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STRUCTURE
AND PROPERTIES

The Origin of the Poisson Ratio of Amorphous Organic Polymers and Inorganic Glasses

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Abstract—Studies concerning the relationship between the value of μ and a number of mechanical and thermal properties of amorphous polymers and glasses are analyzed with the aim to gain information about the origin of Poisson ratio μ in these systems. It is shown that the Poisson ratio features a more pronounced structure-sensitive behavior than the elastic modulus, although the Poisson ratio varies in a narrow range. The relationship between the Poisson ratio and the Grüneisen parameter is substantiated. In this context, the issue of the correlation between harmonic and anharmonic quantities is highlighted. The Poisson ratio is sensitive to lattice dynamics and atomic–molecular structures of polymers and glasses. When light atoms, for example, hydrogen atoms in polyethylene, are replaced with larger and heavier atoms on pendant chains of the macromolecular backbone, anharmonicity increases; that is, lattice Grüneisen parameter γ_D increases. As a result, the Poisson ratio increases because these quantities are related unambiguously. Conditions of preparing an isotropic material with a negative Poisson ratio ($\mu < 0$) are discussed. The relative ultimate strain of the interatomic bond in glassy systems is a function of the Poisson ratio solely. The frozen elastic strain of amorphous polymers and glasses is likewise a single-valued function of the Poisson ratio. The discussed phenomena are interpreted in terms of the Kuz'menko and Pineda theories and the Berlin–Rothenburg–Bathurst model.

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INTRODUCTION

The Poisson ratio μ, by definition, is equal to the ratio of the relative transverse strain of a body to its relative longitudinal elongation under uniaxial tension:

$$\mu = -\frac{\Delta r/r}{\Delta l/l}. \qquad (1)$$

For the overwhelming majority of solids, the Poisson ratio is positive and varies as a rule within the narrow limits $\mu \sim 0.2$–0.3 for both crystals and glasses. For a comparatively small group of solids, like quartz glass, with high yield strength, μ assumes low values on the order of $\mu = 0.15$–0.17. For soft materials with low yield strengths (metals Cu, Ag, Au, and Pb and glassy polymers), this parameter has increased values: $\mu \sim 0.35$–0.44. For porous bodies, for example, foamed plastics and natural cork, $\mu \sim 0$ under uniaxial tension. In contrast, for rubbers, a marked transverse contraction is observed during tension and the Poisson ratio approaches the upper limit, $\mu \sim 0.5$.

As was shown in [1] for isotropic solids, the range of the allowed values of μ is determined through the known formula of the elasticity theory under the condition of elastic-moduli positiveness ($B \geq 0$, $G \geq 0$):

$$\mu = \frac{1}{2}\left(\frac{3B - 2G}{3B + G}\right). \qquad (2)$$

In accordance with this ratio, if isothermal bulk modulus B is zero, the Poisson ratio is equal to the lower limit, $\mu = -1$, and when shear modulus G is zero, we arrive at the upper limit, $\mu = 1/2$. Hence, the value of μ may change in the range

$$-1 \leq \mu \leq 0.5. \qquad (3)$$

Theoretically, a solid with a negative coefficient of transverse strain $\mu < 0$ may exist, but this case is in conflict with common sense.

However, recent publications show that isotropic solids with negative Poisson ratios do exist [2–9]. In 1987, a polymeric isotropic cellular body with $\mu = -0.7$ was synthesized [3, 4]. Recently, glasses of the system Cd–As, for which the values of μ were negative, $\mu = -(0.101 - 0.113)$, have been found [6, 7]. These materials were coined *auxetic* or *auxetics* [2, 9] (derived from the Greek word *auxetos,* which implies swelling).

Along with this unusual phenomenon, other "anomalies" were observed, for example, the unam-

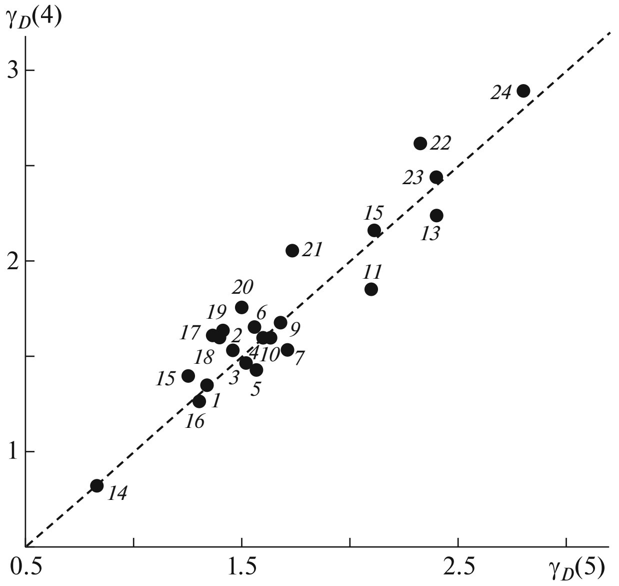


Fig. 1. Comparison of the values of Grüneisen parameter γ_D calculated through Grüneisen equation (4) and Leont'ev formula (5). The numbering of points corresponds to the numbering of solids in Table 1.

biguous relationships of the Poisson ratio with the Grüneisen parameter γ_D, which is a measure of nonlinearity of the interatomic interaction force (anharmonicity) [10, 11], and with the inelastic deformation of solids [12, 13], which is untypical for parameters of the elasticity theory.

This paper presents a brief review and analysis of studies addressing the origin of the Poisson ratio for amorphous polymers and glasses. The main attention is given to the relationship between the value of μ and the structure-sensitive properties of these glassy systems.

THE POISSON RATIO AND THE STRUCTURE-SENSITIVE PROPERTIES OF AMORPHOUS POLYMERS AND GLASSES

This section considers the relationship between the coefficient of transverse strain, μ, and a number of mechanical and thermal properties of amorphous organic polymers and inorganic glasses. These data make it possible to express certain considerations about its origin (see below the section The Origin of the Poisson Ratio). It is remarkable that, in the definition of the Poisson ratio, the case in point is common "soft" static elastic strains; however, the value of μ is a single-valued function of parameters characterizing dynamic and critical processes: for example, the loss of stability of a solid under shearing or the ultimate strain of interatomic and intermolecular bonds in glasses.

The Coefficient of Transverse Strain and the Nonlinearity of the Interatomic Interaction Force

Let us examine the relationship between the coefficient of transverse strain, μ, and the Grüneisen parameter, γ_D, which enters into the equation of state of solids and serves as a measure of anharmonicity of lattice vibrations and nonlinearity of the interatomic interaction force. Grüneisen deduced the formula

$$\gamma_D = \frac{\beta B V}{C_V}, \qquad (4)$$

which can be used to calculate the value of γ_D from the experimental data on the coefficient of volumetric thermal expansion, β; isothermal bulk modulus B; molar volume V; and molar heat capacity C_V.

Along with Grüneisen equation (4), other methods of calculating γ_D were developed. On the basis of the elasticity theory, molecular acoustics, and thermodynamics, K.L. Leont'ev [4] managed to average the frequency of lattice vibrations and to deduce the relationship for the value of γ_D directly from Grüneisen parameter definition:

$$\gamma_D = \frac{3}{2}\left(\frac{B_A}{\rho v_q^2}\right), \qquad (5)$$

where B_A is the adiabatic bulk modulus, ρ is density, and v_q is the average quadratic velocity, whose quadrate is an invariant of the sum of squares of the propagation rates of longitudinal v_L and transverse v_S elastic waves:

$$v_q^2 = \frac{v_L^2 + 2v_S^2}{3}. \qquad (6)$$

Figure 1 compares the results of calculations of γ_D via Grüneisen equation (4) and Leont'ev equation (5) for a number of solids (Table 1) [15]. As is seen, there is satisfactory agreement between these relationships. Deviations from this correlation for several solids are apparently related to the scatter of the γ_D values obtained by different researchers. For example, as follows from three sources, the values of the Grüneisen parameter for aluminum are 2.11, 2.34, and 2.43 [16].

With the use of the expression for the shear modulus, $G = \rho v_S^2$, and formula (6) for v_q^2 let us transform Leont'ev equation (5):

$$\gamma_D = \frac{3}{2}\left(\frac{B_A}{\rho v_S^2}\right)\frac{v_S^2}{v_q^2} = \frac{3}{2}\left(\frac{B_A}{G}\right)\frac{3}{(v_L/v_S)^2 + 2}.$$

Then, with the help of the known expressions of the elasticity theory [1],

$$\frac{B}{G} = \frac{2}{3}\left(\frac{1+\mu}{1-2\mu}\right), \quad \left(\frac{v_L}{v_S}\right)^2 = \left(\frac{2-2\mu}{1-2\mu}\right),$$

Table 1. Comparison of the results of calculation of Grüneisen parameter γ_D via Eqs. (4), (5), and (7) [10, 15, 16]

no.	Elements and compounds	μ	γ_D from the equation according to		
			Grüneisen (4)	Leont'ev (5)	Belomestnykh–Tesleva (7)
1	LiF	0.214	1.34	1.35	1.34
2	NaCl	0.243	1.46	1.53	1.47
3	LiCl	0.245	1.52	1.47	1.48
4	KCl	0.259	1.60	1.60	1.54
5	NaF	0.234	1.57	1.44	1.43
6	NaBr	0.270	1.56	1.65	1.60
7	LiBr	0.256	1.70	1.53	1.53
8	KBr	0.283	1.68	1.67	1.67
9	Fe	0.292	1.68	1.68	1.72
10	KI	0.265	1.63	1.60	1.57
11	Co	0.357	2.10	1.85	2.19
12	Al	0.340	2.11	2.16	2.05
13	Ag	0.379	2.40	2.24	2.40
14	Be	0.034	0.83	0.83	0.82
15	Y	0.245	1.25	1.40	1.48
16	$NaNO_3$	0.257	1.31	1.27	1.53
17	$NaClO_3$	0.270	1.37	1.61	1.60
18	Th	0.254	1.40	1.61	1.52
19	Mg	0.270	1.41	1.64	1.60
20	RbBr	0.267	1.50	1.76	1.59
21	Ta	0.337	1.73	2.05	2.03
22	AgBr	0.396	2.33	2.65	2.58
23	Pd	0.374	2.40	2.44	2.35
24	Au	0.420	2.80	2.90	2.88

and under the approximation $B_A \cong B$ we arrive at the Belomestnykh–Tesleva formula [10]:

$$\gamma_D = \frac{3}{2}\left(\frac{1+\mu}{2-3\mu}\right), \tag{7}$$

which was obtained by the authors of [10] on the basis of other premises.

This formula is attractive because it permits calculations of γ_D from the data on Poisson ratio μ solely. The estimates of γ_D obtained with the help of this formula for many metals and ionic and molecular crystals are in satisfactory agreement with calculations performed through Grüneisen equation (4) (Table 1) [10, 15]. Figure 2 confirms the agreement between the Belomestnykh–Tesleva and Grüneisen equations.

Figure 3 presents the dependence of Grüneisen parameter γ_D that was calculated through the Leont'ev formula (5) on the Poisson ratio determined in accordance with Belomestnykh–Tesleva, $(3/2)(1 + \mu)/(2 - 3\mu)$, for sodium–aluminosilicate glasses containing various amounts of oxides (Table 2 [17]). It is seen that Leont'ev equation (5) and Belomestnykh–Tesleva equation (7) are in good agreement with the experimental data. The same results are obtained for other glasses.

Thus, Poisson ratio μ turns out to be a single-valued function of Grüneisen parameter γ_D.

Noting the agreement between Belomestnykh–Tesleva formula (7) and Grüneisen equation (4), we should be emphasized that this formula unambiguously relates the harmonic (linear) μ and anharmonic (nonlinear) γ_D values.

Attempts to qualitatively explain the existence of the relationship between linear and nonlinear quantities were made in [18–20]. The harmonic a and anharmonic b coefficients in the expansion of the potential energy of interatomic interaction, $U(r)$, are determined by the second and third derivatives of function $U(r)$, respectively, at the equilibrium interatomic distance $r = r_0$. With the use of the Mu potential ($U =$

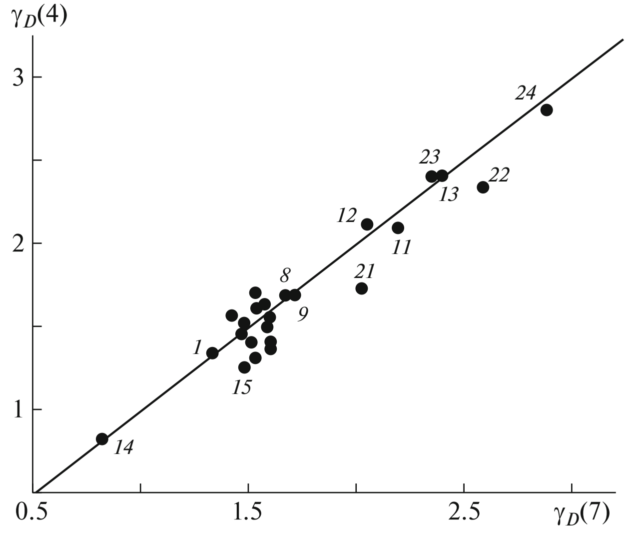


Fig. 2. Comparison of the values of Grüneisen parameter γ_D calculated through Grüneisen equation (4) and Belomestnykh–Tesleva formula (7). The numbering of points corresponds to the numbering of solids in Table 1.

$-Ar^{-m} + Br^{-n}$) in the mentioned derivatives, T.A. Kontorova [18] showed that there is a relationship between the specified coefficients:

$$b = \left(\frac{m+n+3}{2r_0}\right)a.$$

Hence, the considered phenomenon may be explained by the fact that there is a relationship between a and b like the above-mentioned relationship and a related functional dependence of linear and nonlinear properties of solids on a and b.

Thus, the Kontorova approach and the Pineda theory [21] (see below) indicate that correlations may exist between seemingly fully different in origin physical properties of solids, including the difference between harmonic and anharmonic quantities.

The value of γ_D is usually calculated via formula (4), in which the thermal and mechanical characteristics of solids appear. For crystals of the same structural type with the same system of interatomic bonds, relationships obtained by different methods lead to the same values (Table 1): For example, for ionic cubic crystals, $\gamma_D \cong 1.5$–2.0.

In the case of polymer systems, the situation is somewhat different. Strong covalent bonds –C–C– exist along polymer chains between atoms, while weaker intermolecular bonds exist between chains. They have different levels of anharmonicity; therefore, in polymer physics, lattice γ_L and thermodynamic γ_t Grüneisen parameters are distinguished

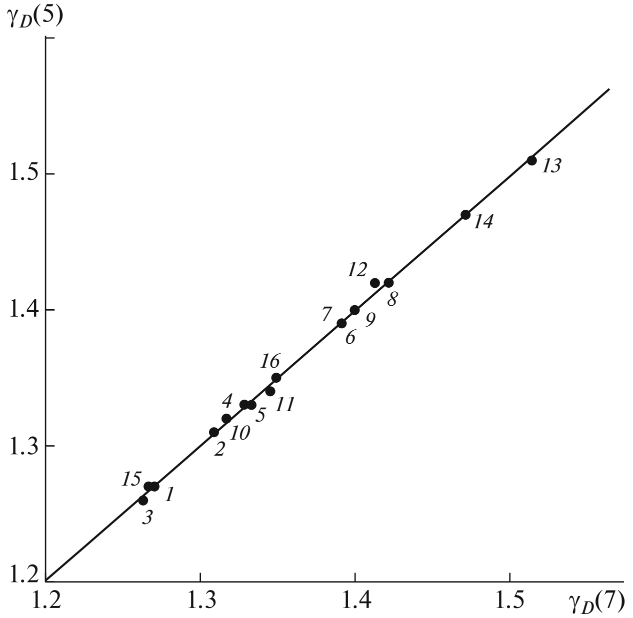


Fig. 3. Comparison of the values of the Grüneisen parameter calculated through Leont'ev equation (5) and Belomestnykh–Tesleva formula (7) for sodium–aluminosilicate glasses. The numbering of points corresponds to the numbering of glasses in Table 2.

([22, 23]). The lattice parameter ($\gamma_L \sim 2$–5) reflects the anharmonicity of low-frequency interchain vibrations related to the intermolecular (van der Waals) interaction, while the thermodynamic parameter ($\gamma_t \sim 1$) expresses anharmonicity averaged over intrachain and other vibrational modes. Thermodynamic Grüneisen parameter γ_t is calculated via Eq. (4), and lattice Grüneisen parameter γ_L is calculated through formulas (7), which relate γ_D to physical quantities determined by the intermolecular interaction.

In alkali–silicate glasses there are two main systems of bonds: ionic–covalent –Si–O–Si– within the silicon–oxygen network and ionic bonds associated with the interaction between alkali-metal ions (R^+) located in voids of the network and nonbridging oxygen ions (Si–O$^-$). The anharmonicity of vibrations of ionic bonds in Si–O$^-R^+$ complexes is more pronounced than that of bonds in an organosilicon network (–Si–O–Si–). This situation is typical for germanate, borate, phosphate, and other inorganic glasses. By analogy with polymers, inorganic glasses may have lattice γ_L and thermodynamic γ_t Grüneisen parameters. The value of $\gamma_L \sim 1.5$–2.0 for alkali–silicate glasses coincides with the data obtained for ionic cubic crystals, and the value of $\gamma_t \sim 1$ coincides with the thermodynamic Grüneisen parameter of amorphous polymers [22, 23].

Table 2. Elastic properties and Grüneisen parameters of sodium–aluminosilicate glasses [17]

no.	Composition with respect to reagent load, mol %			ρ, 10^{-3} kg/m^3	v_L, m/s	v_S, m/s	B, 10^{-8} Pa	μ	γ_D
	Na_2O	Al_2O_3	SiO_2						
1	15	0	85	2.339	5430	3340	342	0.196	1.28
2	15	5	80	2.358	5570	3390	370	0.206	1.31
3	15	10	75	2.410	5697	3510	386	0.194	1.26
4	15	15	70	2.465	5737	3469	416	0.212	1.34
5	15	20	65	2.428	5850	3540	425	0.211	1.34
6	15	25	60	2.472	6000	3568	470	0.226	1.40
7	25	0	75	2.439	5280	3140	359	0.226	1.40
8	25	5	70	2.455	5480	3240	394	0.231	1.41
9	25	10	65	2.461	5610	3330	411	0.228	1.40
10	25	15	60	2.480	5640	3350	418	0.227	1.39
11	25	20	55	2.470	5680	3450	405	0.208	1.32
12	25	25	50	2.499	5790	3490	432	0.215	1.35
13	25	30	45	2.519	6026	3556	490	0.233	1.43
14	35	0	65	2.497	5340	3070	398	0.253	1.52
15	30	5	65	2.486	5500	3200	413	0.244	1.47
16	20	15	65	2.450	5670	3490	390	0.195	1.28
17	17.5	17.5	65	2.447	5746	3458	418	0.216	1.35

The Poisson Ratio and the Ultimate Elastic Strain of the Interatomic Bond

The oscillator theory leads to the following formula for the interatomic interaction force $F = -(dU/dx)$ [24–27]:

$$F \sim -ax + \frac{b}{2}x^2, \tag{8}$$

where $U(x)$ is the potential energy of interaction between atoms and $x = (r - r_0)$ is the displacement of an atom from the equilibrium position. As was noted above, harmonic a and anharmonic b coefficients are determined by the second and third derivatives of function $U(r)$, respectively, at the point of equilibrium, $r = r_0$.

In the region of inflection of curve $U(r)$, the absolute value of force $F(x)$ passes through a maximum (Fig. 4). Hence, the critical elongation of the interatomic bond, $x_m = r_m - r_0$, which corresponds to the maximum of interatomic attraction force F_m, is found from the condition

$$(dF/dx)_{x=x_m} = 0$$

Using relationship (8), we arrive at the following ultimate elongation of the interatomic bond: $x_m = a/b$; therefore, the relative ultimate strain of the interatomic bonds is largely determined by the ratio between harmonic a and anharmonic b coefficients ($x_m = \Delta r_m$):

$$\frac{\Delta r_m}{r_0} = \frac{a}{br_0}. \tag{9}$$

In [27], Ya.I. Frenkel' advanced the following relationship for the coefficient of volumetric thermal expansion of a solid:

$$\beta = \frac{bk}{2ar_0^2B}.$$

After multiplication of the right-hand part of this equality by ratio $(3N_Ar_0/3N_Ar_0)$, it may be represented in the form

$$\beta \cong \left(\frac{br_0}{6a}\right)\frac{C_V}{BV}, \tag{10}$$

where $C_V = 3N_Ak = 3R$ is the molar heat capacity, $V \sim N_Ar_0^3$ is the molar volume, B is the elastic bulk modulus, N_A is Avogadro's number, and R is the gas constant.

A comparison of relationship (10) with Grüneisen equation (4)

$$\beta = \gamma_D\frac{C_V}{BV}$$

Table 3. The Poisson ratios and the calculated characteristics for amorphous and semicrystalline polymers [28]

no.	Polymer	Notation	μ	γ_D (7)	$\Delta r_m/r_0$
1	Polystyrene	PS	0.34	2.1	0.08
2	Poly(vinyl chloride)	PVC	0.35	2.1	0.08
3	Poly(vinyl fluoride)	PVF	0.35	2.1	0.08
4	Poly(methyl methacrylate)	PMMA	0.33	2.0	0.08
5	Epoxy resin (cured)	ER-5	0.35	2.1	0.08
6	Polycarbonate	PC	0.37	2.3	0.07
7	Polyphenylisobutylsilsesquioxane	PPSSO	0.31	1.8	0.09
8	Polyoxymethylene	POM	0.31	1.8	0.09
9	Polypropylene	PP	0.34	2.1	0.08
10	Polytetrafluoroethylene	PTFE	0.32	1.9	0.09
11	Polytrifluorochloroethylene	PTFCE	0.40	2.6	0.06
12	Nylon-6	N-6	0.41	2.7	0.06
13	Nylon-7	N-7	0.38	2.4	0.07
14	Nylon-11	N-11	0.40	2.6	0.06
15	Nylon-12	N-12	0.40	2.6	0.06
16	Poly(4-methyl-1-pentene)	P-4-1-MP	0.39	2.5	0.07
17	Polyvinylidenefluoride	PVDF	0.31	1.8	0.09

leads to the microscopic interpretation of Grüneisen parameter γ_D [24–26]:

$$\gamma_D = \frac{br_0}{6a}. \tag{11}$$

This formula is deduced rigorously with the help of quantum mechanics and covers the low-temperature range ($T < \theta_D$) [24, 25].

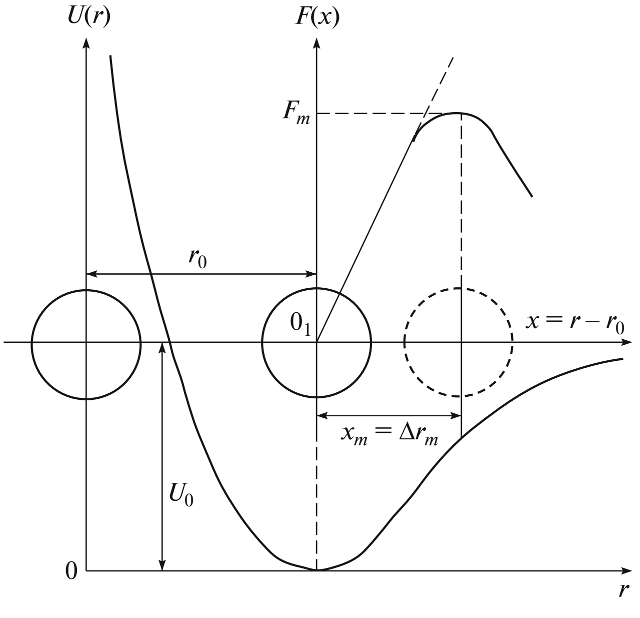


Fig. 4. Scheme of critical atomic displacement Δr_m corresponding to the inflection of the potential $U(r)$ curve.

The substitution of expression (11) into equality (9) leads to the conclusion that the ultimate strain of the interatomic bond is determined by the value of γ_D:

$$\frac{\Delta r_m}{r_0} = \frac{1}{6\gamma_D} \tag{12}$$

With the use of Belomestnykh–Tesleva relationship (7), the relative strain of a bond, $\Delta r_m/r_0$, like γ_D, turns out to be a single-valued function of Poisson ratio μ:

$$\frac{\Delta r_m}{r_0} \sim \frac{(2-3\mu)}{9(1+\mu)} \tag{13}$$

Hence, the Poisson ratios of glassy polymers (Table 3) [28] and inorganic glasses (Table 4) [29, 30] are unambiguously related to the ultimate elastic strain of interatomic and intermolecular bonds.

The value of $\Delta r_m/r_0$ is the strain at which the maximum force of the interatomic (intermolecular) attraction is attained and the transition from elastic deformation to inelastic deformation occurs.

The relative ultimate elastic strain for the studied organic and inorganic glasses varies within small limits (Tables 3, 4):

$$(\Delta r_m/r_0) \sim 0.07 - 0.12.$$

The Loss of Stability of a Solid during Shearing and the Poisson Ratio

As applied to glassy systems, a relationship between the Poisson ratio and Grüneisen parameter γ_D that is

Table 4. The Poisson ratios and the ultimate strains of the interatomic bonds in inorganic glasses [29, 30]

Glass	μ	γ_D	$\Delta r_m/r_0$
Potassium–borate glasses			
$K_2O–B_2O_3$			
K_2O, mol %			
1.1	0.292	1.72	0.10
2.5	0.293	1.73	0.10
3.9	0.293	1.73	0.10
8.5	0.293	1.73	0.10
13.0	0.295	1.74	0.10
18.0	0.301	1.78	0.09
22.8	0.295	1.74	0.10
28.2	0.288	1.70	0.10
33.5	0.303	1.79	0.09
Sulfate–phosphate glasses			
$NaPO_3$	0.294	1.74	0.10
$NaPO_3–Na_2SO_4$			
Na_2SO_4, mol %			
10	0.299	1.77	0.09
20	0.292	1.72	0.10
30	0.288	1.70	0.10
$NaPO_3–K_2SO_4$			
K_2SO_4, mol %			
10	0.316	1.88	0.09
20	0.316	1.88	0.09
30	0.313	1.86	0.09
$0.4NaPO_3 \cdot 0.6Na_2SO_4$	0.320	1.90	0.09
Alkali–silicate glasses			
$Li_2O–SiO_2$			
Li_2O, mol %			
10	0.187	1.24	0.13
25	0.223	1.38	0.12
33.3	0.232	1.42	0.12
$Na_2O–SiO_2$			
Na_2O, mol %			
13	0.205	1.31	0.13
26	0.245	1.48	0.11
33.3	0.255	1.52	0.11
$K_2O–SiO_2$			
K_2O, mol %			
13	0.230	1.41	0.12
25	0.270	1.60	0.10
32	0.250	1.50	0.11

somewhat different from Belomestnykh–Tesleva equation (7) was advanced [23]:

$$\gamma_D = A\left(\frac{1+\mu}{1-2\mu}\right), \tag{14}$$

where multiplier A is determined by the share of fluctuation free volume f_g frozen at the glass-transition temperature:

$$A = \frac{2}{9}\ln\left(\frac{1}{f_g}\right). \tag{15}$$

The value of f_g and, more so, its logarithm weakly depend on the nature of the amorphous compounds [29, 31, 32]. It was found [23] that, in fact, coefficient A is a constant close to unity, $A \sim 1$. Therefore, under the assumption that $A \cong 1$, γ_D may be estimated via formula (14) from the data on the Poisson ratio [23, 32]:

$$\gamma_D \cong \left(\frac{1+\mu}{1-2\mu}\right). \tag{16}$$

After substitution of expression (16) into equality (12) for the ultimate strain of the interatomic bond, we arrive at a relationship analogous to (13):

$$\frac{\Delta r_m}{r_0} \cong \frac{(1-2\mu)}{6(1+\mu)}. \tag{17}$$

The estimate of $\Delta r_m/r_0$ through this formula practically coincides with the results of calculations through Eq. (13).

Relationship (17) is of interest because, as was shown by S.V. Nemilov [33, 34], the Poisson ratio is a single-valued function of the product of parameters of the Mu potential Mu ($U = -\mathrm{A}r^{-m} + \mathrm{B}r^{-n}$), which may be written as

$$\frac{1}{mn} \cong \frac{(1-2\mu)}{6(1+\mu)}. \tag{18}$$

As is seen, the right-hand parts of the last two equalities, (17) and (18), coincide. Hence, it may be suggested that the inverse value of the product of the Mu potential parameters, $1/mn$, characterizes a certain ultimate strain of the interatomic bond:

$$(\Delta r_m/r_0) \sim 1/mn.$$

Indeed, V.B. Lazarev et al. [35] showed that the value of $1/mn$ has the sense of the critical strain at which the solid loses stability during shearing:

$$\varepsilon_c = \frac{1}{mn}.$$

This equality was deduced under the assumption of an elastic–isotropic polycrystalline body with the modified Mu potential, which is not connected with ideas about twoness and centricity of the interatomic interaction [35].

The Poisson Ratio and the Frozen Viscoelastic Strain of Glasses

During the application of a mechanical stress below glass-transition temperature T_g, inelastic deformation appears in silicate glasses; this deformation may be preserved over any time after removal of external stress. It is remarkable that, during heating below softening temperature T_g, strain relaxes and practically disappears. Hence, this is the frozen recoverable retarded elastic strain (Rabotnov's definition). Nevertheless, following some authors, in some cases, the term "plastic" is used (references in [31, 32]).

An analogous frozen recoverable strain is observed for glassy organic polymers. Being "plastically" strained at $T < T_g$, a polymer glass, for example, PMMA, during heating below T_g returns to the initial unstrained state [36, 37], as in the case of silicate glasses.

It is interesting that, for bulky metallic glasses, specifically the glass $Pd_{40}Cu_{30}Ni_{10}P_{20}$, the frozen recoverable strain and its thermally stimulated relaxation at $T < T_g$ are observed [38]. The main features of these processes are in fact the same as those for inorganic glasses and glassy polymers.

Not dwelling on various attempts to explain the origin of the effect of "plasticity" of glasses [31, 32, 36, 37, 39–44], let us demonstrate that, in fact, the frozen retarded elastic strain of glassy materials is unambiguously related to the Poisson ratio.

The microhardness method is suitable for the study of "plasticity" of fragile inorganic glasses. During microindentation of a Vickers diamond tetrahedral pyramid and other pointed indentators into silicate glass, a "plastic" microindentation is formed at $T < T_g$, particularly at 20°C. The Vickers microhardness H_V for silicate, germanate, and other inorganic glasses coincides with ultimate stress $\sigma_{r.el.}$, above which "plastic" (retarded elastic) strain $\varepsilon_{r.el}$ is observed: $H_V \cong \sigma_{r.el}$ [31, 45]. Therefore, for these glasses, the ratio of microhardness to elastic modulus E may be taken as an approximate measure of frozen recoverable strain $\varepsilon_{r.el}$:

$$\varepsilon_{r.el} \cong \frac{\sigma_y}{E} \cong \frac{H_V}{E}. \tag{19}$$

In turn, ratio H_V/E is a function of the Poisson ratio [32] (Table 5):

$$\frac{H_V}{E} \cong \frac{(1-2\mu)}{6(1+\mu)} \tag{20}$$

With consideration for this equality and relationship (19), it may be stated that the frozen retarded elastic strain of glasses is a single-valued function of Poisson ratio μ:

$$\varepsilon_{r.el} \cong \frac{(1-2\mu)}{6(1+\mu)}. \tag{21}$$

Table 5. Elastic moduli μ and E and microhardnesses H_V of inorganic glasses

Glass	Experiment				Calculation (20)	
	μ	E, kg s/mm^2	H_V, kg s/mm^2	$\frac{H_V}{E}$	$\frac{(1-2\mu)}{6(1+\mu)}$	H_V, kg s/mm^2
SiO_2	0.17	7450	692	0.093	0.094	700
Na_2O–SiO_2						
Na_2O, mol %						
16	0.218	6144	442	0.072	0.077	473
20	0.235	5756	405	0.071	0.071	409
33.3	0.255	5993	364	0.061	0.065	376
GeO_2	0.197	4333	360	0.083	0.082	373
Na_2O–GeO_2						
Na_2O, mol %						
5	0.226	5042	370	0.073	0.074	383
20	0.250	6722	450	0.067	0.067	456
30	0.265	5529	350	0.063	0.065	349
K-8	0.225	7920	578	0.073	0.074	586
BK-10	0.250	7516	553	0.075	0.067	505
TF-3	0.219	5469	424	0.075	0.077	420
TF-1	0.225	5355	392	0.077	0.074	395

K-8, BK-10, TF-3, and TF-1 are multicomponent optical glasses.

In accordance with this expression, a linear correlation is observed between the frozen strain $\varepsilon_{r.el}$ and the function of the Poisson ratio $(1 - 2\mu)/(1 + \mu)$ for a number of glasses (Figs. 5, 6). This fact confirms the validity of dependence (21) for at least chalcogenide glasses and a number of inorganic glasses.

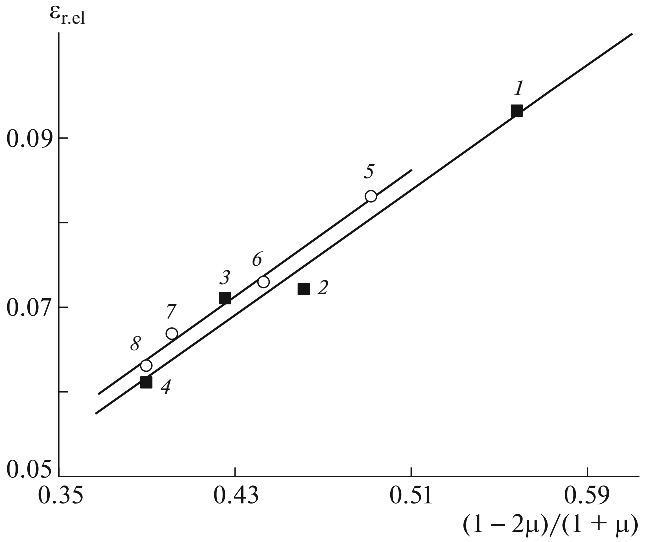


Fig. 5. Dependences of frozen recoverable strain $\varepsilon_{r.el}$ for (squares) sodium–silicate and (circles) sodium–germanate glasses on the function of the Poisson ratio $(1 - 2\mu)/(1 + \mu)$: (*1*) SiO_2; (*2–4*) Na_2O–SiO_2 glasses containing 16, 20, and 33.5 mol % Na_2O, respectively; (*5*) GeO_2; and (*6–8*) glasses Na_2O–GeO_2 containing 5, 20, and 30 mol % Na_2O, respectively.

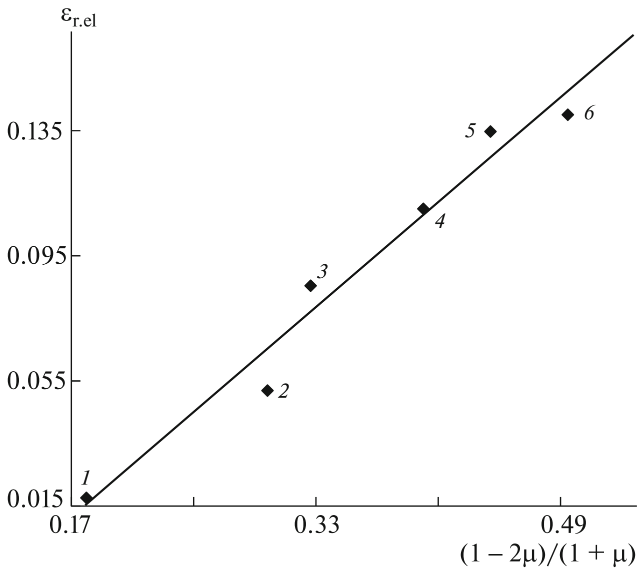


Fig. 6. Plot of $\varepsilon_{r.el}$ vs. function of the Poisson ratio $(1-2\mu)/(1+\mu)$ for chalcogenide glasses: (*1*) $As_{10}S_{90}$, (*2*) $As_{20}S_{80}$, (*3*) $As_{28}S_{72}$, (*4*) $Ge_{13}As_{24}S_{63}$, (*5*) $Ge_{26}Sb_8S_{66}$, and (*6*) $Ge_{32}As_2S_{66}$.

THE ORIGIN OF THE POISSON RATIO

A considerable amount of work on systematization of the experimental data on the Poisson ratio was performed by W. Koster and H. Franz [46] (mostly for metals) and a number of other researchers [2, 4, 21, 47–50]. At the same time, it must be admitted that, at present, the physical meaning of the coefficient of transverse strain of noncrystalline solids is still vague.

The Poisson Ratio and Change in the Volume of a Deformed Body

Ratio μ characterizes primarily a change in body volume during deformation.

A change in the volume $V = V(r, l)$ of a rectangular parallelepiped with length l and a quadratic cross section with side r may be represented as follows [47]:

$$dV = \frac{\partial V}{\partial r}dr + \frac{\partial V}{\partial l}dl. \qquad (22)$$

With consideration for the relationship for volume, $V = r^2 l$, derivatives $(\partial V/\partial r) = 2rl$ and $(\partial V/\partial l) = r^2$ may be found. With due regard for these derivatives, expression (22) may be written as

$$dV = 2rldr + r^2 dl.$$

The transformation of this equality with the use of Poisson ratio definition (1) in the differential form

$$\mu = -\frac{l}{r}\left(\frac{dr}{dl}\right)$$

makes it possible to relate a change in body volume to the value of μ:

$$dV = -\mu 2r^2 dl + r^2 dl.$$

After multiplication of the right-hand part of this relationship by l/l and with consideration for the fact that $r^2 l = V$ and $(dl/l) = \varepsilon_x$, the formula for the relative change in body volume, dV/V, during uniaxial tension may be derived [47]:

$$\frac{dV}{V} = \varepsilon_x(1 - 2\mu). \qquad (23)$$

The Kuz'menko Theory

In accordance with the Kuz'menko approach [48], the Poisson ratio of solids characterizes their ability to withstand a change in volume.

Indeed, as is clear from equality (23), the higher the Poisson ratio of a given solid, the lower its relative volume strain $\Delta V/V$. At $\mu = 0.5$, $\Delta V/V = 0$.

A similar tendency is observed for relative linear strains (expressions (13), (17), (18), and (21)). As μ increases, the critical strain of materials $1/mn$, at which they lose stability during shearing (18), is decreased. The higher the value of μ for this glass, the lower the value of $\Delta r_m/r_0$, at which the transition from the elastic to inelastic deformation occurs (13).

According to the Kuz'menko theory [48], the Poisson ratio, along with the aforesaid, characterizes the fraction of shear energy W_s in total strain energy W:

$$\frac{W_s}{W} = \frac{1 - 3\mu^2 - 3\mu^3}{1 + \mu}. \qquad (24)$$

The higher the value of μ, the lower the relative energy of shear strains, the smaller the shear strength of this material, and the closer it is to a liquid in this respect. Hence, it follows that the Poisson ratio should be related to, for example, such a characteristic of inelasticity of a solid as the yield strength.

If fact, materials with low yield strengths, that is, with increased softness and plasticity (gold, silver, copper, and polymer glasses), feature high values of μ approaching 0.5, while fragile solids with high yield strengths feature low Poisson ratios μ.

The Poisson Ratio and the Lattice Dynamics

During static elastic loading of solids, along with changes in their outer sizes and shapes, "invisible" inner changes of a dynamic character occur: a gain in the frequency of vibrations of atoms in the loaded body and an increase or decrease in its temperature ([51]).

S.I. Mikitishin [50] drew attention to the fact that the value of $1 - 2\mu$ is associated with thermal vibrations of the lattice and (to a certain extent) Debye temperature θ_D; that is, μ depends on the dynamics of the lattice. For the isotropic structures of face-centered and body-centered cubes, the values of $1 - 2\mu$ as a function of ratio $\theta_D\sqrt{m}/T_{vap}$, where T_{vap} is the vaporization temperature and m is the atomic mass, fall on straight lines (Fig. 2 [50]):

$$\frac{\theta_D\sqrt{m}}{T_{vap}} \sim (1 - 2\mu).$$

With respect to this empirical dependence, metals may be grouped in terms of structure type. The value of T_{vap} is apparently used to match dimensionality.

Because product $\theta_D\sqrt{m}$ is closely related to the mean-square displacement of an atom from the equilibrium position, it may be regarded as a peculiar analog of atomic displacement Δr_m and, hence, of atomic-delocalization volume $\Delta V_e = \pi d^2 \Delta r_m$ in glassy solids [52]

$$\Delta V_e = \frac{RT_g}{f_g B},$$

where R is the gas constant, Δr_m is the displacement of the atom from the equilibrium position, f_g is the fraction of fluctuation volume frozen at glass-transition temperature T_g, and B is the bulk modulus.

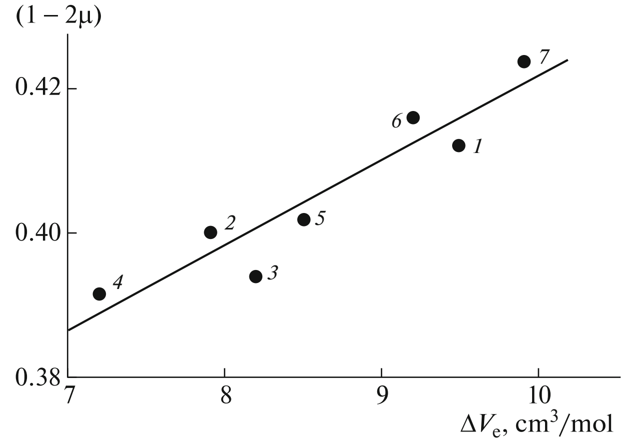


Fig. 7. Plots of the function of the Poisson ratio $(1 - 2\mu)$ vs. the volume of atom delocalization, ΔV_e, for phosphate glasses of the systems $NaPO_3$–Li_2SO_4 and $NaPO_3$–Na_2SO_4. The amounts of Li_2SO_4 are (*1*) 0, (*2*) 10, (*3*) 20, and (*4*) 30 mol %; the amounts of Na_2SO_4 are (*5*) 10, (*6*) 20, and (*7*) 30 mol %.

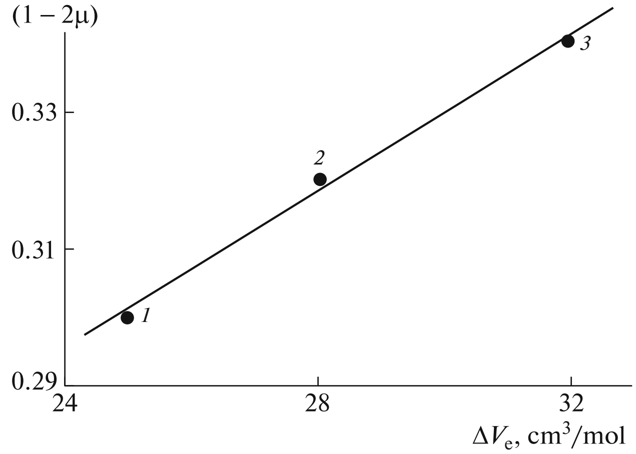


Fig. 8. Dependence of $(1 - 2\mu)$ on ΔV_e for amorphous polymers: (*1*) poly(vinyl chloride), (*2*) polystyrene, and (*3*) poly(methyl methacrylate).

Therefore, by analogy with the above-mentioned linear dependence, a certain correlation between the delocalization volume of the atom, ΔV_e, and the function of Poisson ratio $(1 - 2\mu)$ should be expected

$$(1 - 2\mu) \sim \Delta V_e.$$

Indeed, for a number of inorganic glasses and glassy polymers, there is a linear correlation between the function of Poisson ratio $(1 - 2\mu)$ and the elementary volume ΔV_e needed to displace atoms from the equilibrium position (Figs. 7, 8) [53].

Hence, the value of μ depends on the dynamics of the lattice.

The Pineda Theory

In [21], E. Pineda performed a theoretical study of the effect of structural changes on the elastic constants of metallic glasses. In our opinion, in terms of the Pineda theory, the relationship between the Poisson ratio and Grüneisen parameter (7) may be substantiated at the qualitative level (as in the studies by Kontorova).

The Pineda theory is based on the following three main assumptions. First, the potential of interatomic interaction is composed of harmonic and anharmonic parts:

$$U(r) = a(r - r_0)^2 - b(r - r_0)^3,$$

where a is the harmonic coefficient, b is the anharmonic coefficient, and r_0 is the interatomic distance corresponding to the potential minimum. Second, the distribution of distances between the nearest atoms obeys the Gaussian distribution. Third, elastic properties are determined by the immediate environment of atoms: the first coordination sphere.

The final (cumbersome) formulas of bulk modulus B and shear modulus G contain dimensionless parameters:

$$s = \frac{\delta}{r_0}, \quad \sigma = \frac{\sigma_1}{r_0}, \quad \gamma_1 = \frac{br_0}{a},$$

where $\delta = (r_1 - r_0)$ and r_1 and σ_1 are the average radius and the width of the first coordination sphere, respectively. The values of s and σ characterize deviations of the interatomic distance from its equilibrium value r_0 and the average dispersion in the vicinity of r_0, respectively. Parameter γ_1 implies the degree of anharmonicity of the potential. It is proportional to the Grüneisen parameter $\gamma_D = br_0/6a$ (expression (11)).

The theory was used by Pineda to explain experiments on the structural relaxation and uniform compression of metallic glasses. As a result of structural relaxation, the Poisson ratio decreases (the decrease in parameter σ is stronger), but increases during compression under pressure (where the effect of a decrease in s dominates). On the whole, the theory qualitatively correctly describes change in elastic characteristics in these experiments.

Let us employ the Pineda theory to verify the dependence of elastic-modulus ratio B/G and, hence, Poisson ratio μ on anharmonicity parameter γ_1. It may be inferred that this dependence does exist. In fact, in accordance with formulas, elastic moduli B and G are proportional to harmonic coefficient a, that is, to the parameter of the interatomic potential, and their ratio B/G (and, hence, the Poisson ratio μ) is practically independent of a and mostly determined by anharmonicity parameter γ_1. Hence, it follows that Poisson

Table 6. Mechanical characteristics of Cd–As and Ge–As–S glasses [6, 7]

Composition, at %	v_L, m/s	v_S, m/s	$\rho \times 10^{-3}$, kg/m^3	μ	E, 10^8 Pa	B, 10^8 Pa	G, 10^8 Pa	v_L/v_S	G/E	γ_L
$Cd_{40}As_{60}$	3417	2536	5.97	–0.113	681.1	185.1	383.9	0.74	0.56	0.57
$Cd_{33.3}As_{66.7}$	3393	2510	5.76	–0.104	650.0	179.3	362.9	0.74	0.56	0.58
$Cd_{30}As_{70}$	3370	2490	5.72	–0.101	637.5	176.8	354.6	0.74	0.56	0.58
$As_{10}S_{90}$	2089	930	2.31	0.376	55.1	74.2	20.0	0.44	0.36	2.37
$As_{20}S_{80}$	2229	1180	2.54	0.305	96.3	79.0	35.4	0.53	0.36	1.80
$As_{28}S_{72}$	2255	1228	2.84	0.283	110.0	87.0	42.7	0.54	0.39	1.67
$Ge_{13}As_{24}S_{63}$	2651	1530	3.10	0.250	181.5	121.1	72.6	0.58	0.40	2.50
$Ge_{20}As_{16}S_{64}$	2713	1602	3.05	0.232	192.9	120.1	78.3	0.59	0.41	2.30
$Ge_{26}As_{08}S_{66}$	2745	1720	3.00	0.177	208.9	107.7	88.9	0.60	0.42	1.82

ratio μ depends on the Grüneisen parameter γ_D, that is, on the measure of anharmonicity.

Hence, in terms of the Pineda theory, the calculation of Grüneisen parameter γ_D from the data on transverse-strain coefficient μ (expression (7)) gains an explicit substantiation.

The Model of Randomly Packed Spheres

Among studies devoted to the origin of the Poisson ratio, special emphasis should be placed on the model of randomly packed spheres that interact with each other at the point of contact via two kinds of forces: forces normal to the contact plane (central forces) and tangential forces (friction forces) [4, 49]. It is supposed that normal f_n and tangential f_t forces are proportional to the corresponding displacements of spheres (atoms), x_n and x_t, from the equilibrium position:

$$f_n = a_n x_n, \quad f_t = a_t x_t,$$

where a_n and a_t are the normal and tangential rigidities, respectively. Hence, the Poisson ratio is determined by the ratio of these rigidities, $\lambda = a_t/a_n$ [4]:

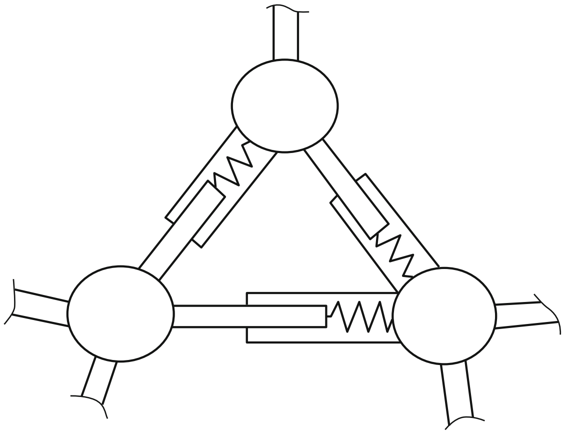
$$\mu = \frac{1-\lambda}{4+\lambda}. \tag{25}$$

At $\lambda = 0$, we have $\mu = 0.25$; this value corresponds to the ensemble of particles with central forces. As λ increases, the value of μ declines, and, at $\lambda = 1$, we have $\mu = 0$; in the limit, at $\lambda \to \infty$, we have $\mu = -1$. It is clear that the model of randomly packed spheres (the model by Berlin et al. [4]) predicts that bodies with negative Poisson ratios $\mu < 0$ may exist and leads to the lower limit $\mu = -1$.

From the viewpoint of this model, auxetic materials (with $\mu < 0$) should possess high flexural rigidities and low axial rigidities in compression–tension: $a_t > a_n$ ($\lambda > 1$). The negative values of the coefficient of transverse strain for Cd–As glasses apparently may be explained by the shape of their main structural unit, which is composed of two interpenetrating tetrahedrons [6, 7]. For this element, tangential rigidity a_t in the region of contact of particles is higher than normal rigidity a_n.

In our opinion, the ratio of shear modulus to the uniaxial compression modulus, G/E, and the ratio of the transverse velocity of sound to the longitudinal velocity of sound, v_S/v_L, may serve to a certain extent as a quantitative measure of the ratio between tangential and normal rigidities $\lambda = a_t/a_n$. As follows from Table 6, ratios $G/E \sim 0.56$ and $v_S/v_L \sim 0.74$ for auxetics, namely, glasses of the Cd–As system, are much higher than those for common chalcogenides As–S ($G/E \sim 0.37$ and $v_S/v_L \sim 0.53$) and glasses of system Ge–As–S ($G/E \sim 0.41$ and $v_S/v_L \sim 0.60$).

For materials with negative Poisson ratios, $\mu < 0$, the main structural units (as supposed by A.A. Berlin et al. [4]) may be, for example, a construction in the form of a triangle at whose apexes interacting atoms linked by elements of the telescopic-antenna type occur. Elements of the construction with $\mu < 0$, which is characterized by rigid angles that couple during deformation [4], are depicted below.



At any strain, the angles of the triangle and the changes in all of its sides are proportional to each other (the condition of geometric similarity).

In fact, all the known potentials of interparticle interaction are either central or much more rigid in the normal direction than in the tangential direction ($\lambda < 1$). Therefore, materials with negative Poisson ratios are few and far between.

In the model of randomly packed spheres, parameter $\lambda = a_t/a_n$, which is equal to the relative tangential (shear) rigidity of the interatomic bond, should be related to the relative energy of shear, W_s/W, in a certain manner in Kuz'menko equation (24). Indeed, the higher the value of Poisson ratio μ, the lower the value of relative tangential rigidity λ (25), and the lower the value of shear strength (24) of the given material. Hence, a relationship between the value of λ and the characteristics of inelasticity of a solid should be expected. Actually, as follows from Belomestnykh–Tesleva formula (7) and relationship (25), there is an unambiguous relationship between λ and the Grüneisen parameter:

$$\gamma_D = \frac{3}{2(1-\lambda)}. \tag{26}$$

In glassy organic polymers, Poisson ratio μ is markedly affected by the side branches of the macromolecular backbone. The minimum values of μ and γ_D are belong to PE, for which light hydrogen atoms play the role of "dangling chains." The replacement of hydrogen atoms with larger and heavier fluorine atoms on passage from polyethylene to polytetrafluoroethylene entails an increase in μ from 0.25 to 0.33 and, accordingly, to an increase in γ_D from 3 to 4. Furthermore, when the fluorine atoms in the repeating connecting unit of polytetrafluoroethylene are replaced with chlorine atoms and, accordingly, on passage to polytrifluorochloroethylene, increases in μ and γ_D are even more pronounced (from 0.33 to 0.37 and from 4 to 5.3, respectively) [54]. Here, γ_D implies the Grüneisen lattice parameter (see above) [22, 23].

When light atoms are replaced with larger and heavier atoms of end or side chain fragments, the nonlinearity of the force of intermolecular interaction and the anharmonicity of lattice vibrations γ_D become more distinct. As a result, the Poisson ratio grows because there is an unambiguous relationship between γ_D and μ (expressions (25), (26)).

In inorganic glasses, the Poisson ratio is closely related to the strain in the structural network of valence bonds, which is related to the displacement of a bridging atom (of the type of oxygen atom in the connecting unit: the bridge –Si–O–Si–). The displacement of the bridging atom is affected to a certain extent by the ions of alkali metals and alkaline-earth metals ("pendant chains").

As the content of sodium oxide Na_2O (sodium ions) in sodium silicate glasses is increased from 0 to 35 mol %, the Poisson ratio and the Grüneisen parameter increase from $\mu = 0.17$ and $\gamma_D = 1.2$ for quartz glass SiO_2 and to $\mu = 0.25$ and $\gamma_D = 1.5$ for Na_2O–SiO_2 glasses containing 35 mol % Na_2O. In accordance with [30, 52], the characteristics of sodium–silicate glasses are as follows:

Na_2O	SiO_2	γ_D	M
0	100	1.2	0.17
15	85	1.3	0.20
25	75	1.4	0.23
35	65	1.5	0.25

These values of μ and γ_D are typical for isotropic bodies with the central forces of interaction of particles, for which the values of λ are small (a_n is much higher than a_t). It is generally agreed that, as the content of alkali-metal ions in alkaline–silicate glasses R_2O–SiO_2 (R = Li, Na, or K) is increased, the ionic character of interatomic bonds becomes more distinct and the transition from the network structure of SiO_2 to the predominantly ionic branched structure of glasses R_2O–SiO_2 is observed ([55]). An increase in μ during this transition may be explained by a reduction in the relative shear rigidity of bonds, λ, in formula (25).

Hence, it is natural that the Poisson ratio depends on the specific features of atomic–molecular structures of glassy systems.

It obvious that, for a number of glasses, a relationship exists between relative tangential rigidity λ and the density of crosslinks, which are determined as the amount of valence bonds per cation, n_n [56]. For linear structures (rubber, polystyrene) with a connectivity of 2 (two anions linked with a cation along the chain), $n_n = 0$ and $\mu \sim 0.4$; for linearly branched structures with a connectivity of 3 (B_2O_3, P_2O_5, As_2O_3), $n_n = 1$ and $\mu = 0.3$; and for structural networks with a connectivity of 4 (SiO_2, GeO_2), $n_n = 2$ and $\mu \sim 0.15$ (i.e., approximately 0.3 : 2.0 = 0.15). The density of crosslink valence bridging bonds additionally provides a clue to the explanation of diametrically opposite melting temperatures of oxides, for which the strengths of bonds are nearly equal. For example, for SiO_2 and GeO_2, the melting temperatures are much higher (1610 and 1115°C) than those for P_2O_5, B_2O_3, and As_2O_3 (580, 450, and 313°C) [56]. The same is true for the softening temperatures of these systems because there is a linear correlation between the melting temperature and the softening temperature: the two-thirds rule $T_g \sim (2/3)T_m$.

The Poisson Ratio and the Fragility of Glasses

It is of interest to consider the linear correlation between the ratio of elastic moduli of glasses, B/G, and so-called "fragility" m, that is, the fundamental characteristic of the temperature dependence of viscosity,

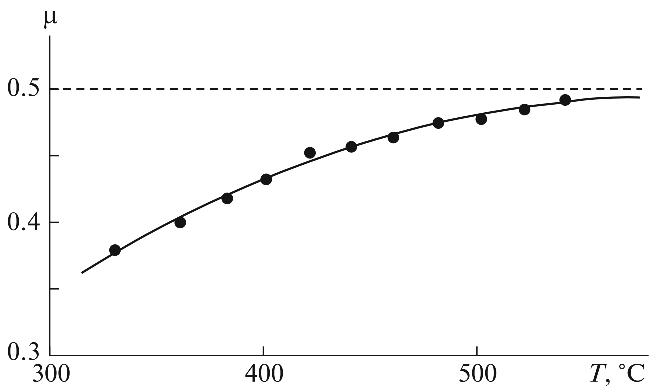


Fig. 9. Temperature dependence of the Poisson ratio, $\mu(T)$, for the sodium–borate glass (mol %) $3Na_2O \cdot 97B_2O$ [59].

$\eta(T)$, in the vicinity of glass-transition temperature T_g [57]:

$$m = 29\left(\frac{B}{G} - 0.41\right), \qquad (27)$$

where fragility is determined through the following relationship [58]:

$$m = \left.\frac{d\log\eta(T)}{d(T_g/T)}\right|_{T=T_g}$$

This correlation was found for various glasses, including glassy systems with covalent, hydrogen, van der Waals, and ionic bonds [57].

This fact implies that the fragility of a melt (the temperature dependence of viscosity in the vicinity of T_g) is determined by the Poisson ratio μ solely, because B/G is a single-valued function of μ (expression (2)) [1]:

$$\frac{B}{G} = \frac{2(1+\mu)}{3(1-2\mu)}.$$

In this context, let us mention the paper by N.S. Andreev and N.A. Bokov [59], in which the experimental data on the temperature dependence of the intensity of light scattering R_g in the glass-transition interval were analyzed in terms of the contribution of elastic energy to the thermodynamic potential. This contribution appears in the viscosity of melts at which the Poisson ratio begins to deviate from $\mu = 0.5$.

The values of μ were calculated through the following formula [59]:

$$\mu = \frac{(2B\alpha_c^2 - 3\varphi_{el})}{(4B\alpha_c^2 - 3\varphi_{el})}, \qquad (28)$$

where $\alpha_c = (1/V)(\partial V/\partial c)$ is the coefficient of concentration expansion, V is volume, c is the molar concentration, φ_{el} is an additional term in the formula for the intensity of light scattering R_g that takes into account the contribution of elastic energy.

The appearance of φ_{el} in the formula for R_g is associated with the need to take into account the appearance of shear elastic strains in the calculation of the minimum work of the formation of fluctuations in solid glasses. With an increase in temperature, the Poisson ratio grows to $\mu = 0.5$, at which the value of φ_{el} turns to zero, $\varphi_{el} = 0$; this situation corresponds to the glass-to-liquid transition.

Figure 9 shows the temperature dependence of the Poisson ratio, $\mu(T)$, for the sodium–borate glass $Na_2O–B_2O_3$ containing 3 mol % Na_2O. Here, dependence $\mu(T)$ was calculated via formula (28) on the basis of light-scattering data. Marked deviations from $\mu = 0.5$ begin to manifest themselves at a temperature of almost 560°C, which is above the glass-transition temperature.

Hence, during cooling of vitrifying melts the shear strain appears at a temperature much higher than glass-transition temperature T_g.

In the future, it will be of indubitable interest to compare the data on the temperature dependence of the coefficient of transverse strain, $\mu(T)$, obtained for the same glasses by two independent methods: diffraction and acoustic.

The theory of phase transitions regards shear strain as a factor suppressing fluctuations in solids. As follows from [59], such suppression of concentration fluctuations likewise occurs during the gradual transition of the vitrifying melt into the solid glass. Unfortunately, the literature lacks experimental data about Poisson ratio $\mu(T)$ in the immediate vicinity of the softening temperature T_g except for calculation of $\mu(T)$ (Fig. 9) [59].

CONCLUSIONS

The Poisson ratio, despite variation of its values within small limits, is among of the most important structure-sensitive properties of glassy solids. The value of μ turns out to be a single-valued function of Grüneisen parameter (7), ultimate strain of the interatomic bond (13), frozen retarded elastic strain (21), fragility (27), fraction of shear energy in the total strain energy (24), and product of Mu potential parameters mn (18). In addition, transverse-strain coefficient μ is unambiguously related to the so-called fractal dimensionality of structural disturbances of the three-dimensional lattice, d_f [35, 60], i.e.,

$$d_f = 2(1+\mu),$$

and to the dimensionality of localization regions of energy stored by the deformed body, D_f [35, 60], i.e.,

$$D_f = \frac{2(1-\mu)}{(1-2\mu)}.$$

At the same time, the physical meaning of the Poisson ratio of glassy solids remains vague [2, 4, 21, 46–50, 56].

Among theoretical developments, the Berlin–Rothenburg–Bathurst model [4], the Kuz'menko theory [48], and the Pineda theory [21] deserve attention. In terms of these approaches it may be explained on the qualitative level why the Poisson ratio is unambiguously related to the Grüneisen parameter, that is, the measure of anharmonicity; why for glasses with high yield strengths, the values of μ are higher, while for soft materials with low yield strengths, the values of μ are smaller; which structural features should be exhibited by isotropic solids with a negative Poisson ratio; and why μ is a single-valued function of the critical strain, at which the transition from the elastic deformation to the inelastic deformation occurs.

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