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THE INFLUENCE OF ANHARMONICITY OF LATTICE VIBRATIONS ON THE GLASS TRANSITION PROCESS

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Abstract. The results obtained using the delocalized atom model established for the first time in the glass transition region a linear temperature dependence of the anharmonicity parameter for a number of glassy materials. The overall effect of thermal motion due to anharmonicity is the occurrence of tensile thermal pressure on interatomic bonds. Internal pressure, which is the main component of thermal pressure in liquids and solids, is the elastic response of the lattice to external influences and is calculated as the rate at which the internal energy of a substance changes when its volume changes at a constant temperature. Using the elastic deformation region at its upper limit, the proposed model was used to determine the maximum thermal pressure. This maximum thermal pressure leads to the ultimate stretching of the interatomic (intermolecular) bond, which is inversely proportional to the anharmonicity parameter. From the equations of state and the delocalized atom model, a linear correlation follows between the reciprocal of the square of the anharmonicity parameter and the glass transition temperature of glassy solids.

Keywords: delocalized atom model, glassy solids, elastic lattice response, internal pressure, glass transition temperature, maximum interatomic bond strain, anharmonic parameter.

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Introduction

The glass transition process remains an under-researched area, as evidenced by numerous theoretical and experimental scientific papers [1-7]. Like any transition process, glass transition is complicated by two factors. First of all, the liquid-to-glass transition itself can be characterized as a relaxation process. Secondly, some authors classify it as a second-order phase transition. However, in the transition region, an increase in the anharmonicity of lattice vibrations occurs, which is discussed in the following articles [8, 9].

In the delocalized atom model [1], the fundamental principle is the transition of an atom, molecule, or group of particles to the nearest neighboring energy state, or, in other words, an elementary act of the process. In particular, such an act occurs during the heating of glassy solids, as follows according to the proposed model. In the delocalized atom model [1], the fundamental principle is the transition of an atom, molecule, or group of particles to the nearest neighboring energy state, or, in other words, an elementary act of the process. In particular, such an act occurs during the heating of glassy solids, as follows according to the proposed model. According to our proposal, the mechanism described above at the molecular level is the factor responsible for the plastic deformation of amorphous organic polymers and inorganic glasses. The results of the cited studies [2, 3] suggest that the interpretation of plastic deformation of amorphous polymers using the proposed model is sufficiently substantiated. Consequently, the relevance of studying the softening of glasses during their heating also extends to the problem of plastic deformation of non-crystalline solids.

The presented article aims to show that the glass transition temperature of glass-forming melts is linearly correlated with the anharmonicity parameter (Grüneisen parameter γ) of the lattice vibrations of glassy solids.

1 Correlation of glass transition temperature with anharmonic parameter

According to the model [1] of delocalized atoms in the region of the liquid-glass transition, the maximum value of the elastic deformation of interparticle bonds can be taken as an elementary act or, in other words, the critical displacement of the kinetic unit Δr_m. In previous studies, we have shown that the critical deformation of an interatomic bond is inversely proportional to the anharmonic parameter γ (the Grüneisen parameter) [10, 11].

$$\frac{\Delta r_m}{r_0} \cong \frac{1}{6\gamma}. \tag{1}$$

Thermal pressure as a consequence of the anharmonicity of lattice vibrations stretches the interparticle bonds [3, 12, 13]

$$p_t = \gamma \frac{U_D}{V} \cong \gamma \frac{3RT}{V}, \tag{2}$$

Where R is the gas constant, and U_D is the Debye energy of the lattice's thermal vibrations, which in the classical region (above the Debye temperature) is equal to $U_D \cong 3RT$.

The sum of the external p and internal p_i pressures compensates for the thermal p_t pressure. The internal pressure of bodies, due to interatomic interactions, greatly exceeds the external atmospheric pressure. Then the thermal and internal pressures will be approximately equal [3, 12]:

$$p_t \cong p_i\,. \tag{3}$$

The internal pressure is equal to the derivative of the internal energy with respect to volume at a constant temperature $p_i = (dU/dV)T$. Since $U(V)$ is composed of the energies of the bonds that unite the atoms (molecules) into a solid, p_i represents the elastic response of the lattice to its all-round extension or compression. Therefore, the magnitude of the internal pressure is determined by Hooke's law $p_i \approx E\varepsilon$, where E is the bulk modulus, ε is the volumetric elastic strain, and for isotropic bodies the volumetric strain is 3 times greater than the linear strain: $\varepsilon \approx 3(\Delta r/r_0)$. Here $\Delta r/r_0$ is the relative strain of the interatomic bond [3, 12].

Considering that, in the approximation, elastic deformation is carried out up to the limit deformation and, taking into account equation (1), for the maximum value of the internal pressure, we have the following relationship

$$p_{im} \approx 3\left(\frac{\Delta r_m}{r_0}\right)E \approx 3\left(\frac{1}{6\gamma}\right)E \approx \left(\frac{1}{2\gamma}\right)E\,. \tag{4}$$

Under the action of thermal pressure at $T=T_g$, the ultimate deformation of the interatomic bond Δr_m occurs, which corresponds to the maximum value of the internal pressure (4). Substituting (2) and (4) into the equation of state (3) at $T=T_g$, for the relationship between the glass transition temperature and the Grüneisen parameter, we finally obtain the following relationship

$$T_g \cong \left(\frac{EV}{6R}\right)\frac{1}{\gamma^2}\,. \tag{5}$$

An alternative interpretation that the average energy of thermal motion of particles at the softening temperature is equal to the work of maximum deformation of the interatomic elastic bond [1] leads to the same result

$$\frac{1}{2}kT_g = \frac{a(\Delta r_m)^2}{2}\,,$$

where a is the coefficient of quasi-elastic force, k is the Boltzmann constant. This equation and equation (1) allow us to conclude that the anharmonicity parameter and the glass transition temperature are linearly correlated

$$T_g = \left(\frac{ar_0^2}{36k}\right)\frac{1}{\gamma^2}\,.$$

2 Comparison with the experiment

Based on the results of [10, 11, 14], it follows that glassy solids can be represented as two-parameter oscillations based on the type of interparticle bond vibrations. One type of vibration is characterized as thermodynamic, with a lower degree of anharmonicity ($\gamma_D \approx 0.5 - 1.0$), while the other type of vibration is lattice, where the degree of anharmonicity is greater ($\gamma_L \approx 3 - 8$). The lattice parameter reflects the anharmonicity of interchain vibrations during intermolecular interactions, while the thermodynamic parameter is responsible for the anharmonicity averaged over intrachain and other vibrational modes.

Inorganic glasses are also characterized by the presence of two types of lattice vibrations.

Therefore, the equation we obtained (5) shows that there is a linear correlation between the reciprocal of the square of the Grüneisen lattice parameter and the glass transition temperature for noncrystalline solids. This correlation holds best for glasses whose structure type is the same, or whose intermolecular interactions are approximately equal (*EV≈const*)

$$T_g \sim \left(\frac{1}{\gamma_L^2}\right). \tag{6}$$

The lattice parameter for polymers is calculated using quantities that depend on intermolecular interactions, in particular, the coefficient of transverse deformation μ [10, 11]

$$\gamma_L = C\left(\frac{1+\mu}{1-2\mu}\right), \tag{7}$$

where $C \approx$ const ≈ 0.7. The article [14] shows the reliability of equation (7) for a number of glassy solids, including some quasi-isotropic crystalline substances.

Figures 1-4 show the linear correlation between the glass transition temperature and the reciprocal of the square of the anharmonic parameter (8) for a number of inorganic glasses. Experimental data on the glass transition temperature and elastic coefficient are taken from the works [15][1]

$$\frac{1}{\gamma_L^2} = 2\frac{(1-2\mu)^2}{(1+\mu)^2}. \tag{8}$$

The data presented in the figures (Fig. 1–4) for the studied glass samples demonstrate an acceptable linear correlation of the glass transition temperature with the value inverse to the square of the anharmonic parameter.

To compare the melting processes of crystalline solids and the softening of glasses, the correlation between the melting temperature T_f of a number of crystalline oxides and the reciprocal of the square of the anharmonic parameter $1/\gamma_L^2$ was calculated using equation (7). The linear correlation found for these substances is shown in Fig. 4. The presence of a linear correlation for both inorganic glasses and crystalline oxides can be interpreted as a similarity between the aforementioned processes.

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[1] Glass property information system SciGlass – 6.6. 2006. Institute of Theoretical chemistry, Shrewsbury, MA, (www.sciglass.info).

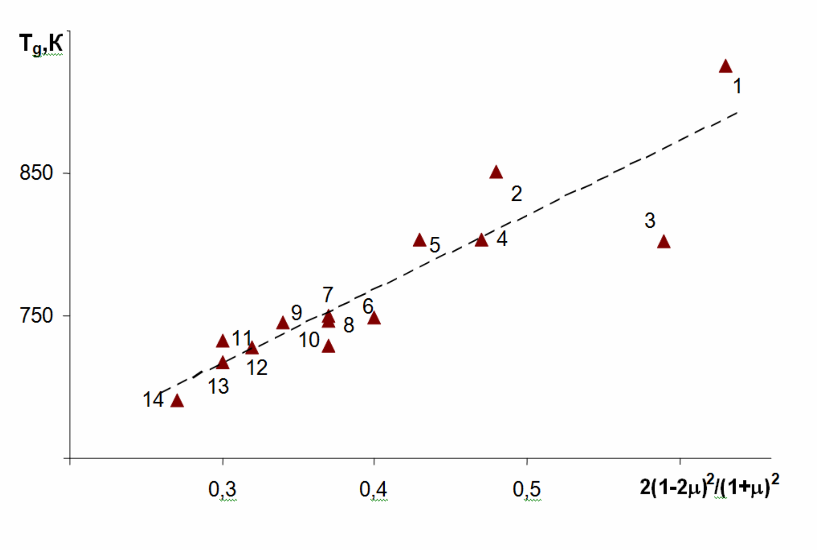

Fig. 1. Correlation between the glass transition temperature and the value of $2(1\text{-}2\mu)^2/(1+\mu)^2$ for $Na_2O\text{-}SiO_2$ glasses. Na_2O content, mol. %: 1- 5, 2- 13, 3- 14.8, 4- 16, 5- 16, 6- 17, 7- 20, 8- 20, 9- 26, 10- 28, 11- 30, 12- 32, 13- 33.3, 14- 40.

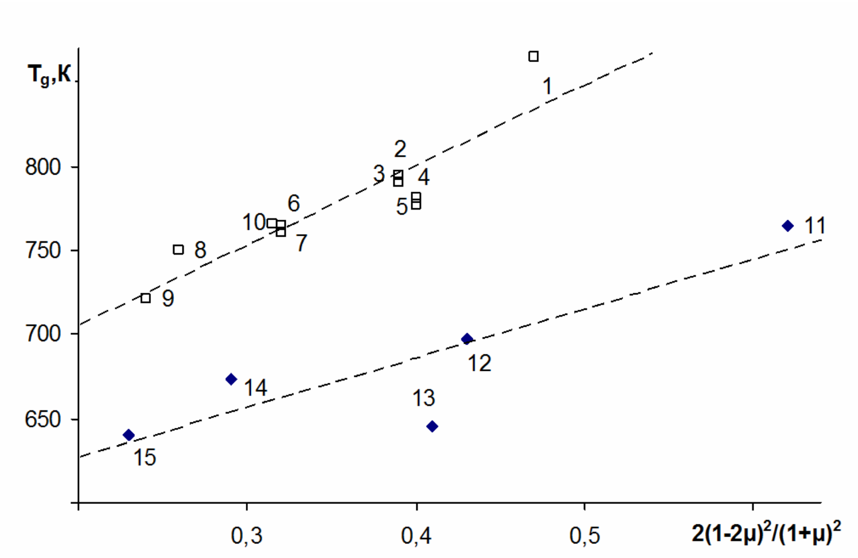

Fig. 2. Dependence of the glass transition temperature on the value of $2(1-2\mu)^2/(1+\mu)^2$ for potassium silicate glasses K_2O-SiO_2 and glasses of the PbO-SiO_2 system. Content of K_2O, mol. %: 1- 5, 2- 13, 3- 13, 4- 15, 5- 16, 6- 20, 7- 20, 8- 25, 9- 30, 10- 32; PbO, mol. %: 11- 30, 12- 45, 13- 50, 14- 55, 15- 60.

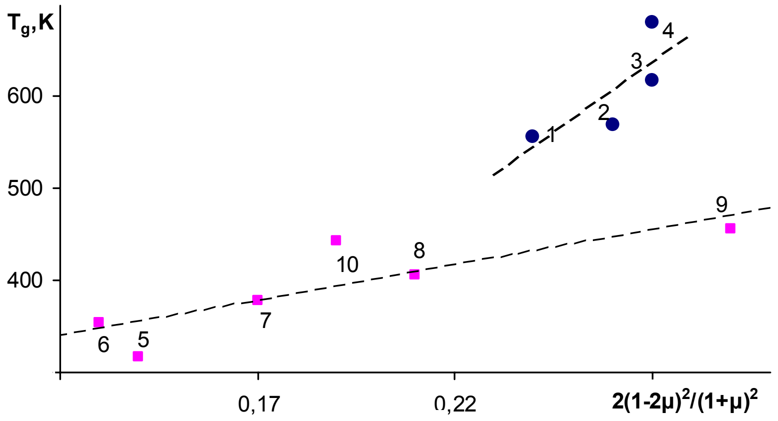

Fig. 3. Correlation between the glass transition temperature and the value of $2(1-2\mu)^2/(1+\mu)^2$ for sodium borate Na_2O-B_2O_2 and chalcogenide As-Se glasses. Na_2O content, mol. %: 1- 10, 2- 15, 3- 20, 4- 25; As, at. %: 5- 5, 6- 10, 7- 20, 8- 30, 9- 40, 10- 50.

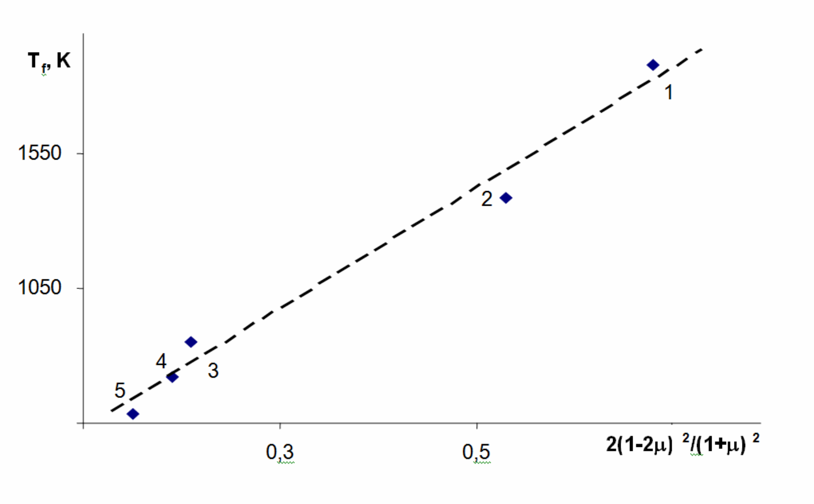

Fig. 4. Dependence of melting temperature T_f on $2(1\text{-}2\mu)^2/(1+\mu)^2$.
1 – SiO_2, 2 – GeO_2, 3 – P_2O_5, 4 – B_2O_3, 5 – As_2O_3 (Data from [16] were used).

Conclusion

When studying the process of glass softening using the model of delocalized atoms, it was shown that for glasses of the same structural type, determined by the same interatomic interaction, a linear correlation should be observed between the softening temperature and the inverse value of the square of the anharmonic parameter.

Comparison with experimental data indeed confirms such a correlation for most of the glasses studied, despite some deviations.

The observed pattern characteristic of the studied inorganic glasses indicates a certain connection between the softening process and the anharmonicity of the lattice vibrations of glass-forming systems. Since the lattice component of anharmonicity is a function of the elasticity, it undoubtedly follows that the transverse strain coefficient plays an important role in the lattice dynamics of glass.

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ВЛИЯНИЕ АНГАРМОНИЗМА РЕШЕТОЧНЫХ КОЛЕБАНИЙ НА ПРОЦЕСС СТЕКЛОВАНИЯ

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Аннотация. Результаты, полученные с помощью модели делокализованных атомов, впервые установили в области стеклования линейную температурную зависимость параметра ангармонизма для ряда стеклообразных материалов. Суммарный эффект теплового движения, обусловленного ангармонизмом, заключается в возникновении растягивающего теплового давления на межатомные связи. Внутреннее давление, являющееся основной компонентой теплового давления в жидкостях и твердых телах, представляет собой упругую реакцию решетки на внешние воздействия и рассчитывается как скорость, с которой внутренняя энергия вещества меняется при изменении его объема при неизменной температуре. Используя область упругой деформации в ее верхнем предельном значении, на основе предложенной модели выявлена максимальная величина теплового давления. Выявленное значение максимального теплового давления приводит к предельному растяжению межатомной (межмолекулярной) связи, которое обратно пропорционально параметру ангармонизма. Из уравнений состояния и модели делокализованных атомов следует линейная корреляция между обратным значением квадрата параметра ангармонизма и температуры стеклования стеклообразных твердых тел.

Ключевые слова: модель делокализованных атомов, стеклообразные твердые тела, упругая реакция решетки, внутреннее давление, температура стеклования, максимальная деформация межатомной связи, ангармонический параметр.

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