

# Nature of Poisson's ratio of amorphous polymers and glasses and its relation to structure-sensitive properties

D S Sanditov

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**Abstract.** A review and analysis of studies concerning the nature of Poisson's ratio  $\mu$  of glassy systems are presented. The value of  $\mu$  is a more pronounced structure-sensitive property than are elasticity moduli. The unique relation of  $\mu$  to the Grüneisen parameter is substantiated. In this connection, the interrelation of harmonic (linear) and anharmonic (nonlinear) characteristics is discussed. Poisson's ratio is a single-valued function of parameters characterizing dynamic properties and critical processes and is sensitive to the lattice dynamics and the atomic–molecular structure of glasses. The structural features of isotropic solids with the negative Poisson's ratio (transverse deformation coefficient) are discussed.

**Keywords:** transverse deformation coefficient, interatomic interaction potential, anharmonicity, elastic constants, auxetics, amorphous organic polymers, inorganic glasses

D S Sanditov Banzarov Buryat State University,  
ul. Smolina 24a, 670000 Ulan-Ude, Russian Federation;  
Institute of Physical Materials Science, Siberian Branch  
of the Russian Academy of Sciences,  
ul. Sakh'yanovoi 6, 670047 Ulan-Ude, Russian Federation  
E-mail: sanditov@bsu.ru

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## 1. Introduction

Poisson's coefficient  $\mu$ , which is sometimes called the transverse deformation coefficient, is equal to the ratio of the relative transverse deformation  $\varepsilon_z = \Delta r/r$  of a body to its relative longitudinal elongation  $\varepsilon_x = \Delta l/l$  under uniaxial stretching:

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

According to Landau and Lifshitz [1], the range of the allowed values of  $\mu$  for isotropic solids is determined from the known expression of the elasticity theory ( $B \geq 0$ ,  $G \geq 0$ )

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

According to this relation, when the volume compression modulus is  $B = 0$ , Poisson's ratio is equal to the lower limit  $\mu = -1$ , and when the shear modulus is  $G = 0$ , we obtain the upper limit  $\mu = 0.5$ . Thus,  $\mu$  can range the interval [1]

$$-1 \leq \mu \leq 0.5.$$

We see that theoretically a solid with a negative transverse deformation coefficient  $\mu < 0$  can exist. This means that under uniaxial stretching of a rod made of such a material,

instead of transverse compression ( $\Delta r < 0$ ), transverse expansion occurs ( $\Delta r > 0$ ), which generally speaking contradicts common sense. However, recent publications (see review [2]) convincingly demonstrate the existence of isotropic solids with negative Poisson's ratio [2–7]. In 1987, a polymeric isotropic foam material with the transverse deformation coefficient  $\mu = -0.7$  [3, 4] was synthesized probably for the first time. Such materials were called auxetic or auxetics [2, 7] (from Greek *auxetos*, swelling).

Along with this unusual phenomenon, other ‘anomalies’ were found, for example, a one-to-one relation of Poisson's ratio to the Grüneisen parameter  $\gamma_D$  characterizing the nonlinearity of the interatomic interaction force (anharmonicity) [8, 9] and to the inelastic deformation of solids [10, 11]. Poisson's ratio (1) is defined for ‘quiet’ static elastic deformations; however,  $\mu$  is a single-valued function of parameters characterizing dynamic, critical processes.

We note that unlike the elastic moduli,  $\mu$  reflects the properties of not only a direct deformation along the external force action but also a transverse deformation in a direction different from the force action direction. The direct deformation  $\varepsilon_x$  is determined by the direct resistance of a body along the deforming force, while the transverse deformation  $\varepsilon_z$  depends on the way this body transfers the external action in other directions. This depends on the properties of the atomic–molecular structure of the body and the lattice dynamics. For these and other reasons, Poisson's ratio proves to be a more distinct structure-sensitive property than elastic moduli, although it varies in a small range.

In this review, studies of the nature of Poisson's ratio of glassy solids are analyzed. The main focus is on the relation of  $\mu$  to the dynamic properties of these systems and its theoretical interpretation.

In Sections 2–7, the relation between the transverse deformation coefficient  $\mu$  and structure-sensitive and thermal properties of inorganic glasses and amorphous organic polymers, as well as some crystalline solids, is considered. In Sections 8–14, which can be conditionally called theoretical, the nature of Poisson's ratio for glassy solids is discussed based mainly on Kuz'menko's and Pineda's theories and the model by Berlin, Rotenburg, and Baserst.

## 2. Relation between Poisson's ratio and the lattice dynamics

Static elastic loading of solids changes their external dimensions and produces ‘invisible’ internal dynamic changes, for example, changing the frequency of atomic vibrations in a loaded body [12].

Mikitishin [13] found that the lattice dynamics depend on Poisson's ratio via the dependence of the latter on the interatomic-potential parameters. The quantity  $1-2\mu$ , closely related to the relative volume deformation (see Section 8), is dependent on thermal vibrations of the lattice and (to some degree or another) on the Debye temperature  $\theta_D$ . For isotropic face-centered and volume-centered cubic structures, the dependence of  $1-2\mu$  on the ratio  $\theta_D\sqrt{m}/T_{ev}$  (where  $T_{ev}$  is the evaporation temperature and  $m$  is the atomic mass) is linear, experimental points lie on straight lines (see Fig. 2 in [13]):

$$\frac{\theta_D\sqrt{m}}{T_{ev}} \sim 1-2\mu.$$

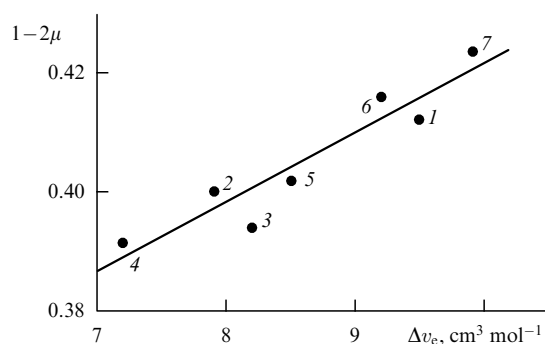
Because the product  $\theta_D\sqrt{m}$  is determined by the root-mean-square displacement  $\langle\Delta r^2\rangle$  of an atom from the equilibrium position, it can be considered a peculiar analog of the atomic displacement  $\Delta r_m$  and therefore of the elementary delocalization volume  $\Delta v_e = \pi d^2 \Delta r_m$  of the atom in a glassy solid [14]:

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

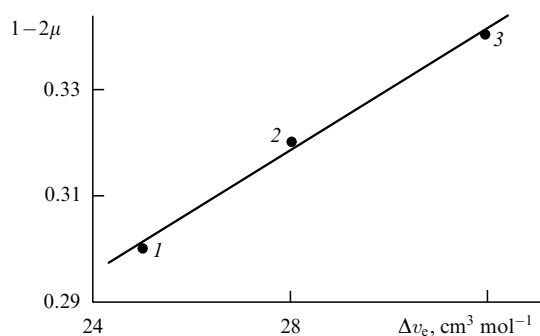
where  $\pi d^2$  is the effective atomic cross section,  $\Delta r_m$  is the maximum displacement of an atom from the local equilibrium position,  $R$  is the gas constant,  $f_g$  is the proportion of the fluctuation volume frozen at the glass-forming temperature  $T_g$ , and  $B$  is the compression modulus. Therefore, similarly to the linear dependence mentioned above, a certain correlation between the delocalization volume  $\Delta v_e$  of the atom and the function  $1-2\mu$  of Poisson's ratio can be expected:

$$\Delta v_e \sim 1-2\mu.$$

Indeed, a number of inorganic glasses and amorphous polymers exhibit a linear correlation between  $1-2\mu$  and the elementary volume  $\Delta v_e$  required for the displacement of an atom from the equilibrium position (Figs 1, 2) [15]. Thus, Poisson's ratio is related to the lattice dynamics, the displacement of a particle from the equilibrium position (within the amplitude of particle vibrations).



**Figure 1.** Dependence of the function  $1-2\mu$  of Poisson's ratio on the atom delocalization volume  $\Delta v_e$  for phosphate  $\text{NaPO}_3\text{-Li}_2\text{SO}_4$  and  $\text{NaPO}_3\text{-Na}_2\text{SO}_4$  glasses. The content of  $\text{Li}_2\text{SO}_4$  (mol %): (1) 0.2, (2) 10, (3) 20, (4) 30;  $\text{Na}_2\text{SO}_4$  (mol %): (5) 19, (6) 20, (7) 30.



**Figure 2.** Dependence of  $1-2\mu$  on  $\Delta v_e$  for amorphous polymers: (1) polyvinyl chloride; (2) polystyrene; (3) polymethyl acrylate.

### 3. Transverse deformation coefficient and the nonlinearity of the interatomic interaction force (Poisson's ratio and the Grüneisen parameter)

We consider the relation between the transverse deformation coefficient  $\mu$  and the Grüneisen parameter  $\gamma_D$  entering the equation of state of solids and characterizing the anharmonicity of lattice vibrations and the nonlinearity of the interatomic interaction force. The parameter  $\gamma_D$  is determined by the change in the frequency  $\nu$  of normal vibrational modes of the lattice, depending on the change in the volume of the system:

$$\gamma_D = -\frac{V}{\nu} \frac{\partial \nu}{\partial V} = -\frac{\partial \ln \nu}{\partial \ln V}. \quad (3)$$

Avoiding difficulties caused by a change in the vibrational frequency of the lattice in passing from one vibrational mode to another, Grüneisen used the equation of state to derive the expression

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

which can be used to calculate  $\gamma_D$  from experimental values of the volume thermal expansion coefficient  $\beta$ , the isothermal volume compression modulus  $B$ , the molar volume  $V$ , and the molar heat capacity  $C_V$ .

Along with Grüneisen equation (4), other methods of calculating  $\gamma_D$  have been proposed. Based on the elasticity theory, molecular acoustics, and thermodynamics, Leont'ev [16] averaged the lattice vibrational frequency and, directly from (3), derived the relation

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

where  $B_A$  is the adiabatic volume compression modulus,  $\rho$  is the density, and  $v_q$  is the average quadratic velocity of deformation waves, whose square is the invariant of the sum of squares of the propagation velocities of longitudinal ( $v_l$ ) and transverse ( $v_s$ ) elastic waves

$$v_q^2 = \frac{v_l^2 + 2v_s^2}{3}. \quad (6)$$

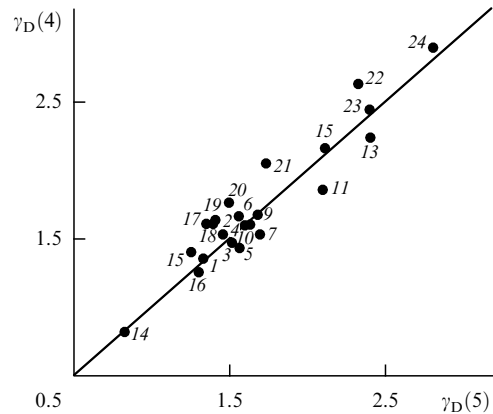
The values of  $\gamma_D$  calculated from Grüneisen (4) and Leont'ev (5) equations are compared for a number of solids in Table 1 [17]. We can see that these relations are in good agreement in the first approximation. Deviations from this correlation for some solids are probably mainly explained by a spread in the values of  $\gamma_D$  obtained by different researchers. For example, the Grüneisen parameter obtained in three different papers was 2.1, 2.3, and 2.4 [18].

Using the expression  $G = \rho v_s^2$  for the shear modulus and formula (6), we transform Leont'ev equation (5) into

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

Then, using the known expressions of elasticity theory [1],

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



**Figure 3.** Comparison of Grüneisen parameters  $\gamma_D$  calculated from Grüneisen equation (4) and Leont'ev expression (5) for different crystals. The numbers of points correspond to the numbers of solids in Table 1.

**Table 1.** Comparison of Grüneisen parameter  $\gamma_D$  values calculated by Grüneisen (4), Leont'ev (5), and Belomestnykh–Teseleva (7) equations [8, 17, 18].

No.	Elements and compounds	$\mu$	$\gamma_D$		
			Grüneisen (4)	Leont'ev (5)	Belomestnykh–Teseleva (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 <sub>3</sub>	0.257	1.31	1.27	1.53
17	NaClO <sub>3</sub>	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

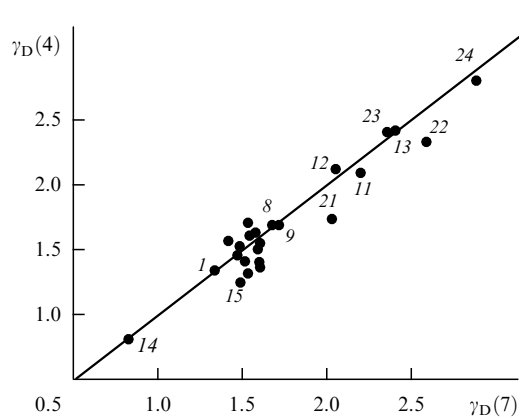
and the approximation  $B_A \approx B$ , we obtain the Belomestnykh–Teseleva expression [8],

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

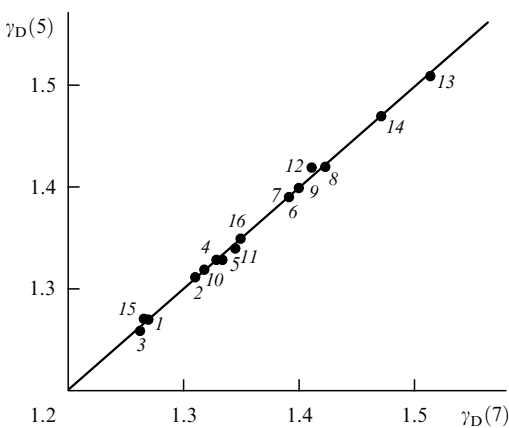
derived in [8] from different initial assumptions.

Thus, from this standpoint, Poisson's ratio  $\mu$  and the Grüneisen parameter  $\gamma_D$  are uniquely related.

Expression (7) is attractive because  $\gamma_D$  is calculated based only on Poisson's ratio  $\mu$ . The estimate of  $\gamma_D$  from (7) for many metals and ions and molecular crystals is in good agreement with calculations from Grüneisen equation (4)



**Figure 4.** Comparison of Grüneisen parameters  $\gamma_D$  calculated from Grüneisen equation (4) and expression (7) for various crystals. The numbers of points correspond to the numbers of solids in Table 1.



**Figure 5.** Comparison Grüneisen parameters  $\gamma_D$  calculated from expressions (5) and (7) for sodium aluminosilicate glasses. The numbers of points correspond to the numbers of solids in Table 2.

**Table 2.** Elastic properties and the Grüneisen parameter of sodium aluminosilicate glasses [19].

No.	Synthesis composition, mol %			$\rho$ , $10^{-3} \text{ kg m}^{-3}$	$v_l$ , m s $^{-1}$	$v_s$ , m s $^{-1}$	$B \times 10^{-8}$ , Pa	$\mu$	$\gamma_D$
	Na $_2$ O	Al $_2$ O $_3$	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

(see Table 1 and Fig. 4) [8, 17]. Figure 5 shows the dependence of the Grüneisen parameter  $\gamma_D$  calculated from expression (5) on the function of Poisson’s ratio  $(3/2)(1 + \mu)/(2 - 3\mu)$  (Belomestnykh–Tesleva) for sodium aluminosilicate glasses with different amounts of oxides (Table 2) [19]. We can see that Leont’ev (5) and Belomestnykh–Tesleva (7) equations are in good agreement. The same results were obtained for other glasses.

**4. Relation between harmonic and anharmonic quantities. Thermodynamic and lattice Grüneisen parameters**

Noting the agreement between expression (7) and Grüneisen equation (4), it must be kept in mind that expression (7) uniquely relates the linear (harmonic) quantity  $\mu$  and a nonlinear (anharmonic) quantity  $\gamma_D$ . Other similar correlations also exist [20–24], for example, the known empirical Barker rule [22] expressing a unique relation between the elasticity modulus  $E$  and the thermal expansion coefficient

squared:  $\beta^2 E \approx \text{const}$ . At the same time, the nature of this phenomenon remains unclear and attempts have been made [20, 21, 23] only to explain it qualitatively.

In a series expansion of the interatomic interaction energy  $U(r)$ , the harmonic  $a$  and anharmonic  $b$  coefficients are determined by the second and third derivatives of  $U(r)$  at the equilibrium interatomic distance  $r = r_0$  (see Section 5). Using the Mie potential  $U = -Ar^{-m} + Br^{-n}$  in these derivatives, Kontorova [20] found the relation

$$b = \frac{m + n + 3}{2r_0} a$$

between these coefficients. Kontorova explains the phenomenon discussed here by the existence of a relation between  $a$  and  $b$  of the type presented above and the dependence of linear and nonlinear properties of solids on these coefficients.

Thus, Kontorova’s approach [20, 21] and Pineda’s theory [23] (see Section 10) demonstrate the fundamental possibility of correlations to exist between apparently totally different physical properties of solids, including correlations between harmonic and anharmonic quantities.

The values of  $\gamma_D$  are usually calculated by expressions like Grüneisen equation (4) containing thermal and mechanical characteristics of solids. For crystals of the same structural type with one system of interatomic bonds, relations obtained by different methods lead to the same values, for example,  $\gamma_D \approx 1.5-2.0$  for ionic cubic crystals (see Table 1).

In the case of polymer systems, the situation is somewhat different. Atoms along a polymer chain are bound by strong  $-C-C-$  type covalent bonds, whereas the chains are bound by weaker intermolecular bonds. The anharmonicity of these bonds is different and therefore the lattice  $\gamma_L$  and thermodynamic  $\gamma_t$  Grüneisen parameters are distinguished in polymer physics (see, e.g., [24, 25]). The lattice parameter ( $\gamma_L \approx 2-4$ ) characterizes the anharmonicity of low-frequency interchain vibrations related to the intermolecular (van der Waals) interaction, while the thermodynamic parameter ( $\gamma_t \approx 1$ ) determines the anharmonicity averaged over the intrachain and other vibrational modes. The thermodynamic Grüneisen parameter  $\gamma_t$  is calculated from Grüneisen equation (4), while the lattice Grüneisen parameter  $\gamma_L$  is calculated from expressions like (7) relating  $\gamma_D$  to physical quantities determined by the intermolecular interaction.

Alkali silicate glasses  $R_2O-SiO_2$  ( $R = Li, Na, K$ ) have two main bond systems: the ion-covalent  $-Si-O-Si$  bonds inside a silicon-oxygen network and ion bonds caused by the Coulomb interaction between alkali-metal ions ( $R^+$ ) located in lattice voids and nonbridge oxygen ions ( $Si-O^-$ ). The anharmonicity of ion bond vibrations in  $Si-O^-R^+$  complexes is stronger than that for bonds in the silicon-oxygen ( $-Si-O-Si-$ ) network. This is typical for germinate, borate, phosphate, and other inorganic glasses in which, similarly to polymers, the lattice  $\gamma_L$  and thermodynamic  $\gamma_t$  Grüneisen parameters are introduced. The value  $\gamma_L \approx 1.5-2.0$  for alkali silicate glasses coincides with that for ion cubic crystals, and  $\gamma_t \approx 1$  coincides with the thermodynamic Grüneisen parameter for amorphous polymers [24, 25].

## 5. Microscopic treatment of Grüneisen parameters. Poisson's ratio and the limit elastic deformation of the interatomic bond

We first consider the diatomic model of a solid [26]. We assume that the left atom is fixed and the right one is free. If the latter is displaced from its equilibrium position  $r = r_0$ , in the case of small displacements  $x = r - r_0$ , it performs harmonic oscillations with a parabolic pair interatomic interaction potential  $U(x)$  corresponding to a linear dependence of the interatomic interaction force  $f(x)$  on the atomic displacement  $x$ .

However, for considerable atomic displacements  $x$ , the assumption about a linear dependence of the force  $f(x)$  is invalid. An anharmonicity appears and the dependence  $f(x)$  becomes nonlinear. The atom performs anharmonic oscillations. Up to third-order terms in a Taylor series, the interatomic interaction energy  $U(x)$  is described as

$$U = \frac{a_0 x^2}{2} - \frac{b_0 x^3}{3},$$

where  $a_0$  is the harmonic coefficient (the bond rigidity). The anharmonicity coefficient  $b_0$  takes the asymmetry of the  $U(r)$  and  $f(r)$  curves into account,

$$a_0 = \left( \frac{d^2 U}{dr^2} \right)_{r=r_0}, \quad b_0 = -\frac{1}{2} \left( \frac{d^3 U}{dr^3} \right)_{r=r_0}.$$

We consider a linear chain of atoms with the 'lattice period'  $l$  (the distance between adjacent atoms). The potential in which atoms of this chain move can be qualitatively represented by the sum of potential curves characterizing the interaction of an atom with its neighbors on the right and left,  $U_-$  and  $U_+$ . Although each of them has its own minimum (at  $r = l_0$ ), near which

$$U = U_0 + \frac{a_0}{2} (r - l_0)^2 - \frac{b_0}{6} (r - l_0)^3 + \dots, \quad (8)$$

their sum gives the total potential  $\Phi = U_- + U_+$  symmetric in the displacement from the equidistant position from both neighbors [25–27]. The returning force  $F$  applied to a given atom is also the sum of forces acting on it from the left and right:  $F = f_- + f_+$ . Each of these is determined by the same derivative

$$f(r) = \frac{dU}{dr}$$

of the pair potential, which can be estimated by differentiating  $U(r)$ . Using expansion (8), it is easy to obtain relation [27] for  $f(r)$  near a lattice point:

$$\begin{aligned} f(r) &\approx a_0 (r - l_0) - \frac{b_0}{2} (r - l_0)^2 \\ &\approx c (l - l_0) + a (r - l) - \frac{b}{2} (r - l)^2, \end{aligned} \quad (9)$$

where  $c = a_0 - b_0 (l - l_0)/2$ ,  $b = b_0$ , and

$$a = a_0 - b_0 (l - l_0). \quad (10)$$

Generally speaking,  $\Delta l = l - l_0 \neq 0$  because the lattice can be in both the compressed and expanded states. The ratio  $\Delta l/l_0$  is usually so small that the noncoincidence of the minima of  $U_-$  and  $U_+$  does not prevent obtaining the sum of the potential curves for small displacements in the form of a parabola inherent in a harmonic potential. It becomes obvious that relatively weak displacements of atoms in a solid should represent harmonic oscillations near equilibrium positions. Debye showed (see, e.g., [26–29]) that the frequency spectrum of an atomic chain extends from 0 to the maximum frequency

$$v_m = \frac{1}{\pi} \sqrt{\frac{a}{m}}, \quad (11)$$

where  $m$  is the atom mass and  $a$  is determined by (10).

Omitting a detailed analysis of the lattice dynamics, we consider a microscopic treatment of the Grüneisen parameter.

When passing from one vibrational mode to another, both the oscillation frequency and phase change. The relation between the oscillation frequency and phase is usually described by the Debye model. In this approximation, the Grüneisen parameter is expressed via the characteristic Debye temperature  $\theta_D = hv_m$  [27–29] ( $h$  is Planck's constant),

$$\gamma_D = -\frac{\partial \ln \theta_D}{\partial \ln V}.$$

Using relation (11), we obtain

$$\gamma_D = -\frac{\partial \ln \theta_D}{\partial \ln V} = -\frac{1}{2} \frac{\partial \ln a}{\partial \ln V} = -\frac{V}{2a} \frac{\partial a}{\partial V}. \quad (12)$$

For isotropic deformations,  $dV/V = 3(d/l)$ . Differentiating in (12) and taking this equality and relation (10) into account, we obtain the microscopic interpretation of the Grüneisen parameter [27, 28]

$$\gamma_D = -\frac{l}{6a} \frac{da}{dl} = \frac{lb_0}{6a}.$$

Because  $l/a \approx l_0/a_0$ , we obtain

$$\gamma_D = \frac{l_0 b_0}{6a_0}. \quad (13)$$

The results obtained for a linear atomic chain remain valid for a three-dimensional solid [26]. Following [26], we consider a crystal model consisting of three layers, the extreme layers being formed by immobile atoms, while atoms in the middle layer oscillate freely. The three-dimensional thermal pressure acting from the middle layer on extreme layers is similar to the thermal pressure of a usual three-dimensional phonon gas. Assuming that this pressure is balanced by elastic forces (internal pressure) due to thermal expansion, we obtain the thermal expansion coefficient of a three-dimensional solid in the form [26, p. 171]

$$\beta = \frac{b_0 k}{2a_0 l_0^2 B}.$$

Multiplying the right-hand side of this equality by  $(3N_A l_0/3N_A l_0)$ , we can represent it in the form [30, 31]

$$\beta = \frac{l_0 b_0}{6a_0} \frac{C_V}{BV},$$

where  $C_V = 3N_A k = 3R$  is the molar heat capacity,  $V = N_A l_0^3$  is the molar volume, and  $N_A$  is the Avogadro number.

By comparing this relation with Grüneisen equation (4),

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

we arrive at the approximate derivation of the microscopic interpretation of the Grüneisen parameter [30, 31] presented above (see expression (13):  $\gamma_D = l_0 b_0/(6a_0)$ ). This expression can be derived rigorously quantum mechanically, including the low-temperature region ( $T < \theta_D$ ) [27, 28].

We consider the anharmonicity and estimate the limit elastic deformation of the interatomic bond  $\Delta l_m = l_m - l_0$ . At  $l = l_m$ , the interaction force of atoms  $f(l)$  passes through a maximum at the inflection point of the  $U(l)$  curve,

$$\left. \frac{\partial f}{\partial r} \right|_{r=l_m} = 0.$$

Using expansion (9) for the dependence  $f(l)$ , it is easy to see that the maximum relative elongation of the interatomic bond has the form [27]

$$\frac{\Delta l_m}{l_0} = \frac{a_0}{l_0 b_0} = \frac{1}{6\gamma_D}, \quad (14)$$

where the Grüneisen parameter is interpreted microscopically, as in (13).

Using relation (7), we see that the relative bond deformation (14), similarly to  $\gamma_D$ , is a single-valued function of

**Table 3.** Poisson's ratio, the Grüneisen parameter, and the limit elastic deformation of the interatomic (molecular) bond calculated for amorphous polymers [52].

No.	Polymer	Abbreviation	$\mu$	$\gamma_D$ (7)	$\Delta l_m/l_0$
1	Polystyrene	PS	0.34	2.1	0.08
2	Polyvinylchloride	PVCh	0.35	2.1	0.08
3	Polyvinyl fluoride	PVF	0.35	2.1	0.08
4	Polymethyl methacrylate	PMMA	0.33	2.0	0.08
5	Epoxy (solidifier)	ED-5	0.35	2.1	0.08
6	Polycarbonate	PC	0.37	2.3	0.07
7	Polyphenyl isobutylsilsequioxane	PPhSSO	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	Polytetrafluorethylene	PTFE	0.32	1.9	0.09
11	Polytrifluorochloroethylene	PTECE	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-methylpentene-1	P4MP1	0.39	2.5	0.07
17	Polyvinylidene fluoride	PVDF	0.31	1.8	0.09

Poisson's ratio:

$$\frac{\Delta l_m}{l_0} = \frac{2 - 3\mu}{9(1 + \mu)}. \quad (15)$$

The relative limit deformation of the interatomic bond in glassy systems calculated by expression (15) changes in a small range (Tables 3 and 4) [31–33] because  $\mu$  oscillates in a narrow interval,

$$\frac{\Delta l_m}{l_0} \approx 0.07 - 0.12,$$

which is in good agreement with other methods of estimating this quantity [24, 29].

Thus, the Poisson ratio of amorphous polymers (Table 3) and glasses (Table 4) is uniquely related to the limit elastic deformation of interatomic and intermolecular bonds. The quantity  $\Delta l_m/l_0$  is the critical deformation at which the interatomic interaction reaches the maximum in passing from elastic to inelastic deformation.

## 6. Loss of stability of a solid under shearing and the transverse deformation coefficient

The relation between Poisson's coefficient and the Grüneisen parameter  $\gamma_D$  for glasses proposed earlier differs somewhat from (7) [25] and has the form

$$\gamma_D = A \frac{1 + \mu}{1 - 2\mu},$$

where the factor  $A$  is determined by the fraction  $f_g$  of the fluctuation free volume frozen at the glass-forming temperature and is close to unity:

$$A = \frac{2}{9} \ln \frac{1}{f_g} \approx \text{const} \approx 1.$$

Therefore, assuming that  $A$  is close to unity in the first approximation, we can estimate  $\gamma_D$  from data on Poisson's

**Table 4.** Characteristics of inorganic glasses [3, 32].

Glass	$\mu$	$\gamma_D$	$\Delta l_m/l_0$
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
$0.4NaPO_3 \times 0.6Na_2SO_4$	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

ratio [25, 29]:

$$\gamma_D \approx \frac{1 + \mu}{1 - 2\mu}. \quad (16)$$

Substituting (16) in equality (14), we obtain the limit deformation of the interatomic bond in a form similar to (15):

$$\frac{\Delta l_m}{l_0} \approx \frac{1 - 2\mu}{6(1 + \mu)}. \quad (17)$$

The estimate of  $\Delta l_m/l_0$  in (17) practically coincides with the results of calculations with (15).

Equality (17) is of interest because it was found in experiments [34, 35] that the right-hand side of (17) (the function of Poisson's ratio) depends only on the product of parameters  $m$  and  $n$  of the Mie potential

$$U = -Ar^{-m} + Br^{-n}.$$

The relation between  $\mu$  and  $mn$  for different substances is described by the following empirical expressions. For metals

with face-centered and volume-centered structures,

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

For alkali-halide salts with an NaCl structure, beryllium fluoride,  $SiO_2$  and  $GeO_2$  oxides, and multicomponent and binary silicate and chalcogenide glasses,

$$\frac{1}{2mn} = \frac{1 - 2\mu}{6(1 + \mu)}. \quad (18a)$$

For diamond, substances with a diamond-like structure, and metals with a hexagonal closely packed structure,

$$\frac{2}{mn} = \frac{1 - 2\mu}{6(1 + \mu)}. \quad (18b)$$

We can see that the right-hand sides of the last three relations coincide with the right-hand side of (17). Therefore, the reciprocal value  $1/mn$  of the product of the Mie potential parameters for these substances is proportional to the limit deformation of the interatomic bond (according to expressions (18), (18a), and (18b):

$$\frac{1}{mn} \approx \frac{\Delta l_m}{l_0},$$

$$\frac{1}{mn} \approx 2 \frac{\Delta l_m}{l_0},$$

$$\frac{1}{mn} \approx \frac{1}{2} \frac{\Delta l_m}{l_0}.$$

Indeed, Lazarev and coauthors [36, p. 100] showed theoretically that the quantity  $(1/mn)$  has the meaning of the critical deformation  $\varepsilon_c$  at which an isotropic polycrystalline solid loses its stability under shearing,

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

This equality was derived in the approximation of an elastically isotropic polycrystalline body with a modified Mie potential, which does not use the concept of the pair and central interatomic interaction [36, p. 97].

"The loss of stability of a solid under shearing" means the critical deformation of the lattice at which the elastic deformation is transformed into inelastic deformation [36].

## 7. Poisson's ratio and the frozen reversible deformation of glasses

Mechanical stress exceeding a certain limit  $\sigma_{el}$  at a temperature of  $20^\circ C$  produces inelastic deformation in silicate glasses under certain conditions; the deformation can remain indefinitely after the lift of the external stress. Notably, under heating (at a temperature slightly below the softening point  $T_g$ ), this deformation relaxes almost to its disappearance. Therefore, it is a frozen reversible deformation. However, following many authors, we use the term 'plastic deformation' (see the references in [29, 33]).

Similar frozen reversible deformations are observed in amorphous organic polymers. A polymer glass, for example, PMMA (polymethyl methacrylate) 'plastically' deformed at a temperature of  $20^\circ C$  and heated to temperatures slightly

**Table 5.** Elastic constants  $\mu$ ,  $E$  and microhardness  $H_V$  of inorganic glasses.

Glass	$\mu$	$E$ , kg s mm <sup>-2</sup>	$H_V$ , kg s mm <sup>-2</sup>	$\frac{H_V}{E}$	$\frac{1-2\mu}{6(1+\mu)}$	$H_V$ , kg s mm <sup>-2</sup>
	Experiment				Calculation by expression (20)	
SiO <sub>2</sub>	0.17	7450	692	0.093	0.094	700
Na <sub>2</sub> O–SiO <sub>2</sub> Na <sub>2</sub> O, 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 <sub>2</sub>	0.197	4333	360	0.083	0.082	373
Na <sub>2</sub> O–GeO <sub>2</sub> Na <sub>2</sub> O, 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
K8 *	0.225	7920	578	0.073	0.074	586
BK10 *	0.250	7516	553	0.075	0.067	505
TF3 *	0.219	5469	424	0.075	0.077	420
TF1 *	0.225	5355	392	0.077	0.074	395

\* Optical multicomponent glass.

below  $T_g$  returns to the initial nondeformed state [37, 38], as do silicate glasses. It is interesting that massive metal glasses, in particular, Pd<sub>40</sub>Cu<sub>40</sub>P<sub>20</sub> glass, reveal a frozen deformation and its thermally stimulated relaxation [39], these processes being in fact the same as in inorganic glasses and amorphous polymers.

Here, we do not discuss attempts to explain the nature of the plasticity effect in glasses [29, 33, 37–42] and show that the frozen reversible deformation of glassy materials is in fact uniquely related to Poisson's ratio.

The 'plasticity' of fragile inorganic glasses is suitable for studying by the microhardness method. The indentation of a diamond Vickers pyramidal indenter and other sharpened indenters into a silicate glass produces a 'plastic' microprint (hole). The Vickers microhardness  $H_V$  of silicate, germanate, and other inorganic glasses coincides with the limit stress  $\sigma_{el}$  above which the 'plastic' deformation is observed:  $H_V \approx \sigma_{el}$  [33, 43]. Therefore, the frozen deformation  $\varepsilon_{el}$  for these glasses can be represented in the first approximation by the ratio of

the microhardness to the elasticity modulus  $E$ :

$$\varepsilon \approx \frac{\sigma_{el}}{E} \cong \frac{H_V}{E}. \quad (19)$$

In turn, the ratio  $H_V/E$  is a function of Poisson's ratio only [29, pp. 52, 227] (Table 5),

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

Taking equality (20) and relation (19) into account, we see that the frozen ('plastic') deformation of glasses is a single-valued function of Poisson's ratio  $\mu$ ,

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

According to (21), the frozen deformation  $\varepsilon_{el}$  of a number of glasses linearly depends on the function  $(1-2\mu)/(1+\mu)$  of Poisson's ratio, as is confirmed in experiments (Figs 6 and 7).

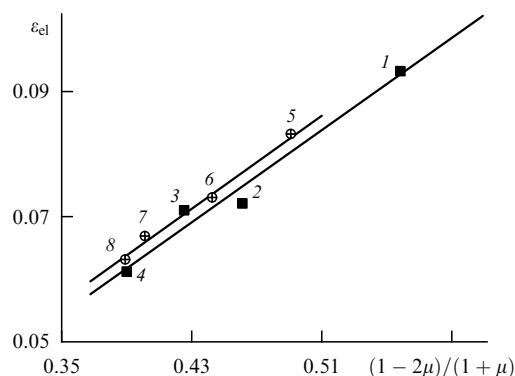
Experimental data on Poisson's ratio were analyzed by Koster and Franz [44] (mainly for metals) and other researchers [2, 4, 13, 45, 46]. At the same time, we must admit that the physical meaning of the transverse deformation coefficient of noncrystalline solids is not completely clear so far. Theoretical studies of Poisson's ratio are discussed in Sections 8–10 [4, 23, 45, 47].

## 8. Transverse deformation coefficient as a characteristic of a change in the deformed-body volume

The transverse deformation coefficient  $\mu$  characterizes, first of all, a change in the deformed-body volume [45, 46].

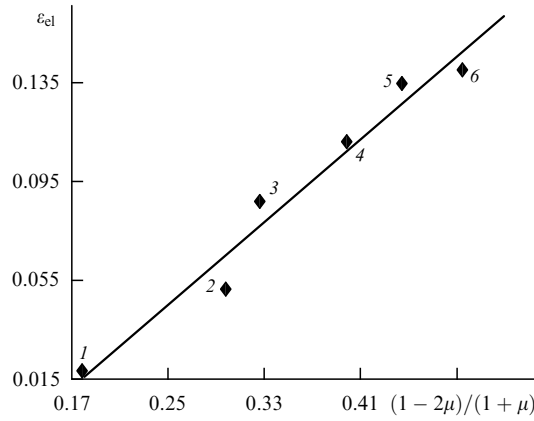
The change in the volume  $V = V(r, l)$  of a rectangular parallelepiped with length  $l$  and a square cross section with side  $r$  can be written in the form [46]

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



**Figure 6.** Dependence of the frozen reversible deformation  $\varepsilon_{el}$  of sodium silicate (squares) and sodium germanate (circles) glasses on  $(1-2\mu)/(1+\mu)$ . (1) SiO<sub>2</sub>; (2–4) Na<sub>2</sub>O–SiO<sub>2</sub> glasses containing Na<sub>2</sub>O in amounts (mol %): (2) 16, (3) 20, (4) 33.5; (5) GeO<sub>2</sub>; (6–8) Na<sub>2</sub>O–GeO<sub>2</sub> glasses containing Na<sub>2</sub>O in amounts (mol %): (6) 5.7, (7) 20, and (8) 30.





**Figure 7.** Dependence of  $\epsilon_{el}$  on the function  $(1 - 2\mu)/(1 + \mu)$  of Poisson's ratio for chalcogenide glasses: (1) As<sub>10</sub>S<sub>90</sub>, (2) As<sub>20</sub>S<sub>80</sub>, (3) As<sub>28</sub>S<sub>72</sub>, (4) Ge<sub>13</sub>As<sub>24</sub>S<sub>63</sub>, (5) Ge<sub>26</sub>Sb<sub>8</sub>S<sub>66</sub>, (6) Ge<sub>32</sub>As<sub>2</sub>S<sub>66</sub>.

Taking into account that  $V = r^2l$ , we find derivatives  $\partial V/\partial r = 2rl$  and  $\partial V/\partial l = r^2$  to express (22) in the form

$$dV = 2rl dr + r^2 dl.$$

Transforming this equality using Poisson's ratio (1) in the differential form

$$\mu = -\frac{l}{r} \frac{dr}{dl},$$

we obtain the dependence of the body volume change on  $\mu$ :

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

Multiplying the right-hand side of this relation by  $l/l$  and taking into account that  $r^2l = V$  and  $dl/l = \epsilon_x$ , we finally obtain the relative change in the volume  $dV/V$  for the uniaxial stretching of a parallelepiped in the form [46]

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

Thus, the function  $1 - 2\mu$  of the transverse deformation coefficient and therefore Poisson's ratio  $\mu$  itself are mainly related to the change in the body volume caused by its uniaxial deformation.

## 9. Kuz'menko's theory

According to Kuz'menko's approach [45], the Poisson ratio of solids characterizes their ability to resist volume change. The larger  $\mu$ , the smaller the volume change of a solid under deformation. The upper bound  $\mu = 0.5$  follows from the condition that the volume change caused by the deformation is completely compensated by the counteraction of the substance ( $\Delta V = 0$ ). This condition concerns liquids, whereas in solids a complete compensation of the volume change does not occur, and therefore  $\mu < 0.5$ .

Indeed, it follows from equality (23) that the greater Poisson's ratio for a given solid, the smaller is its relative volume deformation  $\Delta V/V$ . For  $\mu = 0.5$ , the deformation is  $\Delta V/V = 0$ . Similar properties are also observed for relative linear deformations [see (13), (17), (18), and (21)]. For example, as  $\mu$  increases, the critical deformation  $1/(mn)$  of materials at which they lose stability under shearing

decreases (18). The greater the value of  $\mu$  for a given glass, the smaller is the relative stretching  $\Delta l_m/l_0$  at which the interatomic interaction force reaches its maximum and the smaller the ratio  $\Delta l_m/l_0$  at which the transition from elastic to inelastic deformation occurs (13).

According to Kuz'menko's theory [45], Poisson's ratio characterizes, along with the properties mentioned above, the proportion of the shear energy  $W_s$  in the total deformation energy  $W$ :

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

The greater  $\mu$  is, the smaller the relative shear deformation energy, the smaller the resistance to the shear produced by the given material, and the closer this material is to liquid in this respect. This means that Poisson's ratio should be related, for example, to the characteristic of the inelasticity of a solid such as the fluidity limit.

Indeed, materials with low fluidity limits, i.e., with a high softness and plasticity (gold, silver, and copper) have large values of  $\mu$  close to 0.5, while brittle solids with a high fluidity limit, like silica, have small Poisson's ratios  $\mu$ .

## 10. Pineda's theory

Pineda [23] studied the influence of structural changes on the elastic constants of metal glasses theoretically. Pineda's theory can qualitatively explain (as in [20, 21]) the relation between Poisson's ratio and Grüneisen parameter (7). We briefly consider this question.

Pineda used three main assumptions: (1) The interatomic interaction potential consists 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; (2) the distribution of distances between neighboring atoms is Gaussian; and (3) elastic properties are determined by the environment of atoms, i.e., by the first coordination sphere.

The final (quite cumbersome) expressions for the instantaneous volume compression 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  $\sigma_1$  are the respective mean radius and width of the first coordination sphere. The quantities  $s$  and  $\sigma$  characterize deviations of the interatomic distance from its equilibrium value  $r_0$  and the mean dispersion near  $r_0$ . The parameter  $\gamma_1$  characterizing the potential anharmonicity is proportional to the Grüneisen parameter  $\gamma_D = br_0/(6a)$  (see (11)).

Pineda used his theory to explain experiments on the structural relaxation and all-side compression of metal glasses. Poisson's ratio decreases due to structural relaxation (the parameter  $\sigma$  decreases more strongly) but increases under compression (here, the decrease in  $s$  dominates). As a whole, the theory qualitatively correctly describes the change in elastic characteristics in these experiments.

We use Pineda's theory to verify the dependence of the ratio of elastic moduli  $B/G$  and therefore Poisson's ratio  $\mu$  (see expression (2)) on the anharmonicity parameter  $\gamma_1$ . The theory predicts this dependence, which is in fact single-valued. Indeed, the elastic moduli  $B$  and  $G$  are proportional to the harmonic coefficient  $a$ , a parameter of the harmonic potential, and their ratio  $B/G$  (and therefore Poisson's ratio  $\mu$ ) is in fact independent of  $a$  and is mainly determined by the anharmonicity parameter  $\gamma_1$ . This gives the dependence of Poisson's ratio on the Grüneisen parameter  $\gamma_D$  characterizing anharmonicity.

Thus, Pineda's theory allows us to calculate the Grüneisen parameter  $\gamma_D$  from data on the coefficient transverse deformation  $\mu$  (see (7)).

## 11. Model of randomly packed spheres

Among the studies devoted to the nature of Poisson's ratio, of special interest are papers [4, 47] considering a model of randomly packed spheres interacting with each other in the contact region via two forces: normal to the contact plane (central forces) and tangential (friction forces) acting along the tangent to the given plane. We call this model the BRB (Berlin–Rotenburg–Baserst) model. It is assumed that the normal,  $f_n$ , and tangential,  $f_t$ , forces are proportional to the corresponding displacements  $x_n$  and  $x_t$  of an atom 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 hardnesses. It follows from the BRB model that Poisson's coefficient is determined by the ratio of these shear and bend hardnesses,  $\lambda = a_t/a_n$  [4]:

$$\mu = \frac{1 - \lambda}{4 + \lambda}. \quad (25)$$

For  $\lambda = 0$ , we have  $\mu = 0.25$ , which corresponds to an ensemble of particles with central forces ( $a_n \gg a_t$ ). As  $\lambda$  increases, the value of  $\mu$  decreases and, for  $\lambda = 1$ , we have  $\mu = 0$ , and in the limit  $\lambda \rightarrow \infty$  ( $a_t \gg a_n$ ),  $\mu = -1$ . We see that the model of randomly packed spheres predicts the possibility of the existence of bodies with negative Poisson's ratio,  $\mu < 0$ , and gives the lower bound  $\mu = -1$  [1].

According to the model, auxetic materials (with  $\mu < 0$ ) should have a high bend hardness of bonds and a low axial compression–stretching hardness:  $a_t > a_n$  ( $\lambda > 1$ ). In fact, all the known interaction potentials of particles are either central or are considerably more rigid in the normal than in the tangential direction ( $\lambda < 1$ ). Because of this, materials with a negative Poisson's ratio are very rare in nature.

It is important that BRB expression (25) contains the microscopic parameter  $\lambda$ , which can give certain information on the nature of the transverse deformation coefficient  $\mu$ . Because the shear hardness  $a_t$  is related to the deformation energy dissipation (with the friction force), the dependence of  $\lambda = a_t/a_n$  on nonlinear effects can be expected, in particular, on the anharmonicity described by the Grüneisen parameter  $\gamma_D$ . Indeed, expressions (7) and (25) give a single-valued relation of  $\lambda$  with the Grüneisen parameter:

$$\lambda = \frac{1.5 - \gamma_D}{\gamma_D}. \quad (26)$$

Therefore, BRB equation (25) implicitly contains the dependence of Poisson's ratio on anharmonicity.

The parameter  $\lambda = a_t/a_n$ , equal to the relative tangential (shear) interatomic bond hardness, is certainly related to the relative shear energy  $W_s/W$  in expression (24). According to (24), the greater Poisson's ratio  $\mu$  is, the weaker the resistance of a given material to the shear and the smaller the relative tangential hardness  $\lambda$  (see expression (25)). This also means that  $\lambda$  is related to the inelastic properties of a solid.

We consider the relation of  $\gamma_D$ ,  $\mu$ , and  $\lambda$  to the structural properties of amorphous polymers and glasses at the atomic–molecular level.

Poisson's ratio  $\mu$  in amorphous organic polymers strongly depends on the side branchings of the main chain of a macromolecule ('side appendages' of the main chain). The minimal values of  $\mu$  and  $\gamma_D$  belong to polyethylene, in which the light hydrogen atom plays the role of a side 'appendage'. The substitution of hydrogen atoms by larger and heavier fluorine atoms in passing from polyethylene to polytetrafluoroethylene results in an increase in  $\mu$  from 0.25 to 0.33 and, respectively, in an increase in  $\gamma_D$  from 3 to 4. Then the substitution of fluorine by a chlorine atom in the repeating connecting polytetrafluoroethylene link under transition to polytrifluorochloroethylene leads to an even greater increase in  $\mu$  from 0.33 to 0.37 and  $\gamma_D$  from 4 to 5 [48]. Here,  $\gamma_D$  is the lattice Grüneisen parameter (see above) [24, 25].

The substitution of light atoms by larger and heavier atoms on the side and end sites of chains results in an increase in the nonlinearity of the interatomic interaction force and the anharmonicity  $\gamma_D$  of lattice vibrations, which reduces the relative shear bond hardness  $\lambda$ . In turn, the decrease in  $\lambda$  leads to an increase in Poisson's ratio (see (25) and (26)).

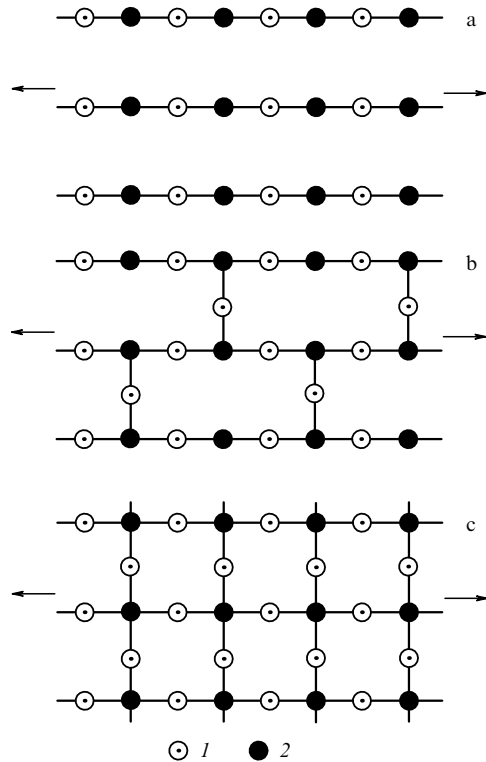
A change in Poisson's ratio in inorganic glasses is caused by the local deformation of the network of valence bonds produced by the displacement of a bridge atom (like the oxygen atom in the  $-\text{Si}-\text{O}-\text{Si}-$  bridge). The bridge atom displacement is affected to a certain degree by alkali and alkali-earth metal ions ('side appendages').

As the content of sodium oxide  $\text{Na}_2\text{O}$  (sodium ions) in sodium-silicate glasses  $\text{Na}_2\text{O}-\text{SiO}_2$  is increased from 0 to 35 mol %, the Grüneisen parameter  $\gamma_D$  increases from 1.2 for a silica  $\text{SiO}_2$  glass to 1.5 for  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses containing 35 mol % of  $\text{Na}_2\text{O}$  (Table 6). This, according to (26), reduces the relative shear hardness  $\lambda$  from 0.25 to 0. In turn, according to (25), the decrease in  $\lambda$  leads to an increase in Poisson's ratio  $\mu$  from 0.17 for a silica  $\text{SiO}_2$  glass to 0.25 for sodium-silicate  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses (see Table 6). Thus, the increase in  $\mu$  in this case is explained by the decrease in the relative shear bond hardness  $\lambda$ .

The relative tangential hardness  $\lambda$  obviously depends on the density of transverse bonds, defined as the number  $n_n$  of valence bonds per cation in some polymers and glasses (Fig. 8) [49]. For linear structures (polybutylene, selenium, polyvinylchloride) with coupling 2 (two anions coupled to a cation along the chain (Fig. 8a)), we have  $n_n = 0$  and  $\mu = 0.4$ ;

**Table 6.** Characteristics of sodium silicate glasses [32].

$\text{Na}_2\text{O}$ , mol %	$\text{SiO}_2$ , mol %	$\gamma_D$	$\mu$
0	100	1.20	0.170
15	85	1.28	0.196
25	75	1.40	0.226
35	65	1.52	0.253



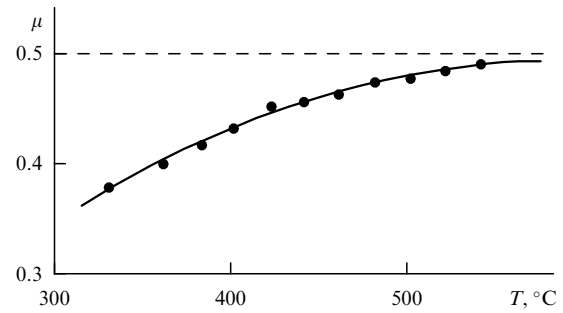
**Figure 8.** Diagrams of (a) linear, (b) linearly branched, and (c) network structures of amorphous materials [49]. The arrows show stretching stresses. (1) anions, (2) cations; Fig. 8a: the density of transverse bonds  $n_n = 0$ ,  $\mu \approx 0.4$ ; Fig. 8b:  $n_n = 1$ ,  $\mu \approx 0.3$ ; Fig. 8c:  $n_n = 2$ ,  $\mu \approx 0.15$ .

for linearly branching structures with the coupling 3 ( $B_2O_3$ ,  $P_2O_5$ ,  $As_2O_3$ ),  $n_n = 1$  (Fig. 8b) and  $\mu = 0.3$ ; for structural networks with coupling 4 ( $SiO_2$ ,  $GeO_2$ ),  $n_n = 2$  (Fig. 8c) and  $\mu \approx 0.15$  (i.e., approximately  $0.3:2 = 0.15$ ). It is clear that as the density of transverse valence bonds increases, the nonlinearity of the interatomic interaction force and anharmonicity  $\gamma_D$  decrease and, according to dependence (26), the relative shear bond hardness  $\lambda$  increases, which, according to BRB expression (25), reduces the transverse deformation coefficient  $\mu$ . The density of transverse bridge bonds also gives a key to explaining strongly different melting points of oxides with approximately equal bond strengths. Thus, the melting points of  $SiO_2$  and  $GeO_2$ , 1610 and 1115 °C, respectively, are much higher than those of  $P_2O_5$ ,  $B_2O_3$ , and  $As_2O_3$  (580, 450, and 313 °C, respectively) [49]. The same can be said about the softening point of these systems, because the melting and softening points  $T_{melt}$  and  $T_g$  are linearly related as  $T_g \approx (2/3)T_{melt}$ .

Thus, Poisson's ratio naturally depends of the properties of the atomic-molecular structure of glassy systems via  $\lambda$ , closely related to the anharmonicity degree  $\gamma_D$ .

## 12. Poisson's ratio and light scattering from glasses

The nature of  $\mu$  was studied, in particular, in [50], where experimental temperature dependences of the light scattering intensity  $R_c$  in the glass-forming range were analyzed taking the contribution of the elastic energy to the thermodynamic potential into account. This contribution appears in the low-temperature region: as the melt viscosity increases, Poisson's ratio begins to deviate from the value  $\mu = 0.5$  (Fig. 9).



**Figure 9.** Temperature dependence of Poisson's ratio  $\mu(T)$  for a sodium borate glass melt with the  $3Na_2O \times 97B_2O$  composition (mol %) [50].

Poisson's coefficient  $\mu$  was calculated from expression [50] as

$$\mu = \frac{2B\alpha_c^2 - 3\varphi_{el}}{4B\alpha_c^2 - 3\varphi_{el}}, \quad (27)$$

where  $\alpha_c = (1/V)(\partial V/\partial c)$  is the concentration expansion coefficient,  $V$  is the volume,  $c$  is the molar concentration,  $\varphi_{el}$  is the additional term in the expression for the light scattering intensity  $R_c$  taking the elastic energy contribution into account, and  $B$  is the elastic volume compression modulus.

The term  $\varphi_{el}$  in the expression for  $R_c$  takes the appearance of shear elastic deformations into account in the calculation of the minimal fluctuation formation work in solid glasses. As temperature increases, Poisson's ratio increases to  $\mu = 0.5$ , where  $\varphi_{el}$  vanishes,  $\varphi_{el} = 0$ , which corresponds to the glass-liquid transition.

Figure 9 shows the temperature dependence of Poisson's ratio  $\mu(T)$  for a sodium borate  $Na_2O-B_2O_3$  glass containing 3 mol % of  $Na_2O$ . Here, the dependence  $\mu(T)$  is calculated from (27) based on light scattering data. We can see that noticeable deviations from  $\mu = 0.5$  appear at temperatures below 560 °C (higher than the glass-forming temperature  $T_g \approx 520$  °C).

A comparison of the temperature dependences of the transverse deformation coefficient  $\mu(T)$  obtained for the same glasses by two independent methods (diffraction and acoustic) will undoubtedly be of interest in the future.

## 13. Elastic moduli and the transverse deformation coefficient

Of interest is the product of the density  $\rho$  and the square of the root-mean-square velocity of deformation waves  $v_q^2$  [17]

$$K = \rho v_q^2,$$

where for cubic crystals  $v_q^2$  is the invariant of the sum of squares of propagation velocities of longitudinal ( $v_l$ ) and transverse ( $v_s$ ) acoustic waves, Eqn (6) (see Section 3).

This section is devoted to the study of the nature of the quantity  $K$  and to finding its relation to elastic moduli and Poisson's ratio for glasses, which gives information about the nature of  $\mu$ .

We consider expressions for the volume compression modulus  $B$  of cubic crystals

$$B = \frac{C_{11} + 2C_{12}}{3}$$

and the root-mean-square sound velocity written in the form [16]

$$\rho v_q^2 = \frac{C_{11} + 2C_{44}}{3},$$

where  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  are second-order elastic constants. It follows from the last two expressions that if the Cauchy condition  $C_{12} = C_{44}$  is satisfied and central forces act between uniformly deformed regions of a cubic lattice, the quantity  $K = \rho v_q^2$  coincides with the volume compression modulus  $K = B$ . In all other cases, the product  $\rho v_q^2$  differs from  $B$ .

We show that being the ratios of elastic moduli of isotropic bodies, in particular, the ratio of the shear modulus  $G$  to the volume compression modulus  $B$  [1],

$$\frac{G}{B} = \frac{3}{2} \frac{1 - 2\mu}{1 + \mu}, \quad (28)$$

the quantities  $G/K$  and  $B/K$  are single-valued functions of Poisson's ratio  $\mu$ .

By dividing the shear modulus  $G = \rho v_s^2$  by  $K = \rho v_q^2$ , we obtain the relation

$$\frac{G}{K} = \frac{v_s^2}{v_q^2}. \quad (29)$$

Using expression (6) for  $v_q^2$ , we express the right-hand side here in terms of the ratio of squares of the longitudinal and transverse sound velocities

$$\frac{v_s^2}{v_q^2} = 3 \left( \frac{v_l^2}{v_s^2} + 2 \right)^{-1}, \quad (30)$$

where for isotropic bodies  $v_l^2/v_s^2$  is a function of Poisson's ratio  $\mu$  [1],

$$\frac{v_l^2}{v_s^2} = 2 \frac{1 - \mu}{1 - 2\mu}. \quad (31)$$

Substituting (31) in (30) and then (30) in (29), we see that the ratio  $G/K$  is a function of only Poisson's ratio:

$$\frac{G}{K} = \frac{3}{2} \frac{1 - 2\mu}{2 - 3\mu}.$$

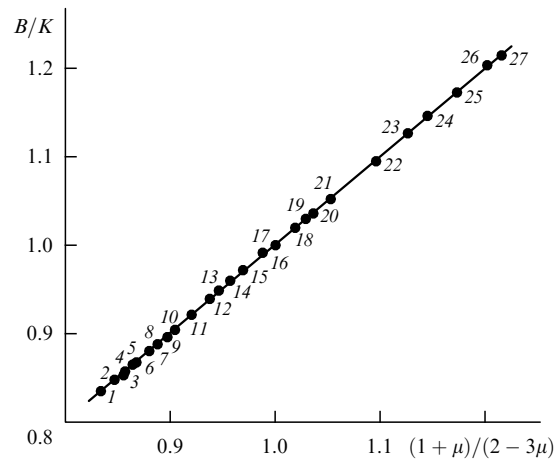
Comparing this expression with equality (28), we see that the ratio  $B/K$  is also a single-valued function of  $\mu$ :

$$\frac{B}{K} = \frac{1 + \mu}{2 - 3\mu}. \quad (32)$$

This result was earlier obtained by a different (more complex) method [17].

Thus, first, like the shear modulus, the quantity  $K = \rho v_q^2$  is the product of the density and the square of the sound velocity and, second, when the Cauchy condition is satisfied, it coincides with the volume compression modulus. Third, as in the case of elastic moduli, the ratios  $G/K$  and  $B/K$  are single-valued functions of Poisson's ratio.

In this connection, the quantity  $K = \rho v_q^2$ , having the characteristic features of elastic moduli, was called the averaged elastic modulus in [17]. This name is not quite appropriate, however, because the known elasticity moduli  $E$ ,  $G$ , and  $B$  are also averaged. Therefore, it is reasonable to



**Figure 10.** Dependence of the ratio  $B/K$  of the volume compression modulus to the effective elastic modulus on the function  $(1 + \mu)/(2 - 3\mu)$  of Poisson's ratio for multicomponent optical glasses: (1) LK7, (2) KF6, (3) F6, (4) KF7, (5) K14, (6) LF5, (7) K8, (8) KF4, (9) F13, (10) K19, (11) F4, (12) TF1, (13) BK6, (14) BF21, (15) BF8, (16) BK10, (17) TF7, (18) FK14, (19) TK13, (20) TK23, (21) BF11, (22) TK17, (23) OF2, (24) STK7, (25) STK9, (26) LK4, (27) TBF4 [51].

call  $K$  the effective elasticity modulus (or the 'characteristic elastic modulus').

The dependence of  $B/K$  on Poisson's ratio in (32) was obtained using relations for isotropic crystals with cubic lattices. Nevertheless, dependence (32) is justified for crystalline solids with other lattices and some inorganic glasses [17]. Figure 10 demonstrates the application of expression (32) to multicomponent industrial optical glasses. The necessary experimental data are taken from handbook [51].

We can see that the ratio  $B/K$  depends linearly on  $(1 + \mu)/(2 - 3\mu)$  and, according to (32), the straight line passes through the origin with the slope equal to unity, confirming the validity of (32).

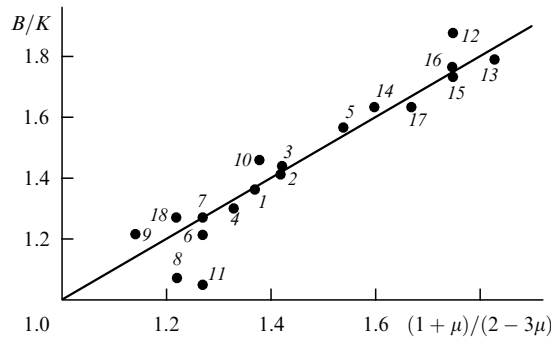
Figure 11 presents a similar dependence for organic glasses. The scatter of experimental points in Fig. 11 is caused by the dependence of the mechanical properties of amorphous polymers on the thermal prehistory of samples and technological conditions of polymerization. Nevertheless, Fig. 11 shows that except for two to three polymers, dependence (32) agrees well with experimental data.

The characteristic feature of the effective elastic modulus  $K$  is its relation to the Grüneisen parameter  $\gamma_D$  describing the anharmonicity of lattice vibrations and nonlinearity of the interatomic interaction force. A close relation between  $K$  and  $\gamma_D$  follows, for example, from a comparison of (32) and (7): the effective elastic modulus is determined by the ratio of the volume compression modulus to the Grüneisen parameter

$$K = \frac{3}{2} \frac{B}{\gamma_D}. \quad (33)$$

When the Cauchy condition  $B = K$  is satisfied, the Grüneisen parameter in (33) is  $\gamma_D = 1.5$ . According to (7), this value of  $\gamma_D$  corresponds to Poisson's ratio  $\mu = 0.25$ . The values  $\gamma_D = 1.5$  and  $\mu = 0.25$  are typical for an ensemble of particles with central interaction forces.

The anharmonicity of lattice vibrations and nonlinearity of the interatomic interaction force are manifested, for example, in the frozen 'plastic' deformation of glassy solids [25] (see



**Figure 11.** Dependence of the ratio  $B/K$  of the volume compression modulus to the effective elastic modulus on the function  $(1 + \mu)/(2 - 3\mu)$  of Poisson's ratio for amorphous organic polymers at  $T = 240$  K: 1—polystyrene; 2—polyvinyl chloride; 3—polyvinyl fluoride; 4—polymethyl methacrylate; 5—polycarbonate; 6—polyphenyl isobutylsilsequioxane; 7—ED-5 epoxy; 8—polyoxymethylene; 9—High-pressure polyethylene; 10—polypropylene; 11—polytetrafluoroethylene; 12—polytrifluorochloroethylene; 13—nylon-6; 14—nylon-7; 15—nylon-11; 16—nylon-12; 17—poly-4-methylpentene-1; 18—polyvinylidene fluoride [52].

Section 7). The fluidity limit  $\sigma_{el}$ —the threshold stress above which glass ‘plasticity’ is observed—is proportional to the ratio of the elastic modulus  $E$  to the Grüneisen parameter  $E/\gamma_D$ , similarly to the ratio  $B/\gamma_D$  in (33) [25]:

$$\sigma_{el} = \frac{1}{6} \left( \frac{E}{\gamma_D} \right). \quad (34)$$

Under plastic deformation of amorphous polymers, the anharmonicity increases ( $\gamma_D$  increases) and intermolecular potential barriers decrease compared to those in the non-deformed state characterized by the intermolecular interaction determined by the elastic modulus  $E$ .

It follows from relations (33) and (34) that the fluidity limit for glassy solids of the same class with  $\mu \approx \text{const}$  is proportional to the effective elastic modulus

$$\sigma_{el} = \frac{1 - 2\mu}{3} K.$$

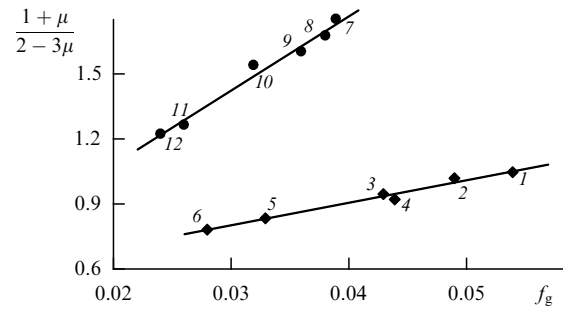
We see that the function of Poisson's ratio  $1 - 2\mu$  characterizes the ‘plastic’ deformation  $\sigma_{el}/K$ .

The Grüneisen parameter can be calculated by expressions (7), (33), and (34) using only mechanical test data, whereas the calculation of  $\gamma_D$  from the known Grüneisen equation is performed mainly from thermophysical characteristics. These expressions are in good agreement with the Grüneisen equation [8, 17].

Thus, the concept of the effective elastic modulus can be useful in studying the mechanical properties of glassy solids, taking their anharmonicity into account.

#### 14. Relation between Poisson's ratio and the viscosity of glass-forming melts in the liquid–glass transition region

At present, the factors controlling the temperature dependences of viscosity and the structural relaxation time in the vitrification region remain not clear enough. In this connection, it is interesting to note a linear relation between the ratio  $B/G$  of the volume and shear elastic moduli and the so-called fragility  $m$ —a fundamental characteristic of the temperature



**Figure 12.** Relation between Poisson's ratio  $\mu$  and the fraction  $f_g$  of the fluctuation volume ‘frozen’ in the glass transition region for inorganic glasses and amorphous organic polymers: 1—SF64 heavy flint, 2—F51 flint glass, 3—SF16 heavy flint, 4—F2 flint glass, 5—8250 glass for soldering with kovar, 6—Duran-50 glass (glass notations from the Schott catalog), 7—polyacrylate, 8—polyvinyl acetate, 9—polyvinyl chloride, 10—polystyrene, 11—polybutadiene, 12—polyisoprene [55].

dependence of the viscosity  $\eta(T)$  near the glass transition point [53]:

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

This linear dependence is found for many glassy systems, including glasses with covalent, hydrogen, van der Waals, and ion bonds [54]:

$$m = 29 \left( \frac{B}{G} - 0.41 \right). \quad (35)$$

This means that the liquid fragility (the temperature dependence of the viscosity at temperatures close to  $T_g$ ) is determined only by Poisson's ratio  $\mu$  because  $\mu$  is a single-valued function of  $B/G$  [1].

It was also found that [54]

$$\frac{T_g}{\Delta F_\infty} \approx 0.037 \left( \frac{B}{G} - 0.41 \right), \quad (36)$$

where  $\Delta F_\infty$  is the high-temperature limit of the activation energy of the viscous flow of glass melts corresponding to the Arrhenius (exponential) dependence  $\eta(T)$  at high temperatures. Relations (35) and (36) give a simple rule according to which the better a glass resists shear stresses rather than all-side compression, the better the usual Arrhenius dependence is satisfied during structural relaxation [54].

There is also another correlation involving  $\mu$ . We can see from Fig. 12 that the function of Poisson's ratio  $(1 + \mu)/(2 - 3\mu)$  depends linearly on the fraction of the fluctuation volume frozen at the glass transition point  $f_g = (\Delta V_e/V)_{T=T_g}$  [55]. The fluctuation volume  $\Delta V_e$  of amorphous materials is caused by the delocalization of atoms: by their limit displacement from equilibrium positions [14] ( $\Delta V_e = N_e \Delta v_e$ , where  $N_e$  is the number of delocalized atoms and  $\Delta v_e$  is the elementary fluctuation volume required for atom delocalization).

#### 15. Conclusions

The data presented above show that Poisson's coefficient, despite its variation in a small range, is one of the most

important structure-sensitive properties of glassy solids. The quantity  $\mu$  proves to be a single-valued function of the Grüneisen parameter, the limit deformation of the interatomic bond, the frozen reversible deformation, the proportion of the shear energy in the total deformation energy, and the product  $mn$  of the Mie potential parameters. In addition, the transverse deformation coefficient  $\mu$  is related to the so-called fractal dimensionality  $d_f$  of structural perturbations of a three-dimensional lattice [36, 56],

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

and also to the dimensionality  $D_f$  of energy localization regions produced in a deformed body [36, 56],

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

At the same time, the physical sense of Poisson's ratio for glassy solids remains unclear [2–10, 44–50, 57–59].

Among theoretical studies, of interest are the Berlin–Rotenburg–Baserst model [4, 47, 58] and the Kuz'menko [45] and Pineda [23] theories. These theories can be used to attempt to explain qualitatively why Poisson's ratio is uniquely related to the Grüneisen parameter; why glasses with a high fluidity limit have smaller values of  $\mu$ , whereas soft materials with a low fluidity limit have higher values of  $\mu$ ; which structural features should be inherent in isotropic solids with a negative Poisson's ratio; and why  $\mu$  is a single-valued function of the critical deformation at which the elastic–inelastic deformation transition occurs.

At this stage, we have to assume a one-to-one relation between Poisson's ratio and the Grüneisen parameter characterizing then anharmonicity, which requires the detailed substantiation in the future. This concerns the general problem of the relation between harmonic (linear) and anharmonic (nonlinear) quantities.

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