>1945</td>
<td>0.013</td>
<td>16.0</td>
<td>16.1</td>
<td>16</td>
<td>175</td>
</tr>
<tr>
<td>9</td>
<td>0.8 NaPO$_3$ - 0.2 K$_2$SO$_4$</td>
<td>453</td>
<td>33500</td>
<td>0.316</td>
<td>0.96</td>
<td>1940</td>
<td>0.014</td>
<td>16.0</td>
<td>16.1</td>
<td>15</td>
<td>185</td>
</tr>
<tr>
<td>10</td>
<td>0.7 NaPO$_3$ - 0.3 K$_2$SO$_4$</td>
<td>473</td>
<td>33400</td>
<td>0.313</td>
<td>0.99</td>
<td>2015</td>
<td>0.014</td>
<td>16.8</td>
<td>16.7</td>
<td>16</td>
<td>180</td>
</tr>
</tbody>
</table>
Parameters \(RD\) and \(Rc\) have the meaning of atom delocalization energy \(\Delta e_{e}\) when deriving the equations of viscosity (3) and (5) in the framework of the delocalized atom model and the activation theory of viscosity [2, 15]:

\[
\eta = \eta_0 \exp\left\{ \frac{\Delta F_\infty}{kT} + \frac{\Delta v_e}{v} \left[ \exp\left( \frac{\Delta e_e}{kT} \right) - 1 \right] \right\} \tag{6}
\]

\[
\eta = \eta_0 \exp\left[ \left( \frac{v}{\Delta v_e} \right) \exp\left( \frac{\Delta e_e}{kT} \right) \right] \tag{7}
\]

Here \(v\) is the volume per atom and \(\Delta F_\infty\) is the high temperature limit of the free activation energy for viscous flow of glass-forming liquids.

In deriving the viscosity equation (6), it was assumed that in liquids and solid amorphous substances, the probability of a kinetic unit \(W\) moving from one local equilibrium position to another is determined, firstly, by the probability \(W_1\) of a configurational change in the structure of for a given kinetic unit and, secondly, by the probability \(W_2\) of the fact that it has sufficient energy \(\Delta F_\infty\) to jump to a new (neighboring) position, so that total probability is: \(W = W_1 W_2\).

At elevated temperatures there are very many “ready-made microregions of structural change” available so that \(W_1 = 1\), and molecular mobility is determined by the probability of a particle jumping into one of these microregions: \(W_2 = \exp (-\Delta F_\infty/kT)\).

As the temperature of melt decreases its structure becomes denser in the glass transition region, and the probability of a local structural change becomes \(W_1 < 1\), therefore it begins to play an important role in the mobility of molecules. The probability \(W_1 (T)\) as a function of temperature is expressed as a double exponential relationship in terms of the model of delocalized atoms. The delocalization of an atom is caused by short-range fluctuations and, in essence, reflects a local configurational structural change. This approach leads to the viscosity equation (6) [2, 7].

At elevated temperatures \((kT >> \Delta e_{e})\), the expression in square brackets vanishes and this equation (6) becomes the usual Arrhenius exponential dependence.

As a result of atom delocalization (atomic displacement) in liquids and amorphous solids, there is formed a fluctuation volume

\[
\Delta V_\epsilon = N_\epsilon \Delta v_\epsilon,
\]

where \(N_\epsilon\) is the number of delocalized atoms. Note that \(\Delta V_\epsilon\) is not the free volume of material. In inorganic glasses, amorphous metallic alloys, amorphous organic polymers, and low-molecular-weight organic glasses, the fraction of the fluctuation volume, \(f_g\), frozen at the glass transition temperature, \(T_g\), weakly depends on the nature of the glass (Table 2) and ranges typically:

\[
f_g = \left( \frac{\Delta V_\epsilon}{V} \right)_{T=T_g} \approx 0.025 \pm 0.030. \tag{8}
\]
Table 2. Parameters of the Williams–Landel–Ferry (WLF) equation ($C_1$ and $C_2$) and fraction of the fluctuation volume, $f_g$, frozen at glass transition temperature, $T_g$ [2, 7, 8, 9]. WLF equation is as follows: $\ln a_T = -\frac{C_1}{T - T_g} / (T - T_g + C_2)$. $a_T = \eta(T) / \eta(T_g)$. $f_g = 1/C_1$, $\Delta \varepsilon_{es} = R T_g \ln(1 / f_g)$.

<table>
<thead>
<tr>
<th>Amorphous substance</th>
<th>$T_g$, K</th>
<th>$C_1$</th>
<th>$C_2$, K</th>
<th>$f_g$</th>
<th>$\ln(1 / f_g)$</th>
<th>$\Delta \varepsilon_{es}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O–SiO$_2$ sodium silicate glasses</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mol % Na$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>782</td>
<td>36</td>
<td>430</td>
<td>0.028</td>
<td>3.6</td>
<td>23</td>
</tr>
<tr>
<td>20</td>
<td>759</td>
<td>36</td>
<td>390</td>
<td>0.028</td>
<td>3.6</td>
<td>23</td>
</tr>
<tr>
<td>25</td>
<td>739</td>
<td>35</td>
<td>355</td>
<td>0.028</td>
<td>3.6</td>
<td>22</td>
</tr>
<tr>
<td>30</td>
<td>721</td>
<td>35</td>
<td>322</td>
<td>0.028</td>
<td>3.6</td>
<td>22</td>
</tr>
<tr>
<td>33</td>
<td>712</td>
<td>35</td>
<td>304</td>
<td>0.028</td>
<td>3.6</td>
<td>21</td>
</tr>
<tr>
<td>35</td>
<td>705</td>
<td>35</td>
<td>291</td>
<td>0.028</td>
<td>3.6</td>
<td>21</td>
</tr>
<tr>
<td>Metallic glasses (amorphous alloys)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$<em>{40}$Ni$</em>{40}$P$_{20}$</td>
<td>602</td>
<td>39</td>
<td>93</td>
<td>0.026</td>
<td>3.6</td>
<td>18</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ni$</em>{15}$P$_{25}$</td>
<td>500</td>
<td>37</td>
<td>95</td>
<td>0.027</td>
<td>3.6</td>
<td>15</td>
</tr>
<tr>
<td>Pd$_{77.5}$Cu$<em>6$Si$</em>{16.5}$</td>
<td>653</td>
<td>38</td>
<td>100</td>
<td>0.026</td>
<td>3.6</td>
<td>19</td>
</tr>
<tr>
<td>Fe$<em>{80}$P$</em>{13}$C$_7$</td>
<td>736</td>
<td>38</td>
<td>120</td>
<td>0.026</td>
<td>3.6</td>
<td>22</td>
</tr>
<tr>
<td>Amorphous organic polymers and selenium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Polyvinyl acetate</td>
<td>305</td>
<td>36</td>
<td>47</td>
<td>0.028</td>
<td>3.6</td>
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</tr>
<tr>
<td>Natural rubber</td>
<td>300</td>
<td>38</td>
<td>54</td>
<td>0.026</td>
<td>3.6</td>
<td>9</td>
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<tr>
<td>Ethyl methacrylate</td>
<td>335</td>
<td>40</td>
<td>65</td>
<td>0.025</td>
<td>3.6</td>
<td>10</td>
</tr>
<tr>
<td>Selenium</td>
<td>303</td>
<td>32</td>
<td>58</td>
<td>0.031</td>
<td>3.5</td>
<td>9</td>
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<td>Low-molecular-weight organic glasses</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propanol</td>
<td>98</td>
<td>41</td>
<td>25</td>
<td>0.024</td>
<td>3.7</td>
<td>3</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>160</td>
<td>44</td>
<td>40</td>
<td>0.023</td>
<td>3.8</td>
<td>5</td>
</tr>
<tr>
<td>Glycerol</td>
<td>185</td>
<td>42</td>
<td>53</td>
<td>0.024</td>
<td>3.7</td>
<td>6</td>
</tr>
</tbody>
</table>

The fraction of the fluctuation volume is essentially constant for a given type of glass. For example, $f_g \approx const = 0.028$ for the sodium silicate glasses (see Table 2). The value of $f_g$ can be determined from viscosity data in the glass transition region [7, 8]. The $f_g$ of the sulfurphosphate glasses also varies in a narrow range ($f_g \approx const$), but it is markedly smaller than that of the silicate glasses (Table 1). The fraction of the fluctuation volume $f_g$ appears in formulas of the delocalized atom model (see, for example, (9)).

Glass softening leads to the formation of states atypical of glassy solids [16, 17]. The notion has been developed that, above $T_g$, glass-forming liquids are in an excited state, which differs from the ground state by a small excess of energy [17]. Based on such work, we assume that
viscous flow of inorganic glass melts above $T_g$ is due to excited delocalized bridging atoms with excitation energy $\Delta \varepsilon_e$. In alkali silicate glasses, this energy is (Table 2) [2, 7] approximately

$$\Delta \varepsilon_e \approx RT_g \ln \left( \frac{1}{f_g} \right) \approx 20 \text{ kJ/mol}. \quad (9)$$

The atom delocalization energy calculated by formula (2) using an empirical constant $D = 2500$ K (Table 3) [11] for the alkali silicate glasses is

$$\Delta \varepsilon_e = RD = 21 \text{ kJ/mol}.$$ 

This is in agreement with data calculated using equation (9) of the delocalized atom model.

Table 3. The empirical constants of Enkel equation (3) and characteristics of the viscous flow and glass transition of amorphous substances calculated from them ($\Delta F_\infty = RB$ and $\Delta \varepsilon_e = RD$)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$B$</th>
<th>$D$</th>
<th>$\Delta F_\infty$</th>
<th>$\Delta \varepsilon_e$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicate glass</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>No15</td>
<td>13226</td>
<td>2500</td>
<td>110</td>
<td>21</td>
<td>[11]</td>
</tr>
<tr>
<td>No18</td>
<td>13348</td>
<td>2500</td>
<td>111</td>
<td>21</td>
<td>[11]</td>
</tr>
<tr>
<td>Na$_2$O 3SiO$_2$</td>
<td>-</td>
<td>1840</td>
<td>-</td>
<td>15</td>
<td>[10]</td>
</tr>
<tr>
<td>Mineral oil:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>1195</td>
<td>800</td>
<td>10</td>
<td>7</td>
<td>[11]</td>
</tr>
<tr>
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<td>928</td>
<td>700</td>
<td>8</td>
<td>6</td>
<td>[11]</td>
</tr>
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<td>741</td>
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<td>6</td>
<td>5</td>
<td>[11]</td>
</tr>
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<td>600</td>
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<td>[11]</td>
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<td>615</td>
<td>600</td>
<td>5</td>
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<td>-</td>
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<td>[10]</td>
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<tr>
<td>Polyisobutylene</td>
<td>-</td>
<td>460</td>
<td>-</td>
<td>4</td>
<td>[10]</td>
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</table>

$\Delta F_\infty$ is the high-temperature limit of the free activation energy of the viscous flow of glass-forming liquids.

It is noteworthy that the atomic delocalization energy $\Delta \varepsilon_e$ is comparable by its order of magnitude with the average energy of thermal vibrational motion of the disordered lattice in the glass transition region, which, for example, according to the law of equal distribution of energy over degrees of freedom (according to the classical expression $\Delta \varepsilon_D = 3N_AkT = 3RT$) for silicate glasses for which $T_g \approx 700 - 900$ K, is about: $\Delta \varepsilon_D = 3RT_g \approx 17 - 22$ kJ/mol. In organic glasses ($D = 480-800$ K, Table 3), the value $\Delta \varepsilon_e = RD \approx 4 - 7$ kJ/mol. This is close to the thermal motion energy in the glass transition region of these systems ($T_g \approx 200-300$ K): $\Delta \varepsilon_D = 3RT_g \approx 5 - 7$ kJ/mol. The data presented are in agreement with the idea of freezing of atomic delocalization process in the glass transition region, when the energy of thermal vibrations of
atomic lattice assigned to an atom becomes equal to or less than the energy (enthalpy) of atomic delocalization (1).

Thus, within the framework of the developed concepts, the glass transition of a liquid is associated with the freezing of the atom delocalization process. From Figures 1 – 3 it follows that for the glasses under study, the delocalization energy of the atom $\Delta e$ linearly depends on the glass transition temperature.

However, it is noteworthy that the straight lines $\Delta e - T_g$ for the glasses studied do not pass through the origin. The glass transition criterion (1) in these cases can be brought in line with experiment if the empirical term $\Delta e_0$ is added

$$\Delta e = \frac{i}{2} kT_g + \Delta e_0,$$  \hfill (10)

whose physical meaning is not yet fully clear. Consider one of the possible options for its interpretation. If the system is under the influence of external pressure $p$, for example, atmospheric pressure, it must be taken into account that the work on limiting displacements of an atom (its delocalization) is performed not only against the internal pressure $p_i$, but also against the external pressure $p$. Therefore, in the glass transition criterion (1) in this case, the energy $\Delta e$ should be replaced by the delocalization enthalpy of the atom $\Delta H_e$

$$\Delta H_e = \frac{i}{2} kT_g,$$ \hfill (11)

where $\Delta H_e$ is determined by the relation [7]

$$\Delta H_e = (p_i + p)\Delta v_e = \Delta e + p\Delta v_e.$$ \hfill (12)

Criterion (11), taking into account (12), is transformed into equality (10)

$$\Delta e = \frac{i}{2} kT_g - p\Delta v_e$$ \hfill (13)

and the empirical term $\Delta e_0$ is related to work performed against external pressure in the process of atom delocalization: $\Delta e_0 = - p\Delta v_e$. Hereinafter, we understood that the volume and energy of the delocalization of an atom refers to a mole of matter.

Thus, using certain approximations and assumptions, in the framework of the model of delocalized atoms at a qualitative level, in principle, a linear correlation between the glass transition temperature and atomic delocalization energy $\Delta e$ can be substantiated.

3. Glass “plasticity” and atom delocalization

Plasticity of inorganic glasses was first detected by Bridgman and Simon [18] and later studied in detail by other researchers [19, 20]. There is experimental evidence that glass can be “plastically” densified during both uniaxial and hydrostatic compression if the applied mechanical stress (pressure) exceeds some threshold $\sigma_i$. In the case of silicate glasses at 20°C the threshold is about
\[ \sigma_y \approx 500 \text{ kg/mm}^2 \left( 5 \times 10^4 \text{ atm} \right), \]

which is of the same order as their Vickers microhardness \( H_V \). Thus, at \( \sigma > \sigma_y \) glass undergoes plastic deformation, which at 20°C lasts indefinitely.

It is remarkable that, during heating to below the glass transition temperature and near \( T_g \), the deformation relaxes to the point of disappearing. Therefore, it turns out to be frozen reversible deformation (see [3]). Nevertheless, following many researchers we will use the term “plastic deformation”, and \( \sigma_y \) will be referred to as the yield (“plastic” flow) stress.

Similar frozen reversible deformation (referred to as stimulated elastic deformation in early reports [21]) is observed in amorphous organic polymers [21 – 23]. Frozen deformation and its thermally stimulated relaxation were recently reported for bulk metallic glasses [24], and the main inherent features of these effects are essentially identical to those in glassy organic polymers and inorganic glasses.

It should be noted that in some cases, when heated near \( T_g \), the frozen strain does not completely relax. Therefore, along with it, sometimes true residual deformation is also observed. This fact requires a detailed study. It is possible that it may be due to partial destruction of the glass, and not a true plastic deformation. In this work, we restrict ourselves to the consideration of frozen deformation, which, when heated near \( T_g \), turns out to be completely reversible.

The rate of processes of “plastical” deformation and its thermally stimulated relaxation is an exponential function of temperature [18, 19, 23]. The activation energy for these processes in the alkali silicate glasses is about \( \Delta u \approx 20 \text{ kJ/mol} \). Thus, frozen reversible deformation of glasses turns out to be a relaxation process with a low activation energy.

Various approaches have been proposed to explain the effect of plasticity of glasses (see, for example, [19–22, 25–30]). According to a number of researchers, it is associated with the mobility of small-scale elementary shears, called: “Somilian dislocations,” “incomplete shears,” and “plastic shear transformations” (see [22]). It is interesting to note that the “plastic” deformation of glasses is quite satisfactorily described formally using the dislocation theory of crystal plasticity [27, 28]. However, until now no defects have been found in glassy systems, similar to an edge dislocation, which is a linear defect of ordered (periodic or aperiodic in quasicrystals) crystal lattice (there is no such lattice in glasses). Nevertheless, the dislocation analogy undoubtedly deserves attention. A possible solution of analogies with dislocations in crystals could be sets of interconnecting broken bonds or delocalised atoms that form complex structures extended in space (see below Fig. 8).

It is convenient to study the “plasticity” of brittle inorganic glasses using microhardness measurements. Indenting a Vickers diamond pyramid and other sharp indenter into silicate glass at 20°C produces a “plastic” pit—a microindent (Fig. 4). Note that the Vickers microhardness \( H_V \) of silicate, germanate, and some other inorganic glasses coincides with their yield stress, \( H_V \approx \sigma_y \), above which “plastic” deformation is observed [3, 31].
As would be expected, during heating to below $T_g$ and near it a microindent decreases and gradually disappears (becomes eliminated) (Fig. 4). The activation energy for this process in silicate glass is $\sim 20$ kJ/mol [3].

The notion that an elementary frozen deformation event in glass reduces to delocalization of an atom (a kinetic unit) is quite consistent with experimental data: the calculated yield stress and the activation energy for this deformation agree with experimental data [3, 31]. The activation energy for “plastic” deformation of silicate glass, $\Delta u \approx 20$ kJ/mol, coincides with the atom delocalization energy in them: $\Delta u \approx \Delta \varepsilon_e$.

The yield stress $\sigma_y$ has the meaning of stress necessary for critical displacement (delocalization) of a kinetic unit. The magnitude of $\sigma_y$ coincides with that of internal pressure,

$$p_i = \Delta \varepsilon_e / \Delta V_e,$$

against which the work of atom delocalization is done. Taking into account the equality $\sigma_y = p_i$ and relation (9) for the atom delocalization energy $\Delta \varepsilon_e$, we conclude that the yield stress $\sigma_y$ and softening temperature (glass transition temperature) $T_g$ are related by

$$\sigma_y = \frac{k \ln(1/f_g)}{\Delta V_e} T_g. \quad (14)$$

As pointed out above, bridging “pivot” atoms, such as oxygen atom in a Si–O–Si bridge, act as kinetic units capable of delocalization in inorganic glasses. Because of this, the atom delocalization volume $\Delta V_e$ in a given class of glasses is essentially constant: $\Delta V_e \approx \text{const}$ [2, 7, 8].

According to formula (14), at $f_g \approx \text{const}$ and $\Delta V_e \approx \text{const}$ there should be a linear correlation between $\sigma_y$ and $T_g$, as well as between $H_V$ and $T_g$, for a particular type of glass. Indeed, there is a linear correlation between the $\sigma_y$ and $T_g$ of amorphous polymers (Fig. 5) [3, 31, 32]. As seen in Figs. 6 and 7, the microhardness (yield stress) of a number of glasses is also a linear function of their glass transition temperature $T_g$ [3, 33].

Thus, the approach under consideration provides a plausible explanation of the linear correlation between the yield stress and softening temperature of glass.

The rate of thermally stimulated recovery of “plastically” deformed glassy polymers, $v_{rel}$, as a function of temperature and pressure meets the following exponential relation [23]:
\[ v_{rel} = A \exp\left( -\frac{\Delta u + p\Delta v_y}{kT} \right). \]  

(15)

For an amorphous cross-linked epoxy polymer, the activation volume of this relaxation process is obtained [23]:

\[ \Delta v_y = (55 \pm 8) \text{ Å}^3. \]  

(16)

In the delocalized atom model, the rate of the thermally stimulated recovery of the initial, undeformed state of glass (15) is determined by the rate of change in the number of delocalized atoms in this process:

\[ v_{rel} \sim \left( \frac{dN_e}{dt} \right), \]

therefore, relation (15) can be derived from the model equation for the relative number of delocalized atoms [7]:

\[ \frac{N_e}{N} = \exp\left( -\frac{\Delta \varepsilon_e + p\Delta v_e}{kT} \right). \]  

(17)

The activation volume \( \Delta v_y \) then receives the following interpretation: \( \Delta v_y = \Delta v_e \). In the case of crosslinked epoxy polymers, such as ER-16 modified epoxy, the atom delocalization volume \( \Delta v_e \) calculated using the model formula [7, 8]:

\[ \Delta v_e = \frac{3(1-2\mu)kT_g}{f_g E} \approx 45 \pm 74 \text{ Å}^3, \]  

(18)

where \( \mu \) is Poisson’s ratio and \( E \) is the modulus of elasticity for uniaxial deformation, is on the same order as the above activation volume \( \Delta v_y \). For the epoxy polymers in question, \( \Delta v_e \) was calculated using data from Filyanov [34]: \( T_g = 358 \text{ K} \), \( \mu = 0.33 - 0.37 \), \( E = (28-35) \times 10^8 \text{ Pa} \), and \( f_g = 0.025 \).

Thus, an ultimate displacement of a small segment of the main chain of the macromolecule (an atomic group in a linking unit) [7, 8] contributes to atom delocalization process in glassy organic polymers.

4. Structural changes near the glass transition temperature

Analysis of entropy, volume, and free energy changes accompanying glass transition in liquids led Kauzmann to conclude that a transition across \( T_g \) leads to freezing of internal degrees of freedom of kinetic units [35]. Most likely, these are configurational degrees of freedom, because only configurational degrees of freedom (and not translational or rotational ones) can contribute to the potential energy of the system [16]. In glass, an excess of potential energy and entropy becomes frozen.
Atom delocalization is due to the rearrangement of neighboring particles and reflects local configurational structural changes. Thermal stimulation of glass (heating to \( T_g \)) unfreezes the atom delocalization process, and the atoms revert back to their equilibrium position. Moreover, near the glass transition temperature there are reversible configurational structural changes that occur at small displacements of atoms or structural groups (kinetic units).

Similar reversible configurational structural changes occur in the case of reversible frozen glass deformation and its thermally stimulated relaxation. This is confirmed by the linear correlation between the softening temperature (glass transition temperature) \( T_g \) and the yield stress \( \sigma_y \), above which “plastic” deformation of glass is observed (Figs. 5–7). Glass softening near \( T_g \) and “plastic” deformation of glass under the effect of mechanical stress \( \sigma > \sigma_y \) at 20°C follow the same molecular mechanism: atom delocalization related to local configurational structural changes.

Fig. 5. Linear correlation between the yield strength \( \sigma_y \) and the glass transition temperature \( T_g \) of amorphous polymers.1 - polytetrafluoroethylene, 2 - polyethylene, 3 - polypropylene, 4 - polyamide, 5 - polyethylene terephthalate, 6 - polyvinyl chloride, 7 - polycarbonate, 8 - polyarylate sulfone, 9 - polysulfone, 10 - polyarylate.
Fig. 6. Correlation between the microhardness $H_V$ and the glass transition temperature of silicate glasses. 1 - lead silicate, 2 - alkaline silicate, 3 - aluminosilicate, 4 - quartz.
Thus, comparison of glass softening with reversible frozen deformation of glassy solids lends support to the assumption that, in the vicinity of the glass transition temperature, the glass undergoes reversible configurational structural changes related to displacement (delocalization) of atoms from their equilibrium position.

In this context, note Belen’kii’s model [36], which was used to demonstrate that, in the vicinity of glass transition temperature, metallic glasses undergo structural changes consisting in a reversible rearrangement of structural units characterized by local dilation (expansion and compression). This conclusion applies to other glass-forming systems as well, because the main general aspects of the glass transition process are qualitatively identical for all amorphous substances, independent of their nature: for amorphous organic polymers, inorganic glasses, metallic amorphous alloys, aqueous solutions, chalcogenides, and others [2, 3]. In particular, this is confirmed by the fact that, in the glass transition region, universal equations and rules work well: Simha–Boyer rule, Bartenev–Ritland equation, “two-thirds” rule, Williams–Landel–Ferry (WLF) equation, and others [3].

However, at the same time, it should be noted that for different classes of glasses at $T_g$ the mobility of various kinetic units related to the different nature of interactions between particles is frozen.

Fig. 7. Linear correlation between $H_V$ and $T_g$ for oxygen-free chalcogenide glasses of arsenic-tellurium-aluminum system at various component contents [33].
The glass transition of linear amorphous organic polymers is a physical relaxation process associated with the loss of segmental mobility at the glass transition temperature, and the glass transition of inorganic glasses with a network structure is a chemical relaxation process and is due to the freezing of the process of switching valence bonds of the type silicon - oxygen - silicon. The glass transition of densely crosslinked cross-linked polymers (for example, epoxides) has also its own specifics, although in qualitative terms they obey the general universal laws of glass transition, like the glassy systems mentioned above [37].

In discussing the nature of the liquid–glass transition, in particular, structural changes in the glass transition region, one should keep in mind that $T_g$ is not constant (in contrast to the crystallization temperature): it is influenced by the process temperature and time, for example, by the temperature scan rate during cooling of glass-forming liquids.

Since the glass transition temperature $T_g$ depends on the melt cooling rate, a number of researchers in the field of glass dilatometry proposed using the concept of a standard cooling rate,

$$q = 3 \text{ K/ min} = 0.05 \text{ K/s},$$

accepted in glass technology (see, for example, [3, 37, 38]). Since $T_g$ is a relatively weak (semilogarithmic) function of $q$, small deviations of $q$ from the standard value have little effect on $T_g$ with rare exceptions. A change in $q$ by ten times shifts the glass transition temperature only slightly, by just $\Delta T \approx 0.03T_g$ [37, 38]. It is commonly believed that the vast majority of $T_g$ data refers to the standard cooling (heating) rate. There is little data for other $q$ values.

The effects of various factors, primarily temperature and time, on the glass transition temperature were discussed in detail by Mazurin [39]. He has recommended the optimal conditions for glass transition temperature measurements. For example, in the case of dilatometry the recommended heating rate is 5 K/min (which is near the standard value). As follows from analysis by Mazurin, the widespread idea that the glass transition temperature of all glasses corresponds to the temperature at which glass viscosity is $10^{12}$ Pa·s ($10^{13}$ Pois) is not justified although it is being stated that “at the same time, for most of the glasses studied to date their $T_g$ (determined under near-standard conditions) corresponds to temperatures at which their viscosity lies in the range from $10^{12}$ to $10^{13}$ P” [39]. However, this is not the case either as can be seen from Table 4 that reveals that the actual viscosities at glass transition temperatures vary from $10^{8.8}$ to $10^{13}$ Pa·s which is far different from arbitrarily agreed viscosity of $10^{12}$ Pa·s.

**Table 4.** The viscosity of amorphous materials at the glass transition temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$, K</th>
<th>Log(η)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>1475; 1480</td>
<td>11.7</td>
<td>[40, 41]</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>786</td>
<td>13</td>
<td>[42]</td>
</tr>
<tr>
<td>70SiO$_2$·21CaO·9Na$_2$O</td>
<td>870</td>
<td>8.8</td>
<td>[43]</td>
</tr>
<tr>
<td>Salol</td>
<td>220</td>
<td>9.8</td>
<td>[44]</td>
</tr>
<tr>
<td>Cresol</td>
<td>220</td>
<td>8.83</td>
<td>[44]</td>
</tr>
</tbody>
</table>
5. Connection with configuron concept

Microscopical delocalization of atoms occurs when chemical bonds are broken by temperature fluctuations (also pressure or irradiation). Broken bonds once formed accommodate surrounding displacements of atoms in an amorphous material. Elementary excitations in amorphous materials caused by bond breaking and resulting relaxed surroundings are termed configurons [45-47]. Glass-liquid transition is treated in terms of configurons as corresponding to condition (e.g. temperature) when so many bonds are broken that a kind of “fragmentation” of solid occurs by some imaginary structures (sets) made of broken bonds [48, 49]. These sets of broken bonds are characterized by their dimensionalities (that appears to be fractal), moreover these sets change the connectivity between building blocks of amorphous materials [50] (Fig. 8).

Fig. 8. Schematic “fragmentation” of solids, that have 1D (linear), 2D (surface) or 3D (body) dimensionalities of bonds, by broken bonds (configurons) that form separate structures (sets). These structures (shown here in red colour) are schematically characterized by 0D, 1D or 2D dimensionalities. In the case of a 3D amorphous solid material (glass) the structure formed out of configurons at glass transition temperature is a percolation cluster (a macroscopic fractal structure) which has the dimensionality \( \approx 2.5 \) [45-47, 50].

The configuron percolation theory of glass transition [45-47, 50] gives for glass transition temperature an explicit equation (19) which is similar in nature to equations (1), (10) and (13) given above

\[
T_g = \frac{H_d}{S_d + R \ln[(1-\phi_c)/\phi_c]}
\]

(19)

Here \( H_d \) and \( S_d \) are quasi-equilibrium enthalpy and entropy of configurons, \( \phi_c \) is the percolation threshold e.g. the critical fraction of space occupied by configurons at percolation. In our treatment herewith we considered coefficient \( i \) in above equations (1), (10) and (13) as the number of degrees of freedom of kinetic unit responsible for the glass transition. In the Tournier model the kinetic units are homogeneously formed superclusters [4], in this case the coefficient \( i \) should be replaced by an effective coefficient normalised to the number of atoms \( n \) in the supercluster \( i_{eff} = i/n \). The coefficient \( i_{eff} \) is hence expected to strongly depend on the material as well as on cooling/heating rate \( q \) particularly for fragile liquids (see Figure 7 in Ref. [4]).
It is important to note that the configuron percolation theory of glass transition [45-47, 50] operates with the volumes of configurons rather than with non-occupied (free) volume therefore no controversies occur for materials characterized by any free volume such as silica glass.

Configurons are elementary excitations in amorphous materials and cannot be readily observed or detected. Therefore, we suggest detection of main results of configuron formation – namely to analyse atomic displacements caused by configuron and clusters of configuron formation using Χ-rays or neutron scattering and processing pair distribution functions obtained. Indeed, structural changes in amorphous materials can be described in real space in terms of pair distribution function $g(r)$ which is proportional to the probability of finding an atom at a position $r$ relative to a reference atom taken to be at the origin [51]. The first sharp diffraction peak (FSDP) e.g. the first peak of pair distribution function $g(r)$ corresponds to atoms in the first coordination shell, whereas the first sharp diffraction minimum (FSDM) is positioned at the end of first coordination shell. The pair distribution function is related to static structure factor $S(q)$ via expression

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty q[S(q) - 1] \sin(qr) \, dq,$$

where $\rho_0$ is the density, $q$ is the scattering vector which for a quantum of incident wavelength $\lambda_0$ is related to the scattering angle $2\theta$ as

$$q = \frac{4\pi}{\lambda_0} \sin(\theta).$$

The larger the $g(R_{FSDM})$, which is proportional to the height of FSDM, the larger the number of atoms shifted from the first coordination shell. Indeed, the average number of atoms in a shell of radius $R_{FSDM}$ near the FSDM of thickness $\delta \ll R_{FSDM}$ is given by equation

$$N_{FSDM} = 4\pi \rho_0 g(R_{FSDM}) R_{FSDM}^2 \delta$$

Therefore, the FSDM height corresponds to those bonds connecting atoms that are broken and enable delocalization of atoms and their shifting (displacements) out of the first coordination shell. It is expedient therefore to analyse behaviour of FSDM as a function of temperature in the vicinity of $T_g$. For metallic glasses, an empirical criterion of glass transition was earlier established by Wendt and Abraham based on changes in the temperature behaviour of pair distribution function minimum divided to its maximum (FSDM/FSDP) seen as a kink at $T_g$ [52]. The Wendt and Abraham criterion has been confirmed by numerous experimental data [53, 54]. It is therefore advisable to analyse the behaviour of FSDM (e.g. of $g(R_{FSDM})$) as a function of temperature near $T_g$ for oxide (including water) and organic glasses either. It is expected to observe a notable kink at $T_g$ for FSDM on heating up oxide and organic glasses which is due to formation of a percolation cluster made of configurons and to delocalisation of atoms at glass-liquid transition. The kink in the temperature behaviour of $g(R_{FSDM})$ is a direct consequence of formation of macroscopic (percolation) clusters made of configurons.

6. Conclusions

It follows from the delocalized atom model that there is a linear correlation between the glass transition temperature $T_g$ of a liquid and the yield stress, a mechanical stress $\sigma_y$ above which reversible frozen deformation of glass is observed at 20°C, as confirmed by experimental data. It is, therefore, reasonable to assume that, in the vicinity of the temperature $T_g$, glass undergoes the same reversible configurational structural changes as those observed in the case of reversible frozen deformation of glass. Glass softening during heating near $T_g$ and reversible frozen deformation of glass under the effect of mechanical stress at 20°C are governed by the
same molecular mechanism: atom delocalization—an ultimate displacement of an atom from its equilibrium position, which is related to local configurational structural changes.

We have developed the notion that atom delocalization, an ultimate displacement of an active atom, is a necessary condition for an elementary event in the process of viscous flow of glasses and melts. For this reason, as a result of freezing of atom delocalization process (creep “triggering mechanism”) in the glass transition region, viscous flow stops and the melt vitrifies e.g. passes into a glassy state. This occurs when the energy of thermal vibrations of the disordered lattice per atom becomes equal to or lower than the atom delocalization enthalpy. This provides a certain glass transition criterion.

We have discussed the connection of atom delocalization with the concept of broken chemical bonds – configurons and suggested to analyze the temperature behaviour of first minimum of pair distribution function for oxide and organic glasses, which is expected to exhibit a notable kink at $T_g$ due to delocalisation of atoms e.g. formation of percolation clusters made of configurons at liquid-glass transition.

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References