Micro- and nanoinhomogeneities in glasses and their melts studied by optical, SAXS, acoustical and thermodynamic methods

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Abstracts. Ultrasonic waves velocities are studied in glasses of the systems Na$_2$O - GeO$_2$ and K$_2$O - GeO$_2$ and in glasses and melts of the system PbO-GeO$_2$. Our Rayleigh-Mandelstam-Brillouin light scattering (RMBS), small angle X-ray scattering (SAXS) and Raman scattering (RS) experimental data for glasses of the system PbO-GeO$_2$ have been analyzed. At small concentrations of metallic oxides a “water-like anomaly” is observed, i.e. the increase of sound velocity with raising temperature. The results of scattering are compared with calculations based on the concept of “frozen-in” equilibrium thermal fluctuations as the origin of static inhomogeneities in glasses. Discussion of glass composition dependences of the data obtained was performed in terms of “freezing” equilibrium thermodynamic fluctuations of density and concentration (chemical composition) in a glass melt at the process of its cooling and transformation into solid state. Usage of acoustic and electrochemical data for glass melts makes it possible to estimate contributions of “frozen-in” density and concentration fluctuations into Rayleigh scattering losses separately. Combining RMBS and RS data gave the answer to the important question: concentration of which structural species fluctuates in a glass melt? It was found that RS spectra of glasses contain information about units of a glass – groups with constant stoichiometry. These groups are characterized by components of the RS spectra intensities of which correspond with concentration of these groups. It means that some multicomponent glasses built from the groups of a single type. As a rule, these glasses are characterized by high level of chemical (and optical) homogeneity

1. Introduction

Study of physical nature of micro- and nanoscale molecular inhomogeneities (IH) in glasses and in their melts provides glass designers with basis for elaboration of glasses with required IH: from optically homogeneous glasses for optical fiber drawing to nano-porous glasses for application as

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sorbents, molecular filters, matrixes for nanoscale crystals, etc. IH of inorganic glasses are caused by technological, physical and chemical origins and should be investigated by a set of experimental methods sensitive to IH of various scales and structure.

The present paper is devoted to two problems: on the anomalous temperature dependence of the sound velocity, and the nature of “frozen-in” IH in GeO$_2$--based glasses (cf. e.g. Ref. [1-4] for other glassforming systems). Behind these specific and seemingly not interconnected questions a general problem (which is not a direct subject of this report) is hidden: the structural relaxation in highly viscous liquids and glasses and its influence on the properties of glasses pertinent in applications. We want to draw attention, using the example of specific questions, to the need of detailed studies of relaxation properties of glassforming liquids and glasses: in the absence of comprehensive information on such properties for concrete materials one is obliged, when discussing the mechanisms responsible for pertinent applied characteristics of such important technical materials as glasses, to limit oneself to enumerating the possible alternatives; naturally, one cannot then hope for a perspective of knowledgeable controlling these characteristics. Modern development of the experimental techniques, particularly conjugation of acoustical and optical spectroscopic methods, permits to fill up the said deficiency but there is yet no, or almost no, examples of systems for which all information necessary for discussing questions like those studied in the present paper can be said to exist.

2. Experimental
Velocity of longitudinal ultrasonic waves in GeO$_2$ and PbO-GeO$_2$ melts was measured by specially designed high temperature (to 1450$^\circ$C) acoustic interferometer [1, 2]. Velocity in solid germanate glasses was measured by pulse-phase acoustic interferometer and pulse ultrasonic method described in [2, 4, 5, 8]. RMBS spectra were measured by light scattering spectrometer including a laser, pressure scanned Fabry-Perot interferometer, and photon counting system. RMBS spectra were processed with deconvolution technique [2, 5, 9]. Rayleigh scattering losses in the glasses under study were estimated in accordance with procedure developed in [2, 5, 9]. Ratio of Rayleigh scattering intensity to intensity of two Mandeshtam-Brillouin scattering components (so-called “Landau — Plazcek ratio” $R_{L-P}$) was measured within $\pm 5\%$ accuracy. SAXS intensity measurements in PbO-GeO$_2$ glasses were performed at room temperature. Measurements of X-rays scattering intensity as function of $q$ were performed on the small-angle apparatus described in [8] and supplemented by high-temperature facility. CuK$_\alpha$-radiation were used. Polarized Raman spectra were measured with 2 cm$^{-1}$ step at room temperature on a two-beam spectrometer at a 90$^\circ$ scattering geometry with a spectral resolution of 4 cm$^{-1}$, using photomultipliers in photon counting mode and the 488 nm line of an argon ion laser for excitation. Relative intensities of Raman spectra of the PbO-GeO$_2$ glasses were compared at a maximum of a band in the range 700 - 900 cm$^{-1}$ with the intensities of fused silica at a frequency of 440 cm$^{-1}$ and fused germanium dioxide at a frequency of 418 cm$^{-1}$ as references.

3. Water-like anomaly of elastic properties of oxide glasses and their melts
Germanium oxide, like silicium and boron oxides, belongs to the group of glassformers whose structure is characterized by the existence of an open-worked network of covalent bonds (oxigene bridges). General property of such systems seems to be the existence of so-called “water-like anomaly” (WLA) in molten and glassy states; the anomaly shows itself most prominently as the increase of sound velocity $v$ with raising temperature. It is not yet clear whether it is possible to separate a common for all systems main mechanism of the anomaly. It is assumed that with raising temperature $T$ a structural rearrangement (often modeled as the increasing content of the second structure) takes place leading to a denser packing and higher instantaneous rigidity; besides, if the process of viscoelastic relaxation is connected with the transition between states with small enthalpy difference, the increasing $T$ can lead to decrease of the relaxation contribution to the equilibrium compliances (both volume and shear). These effects must be sufficiently strong to show against the
background of “normal” temperature dependence — decreasing $v$ with raising $T$. Increasing the content $x$ of metallic oxides-modifiers in the glass destroys the network by substituting ionic bonds for covalent ones, and then WLA is weaken; at sufficiently high $x$ the glass or melt shows a normal behaviour — $dv/dT<0$.

Tables 1–3 show results of our measurements of the density $\rho$ and velocities of sound (longitudinal $v_l$ and transversal $v_t$) in some GeO$_2$-based glasses The data is referred to room temperature, values $dv/dT$ were obtained in 20—100°C. For Na$_2$O - GeO$_2$ and K$_2$O - GeO$_2$ one can clearly see the effect of a gradual weakening WLA with network destruction with increase in modifier percentage. A similar behaviour in melts of the system PbO - GeO$_2$ can be seen in the column 3 of Table 4 discussed below.

### Tables 1–3: Density $\rho$ and sound velocities: longitudinal $v_l$ and transversal $v_t$.

| $x$ | $\rho$ (g/cm$^3$) | $v_l$ (m/s) | $dv/dT$ (m/s)/K | $v_t$ (m/s) |
|-----|------------------|-------------|-----------------|-------------|
| 0   | 3.66             | 3770        | +0.19           | 2282        |
| 1   | 3.72             | 3880        | +0.02           | 2350        |
| 2   | 3.76             | 3940        | -0.04           | 2380        |
| 5   | 3.815            | 4190        |                 | 2470        |
| 15  | 3.96             | 4730        | -0.21           | 2700        |
| ±0.01| ±20             | ±0.02       | ±20             |             |

| $x$ | $\rho$ (g/cm$^3$) | $v_l$ (m/s) | $dv/dT$ (m/s)/K | $v_t$ (m/s) |
|-----|------------------|-------------|-----------------|-------------|
| 1   | 3.72             | 3860        | +0.07           | 2355        |
| 2   | 3.775            | 3990        | 0               | 2370        |
| 5   | 3.80             | 4100        | -0.03           | 2140        |
| 7   | 3.85             | 4200        | -0.03           | 4336        |
| 10  | 3.88             | 4330        | -0.05           | 2480        |
| 17  | 3.87             | 4370        | -0.06           | 24900       |
| ±0.01| ±20             | ±0.02       | ±20             |             |

For glassy SiO$_2$ and B$_2$O$_5$ the existence of WLA is also well known both for longitudinal and transversal sound, and in some groups of multicomponent optical SiO$_2$-based glasses the existence of WLA effect diminishing with the increase of total concentration of modifiers has been found, see Ref. [2-4]. We observed the similar behavior in SiO$_2$ glasses [5] treated by the fast neutrons irradiation (the radiation damage, like the addition of modifiers, tends to destroy the network, at intermediate doses causing strong inhomogeneity, and at large ones substantially, up to 10%, increasing the density of the glass). The value $(1/v_l dv/dT)$, which in the native glass equals $+1.0 \cdot 10^{-4}$ K$^{-1}$ (practically the same for $v_l$ and $v_t$), decreases by a factor of 10 after irradiating with the dose of $10^{20}$ neutrons/cm$^2$. The totality of these evidences can be accepted as indirect but sufficiently convincing proof of the connection of WLA with the existence of the open network structure.

As to the possibility to choose between the mechanisms of WLA in glassformers with the undamaged network, it requires, as stated above, extensive studies of the acoustic relaxation. The simplest theoretical scheme devised for explaining the effect for volume strain on the basis of two-state (or “two structure”) model is described, e.g., in Ref. [6], § 14. Direct application of this model to the case of shear strain, as far as we know, is absent in literature, since the relaxation variable introduced in it — the number of molecules in the excited state — is a scalar and cannot be directly coupled to the traceless tensor of shear strain (though a qualitative understanding of the kinship between mechanisms of shear and structural volume relaxations was put forward by Debye and Frenkel & Obraztsov as early as 1939, see in Ref. [6]). This difficulty can be avoided on the molecular level assuming that in the excited state of a molecule its environment becomes substantially anisotropic, assuming e.g. a symmetry of a uniaxial ellipsoid. Transforming the tensor of the ellipsoid to the laboratory coordinate system and averaging over the axes orientations, one obtains a relaxation variable possessing a symmetry of the full second rank tensor, including isotropic and anisotropic parts. This scheme (which will be presented in full elsewhere) will lead to similar temperature dependences of relaxational contributions to the compressibility and to shear compliance. Thus both
The abovementioned mechanisms of the WLA origin may work in a similar fashion for longitudinal and transversal waves.

The existence of WLA in glassforming melts of PbO - GeO₂ system is demonstrated in the columns 1–3 of Table 4. Here \( v_{\text{eq}} \) — is the equilibrium sound velocity which can be measured only at comparatively high temperatures \( T \); when \( T \) is lowered below the range indicated in the column 2, relaxational (frequency dependent) increase of velocity is observed. We shall not use here the information concerning the relaxation properties which would have been justified (and most interesting) if the frequency range had been much wider than studied in the present work (1–5 MHz). Rather, we shall limit ourselves to using the data cited in Table 4 for obtaining the information on the nature of the inhomogeneities in glasses of this system; information of this kind is important for the possibility of controlling the degree of inhomogeneity of glasses responsible, e.g., for the light losses due to scattering in optical systems.

### Table 4: To the estimation of frozen-in density fluctuations in glasses of the system \( x \text{PbO} – (1-x)\text{GeO}_2 \)

| \( x \) mol.% PbO | Temperat. range for \( v_{\text{eq}} \) | \( v_{\text{eq}}(T_{\text{average}}) \) | \( d v_{\text{eq}}/dT \) | \( T_g \) | \( v_{\text{eq}}(\text{at } T_g) \) | \( R_{L,P_{\text{pp}}} \) | \( I_{pp} \) |
|-----------------|-----------------|-----------------|-----------------|------|-----------------|-----------------|------|
| 0               | 1218±42         | 1417            | (+0.08)         | 565  | (1370)          | (19)            | (1.5) |
| 5               | 1200±100        | 1385            | +0.04           | 439  | 1345            | –               | –    |
| 10              | 1075±75         | 1360            | 0               | 436  | 1345            | –               | –    |
| 20              | 995±165         | 1320            | –0.08           | 438  | 1340            | 21              | 1.7  |
| 25              | 995±165         | 1335            | –0.02           | 441  | 1355            | 21              | 1.7  |
| 35              | 835±165         | 1382            | 0               | 416  | 1375            | 15              | 1.7  |
| 40              | 835±165         | 1383            | –0.3            | 398  | 1420            | 11.5            | 1.6  |
| 50              | 832±152         | 1420            | –0.8            | 362  | 1450            | (8.5)           | (1.6) |
| ±15             | ±15             | ±0.05           | ±50             | ±2   | ±0.2            | (Values in parenthesis in the table are those obtained with insufficient precision)

### 4. Molecular inhomogeneities in glasses and in their melts

We are using for analysis the concept of “frozen-in” fluctuations (FF) [7-10] assuming that static inhomogeneities in glasses include a contribution, unremovable in principle, comprising the fixed by vitrification equilibrium thermal fluctuations (which in the melt have a dynamical character and can be evaluated if thermodynamic properties of the melt above the glass transition point \( T=T_g \) are known). With sufficient precision one can limit oneself to estimation of two statistically independent contributions — those of density fluctuations \( <\delta \rho^2>_{q} \) and concentration fluctuations \( <\delta x^2>_{q} \); here symbol \( \delta \) means the deviation from the average value of the corresponding property, and \( <...>_{q} \) denotes the spectral density for the wave vector \( q \) in the spatial Fourier spectrum of fluctuations (in the observations of scattering is determined by the geometry of the experiment). Acoustic studies of glasses and their melts are used in the frames of FF concept to estimate the contribution to light scattering from the frozen fluctuations of density \( \rho \). It is assumed that the “freezing-in” fluctuations are those of relaxational variables (order parameters) responsible for structural relaxation in the melt. The corresponding part of \( <\delta \rho^2>_{q} \) is proportional to the difference of values of isothermal compressibilities \( \beta_T \) at the glass transition temperature \( T_g \) between the equilibrium melt (\( \beta_{T_{\text{eq}}} \)) and glass (\( \beta_{T_{\text{glass}}} \)): compressibilities are estimated from the measurements of sound velocities \( v \).

The main source of indefiniteness in the estimations is connected with the relaxational behavior of the melt which precludes the possibility of direct measurements of equilibrium sound velocity in the melt at \( T=T_g \). As a plausible hypothesis we shall assume, as is usually done in FF...
estimations, the admissibility of linear extrapolation to \( T_g \) (column 4 in Table 4) from the range shown in column 2. Column 6 shows the results of such extrapolation. (We think it premature to accept the point of view of Kieffer [11], who assumes for some systems a sharp increase of \( v_{\text{equ}} \) at \( T \to T_g \)).

The value of the frozen-in density fluctuations shall be characterized by two quantities: their contribution \( R_{L-P}^{\rho \rho} \) determined from Rayleigh-Mandelstam-Brillouin light scattering (RMBS) spectrum — column 7, and their contribution \( I_{\rho \rho} \) to small-angle X-ray scattering (SAXS) — column 8. These quantities are calculated by the equations:

\[
R_{L-P}^{\rho \rho} \approx \left( \frac{T_g}{T} \right) \left( \frac{v_l^2}{v_{\text{equ}}^2} - 1 \right),
\]

\[
I_{\rho \rho} \approx \rho k T_g \left( \frac{Z N_A}{M} \right)^2 \left( \frac{1}{v_{\text{equ}}^2} - \frac{1}{v_l^2} \right),
\]

where \( T \) is the measurement temperature, \( k \) is the Boltzmann’s constant, \( N_A \) is the Avogadro’s number, \( M \) is the average molar mass, \( Z = Z_1 x + Z_2 (1-x) \), \( Z_1 \) and \( Z_2 \) are the numbers of electrons in the molecules \( \text{PbO} \) and \( \text{GeO}_2 \) respectively; as \( v_l \) and \( v_{\text{equ}} \) (at \( T_g \)) the values from Tables 3, 4 are used. For the deduction of these equation and discussion of the assumed approximations (unimportant in the precision limits of the order 10%) see Ref. [2,4,7-10].

In Figure 1 the values \( I_{\rho \rho} \) are compared to the total measured SAXS intensity \( I \). The difference \( I - I_{\rho \rho} \) gives the value of scattering by concentration fluctuations which can be calculated according to the equation

\[
<\Delta x^2> = \frac{(I-I_{\rho \rho}) V^2}{[Z_1 V_1 - Z_2 V_2 (1-x)]^2},
\]

where \( V_1, V_2 \) and \( V \) are the molar volumes respectively of \( \text{PbO}, \text{GeO}_2 \) and of mixture.

One should note that the difference between the measured \( I \) and calculated \( I_{\rho \rho} \) in the pure \( \text{GeO}_2 \) is probably connected with the noticeable influence of nonstoichiometry — the presence of admixture of \( \text{GeO} \). As shown in Ref. [2,9], this very reason is responsible for a similar discrepancy in the values of \( R_{L-P} \) measured in a number of preceding studies. Light scattering measurement in the \( \text{GeO}_2 \) sample synthetized with a technology suppressing the formation of \( \text{GeO} \) [2,9] gave \( R_{L-P} \) value agreeing with that given in Table 4.

In Figure 2 the values \( R_{L-P}^{\rho \rho} \) are compared to the total measured Landau — Plazcek ratio \( R_{L-P} \). The difference \( R_{L-P} - R_{L-P}^{\rho \rho} \) gives the value of scattering by concentration fluctuations \( R_x \)

\[
R_x \sim \frac{T_D \left( \frac{\partial\Delta n}{\partial \Delta x} \right)^2_{\text{RMS}} \langle \Delta x^2 \rangle}{I_{\text{RMS}}},
\]

where \( \langle \Delta x^2 \rangle \) is the mean square fluctuations of concentration, \( x \), and \( n \) is the refractive index, \( T_D \) is the temperature of “arresting” diffusion processes.

Usage of acoustic and electrochemical data for glasses melts makes it possible to estimating contributions of “frozen-in” density and concentration fluctuations into Rayleigh and small-angle X-ray scattering losses separately. It opens the way to designing multicomponent glasses for fiber drawing with Rayleigh scattering losses less than that of silica glass. Data for independent (from RMBS and SAXS experiments) evaluating of the spectral intensity of frozen-in concentration fluctuations can be obtained from the thermodynamic studies of melts, i.e. measurements of electromotive forces of electrochemical cells [10].
**Figure 1.** The intensity of small-angle X-ray scattering (line CuK$_\alpha$, angle 0' (extrapolation)) in glasses of the system PbO-GeO$_2$ as a function of concentration. Dashed line — calculated contribution of density fluctuations $I_{\rho\rho}$.

**Figure 2.** The Landau-Placzek ratio, $R_{L-P}$, (1) (RMBS experiment), Rayleigh scattering intensity relative to that of silica glass (2), and calculated contribution of "frozen-in" density fluctuations, $R_{L-P_{\rho\rho}}$, (3) as functions of PbO – GeO$_2$ glass composition.

There exist paper [12] on the thermodynamic study of the PbO-SiO$_2$ melts at temperatures 900-1100°C; these temperatures correspond however to viscosities much smaller (and strongly dependent on composition) than estimations given above for “freezing-in” of concentration fluctuations. These results can be used for qualitative estimations of the concentration fluctuations (Figure 3). In 5-20 mol.% PbO range the calculated intensity $\langle \delta x^2 \rangle_q$ (Figure 3) goes through a maximum and increases with the decreasing of temperature. Such behavior implies tendency to the phase separation, or the increase of supercritical composition fluctuations in PbO-GeO$_2$ melts with
decreasing of their temperature. It is in a good qualitative agreement with the experimental data of light scattering and SAXS in glasses of the same compositions (see, Figures 1, 2).

Analysis of experimental data and our calculations allows us to conclude that chemical composition fluctuations play dominant role in Rayleigh light scattering and SAXS in PbO-GeO$_2$ glasses; density fluctuations are important mainly in pure GeO$_2$ and around 40% of PbO. At high PbO contents the system is, according to these data, substantially more homogeneous, whereas at low contents it is more inhomogeneous than the latter though it is still far from demixing.

![Figure 3](image.png)

**Figure 3.** Chemical composition fluctuations in PbO-GeO$_2$ glass melts at the temperatures 1073, 1173 and 1273 K (calculations from the electrochemical data [12]).

Combining RMBS and Raman spectroscopy (RS) data gave the answer to the important question: concentration of which structural species fluctuates in a glass melt? It was found that RS spectra of glasses contain information about units of a glass – groups with constant stoichiometry [13]. Figure 4 shows the diagram of the content for groups with constant stoichiometry in PbO – GeO$_2$ glasses according RS data [13]. These groups are characterized by RS spectra components the intensity of which corresponds with the concentration of these groups. It means that exist some multicomponent glasses built from the groups of a single type. These glasses should be characterized by high chemical (and optical) homogeneity.
Figure 4. Diagram of the content for groups with constant stoichiometry in PbO – GeO$_2$ glasses in accordance with RS data [13].

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6. References
[1] Bogdanov V N, Nemilov S V, Mikhailov I G and Sokolov L N 1975 Fizika i Khimiya Stekla 1 511
[2] Anan’ev A V, Bogdanov V N, Champagnon B, Ferrari M, Karapetyan G O, Maksimov L V, Smerdin S N and Solovyev V A 2007 J. of Non-Crystalline Solids (Submitted)
[3] Bogdanov V, Golovnev A, Smerdin S, Solovyev V, Anan’ev A and Champagnon B 2006 Abstracts of 10th International Conference on the Structure of Non-Crystalline Materials (NCM 10-Praha 2006) September 18-22 2006 Prague, Czech Republic (Invited lecture)
[4] Smerdin S N 1986 Acoustical properties of optical glasses and their melts PhD Thesis (Leningrad: Leningrad State University)
[5] Bogdanov V N, Brovchenko I M, Maksimov L V, Silin A R and Yanush O V 1990 Phys. Status Solidi A 119 621
[6] Mikhailov I G, Solovyev V A and Syrnikov Yu P 1965 Bases of molecular acoustics (Moscow: Nauka Publ.) pp 514
[7] Schroeder J 1977 Light Scattering of Glass: Treatise on Materials Science and Technology 12 Glass I (New York) pp 157-222
[8] Golubkov V V, Bogdanov V N, Pakhnin A Ya, Solovyev V A, Zhivaeva E V, Kabanov V O, Yanush O V, Nemilov S V, Kisliuk A, Soltwisch M and Quitmann D 1999 J. Chem. Phys. 110 4879
[9] Maksimov L V 1997 Rayleigh and Mandelstam-Brillouin scattering by the inhomogeneities of inorganic glasses Dr. Sci. Thesys (Saint Petersburg: Institute of Silicate Chemistry, Russian Academy of Sci.)
[10] Bogdanov V N, Nemilov S V, Solovyev V A, Mikhailov I G, Borisov B F and Nikonov A M 1978 Fizika i Khimiya Stekla 48 44
[11] Kieffer J, Masnik J E, Nikolayev O and Bass J D 1998 Phys. Rev. B 58 694
[12] Iwase M, Miki S-I and Mori T 1979 J.Chem.Thermod. 11 101
[13] Mukhitdinova I A, Sycheva G A, Yanush O V, Maksimov L V and Markova T S 2006 Optical materials 28 1309