

Correlation of fragility of supercooled liquids with elastic properties of glasses

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We present a detailed analysis of correlations between fragility and other parameters of glass-forming systems. The analysis shows the importance of the ratio between the instantaneous bulk and shear modulus of glass-forming systems, or their Poisson ratio, for structural α relaxation and fast dynamics. In particular, for simple glass formers, the bulk to shear modulus ratio in the glassy state correlates with fragility in the liquid state and is inversely proportional to the intensity of the boson peak. A simple relationship between the temperature dependence of the viscosity of liquids at high temperatures and near the glass transition is used to rationalize these correlations. We argue that the ratio of the moduli controls the high-temperature activation energy of the structural relaxation and in this way affects the fragility. The ratio also defines the amplitude of the structural relaxation (i.e., the nonergodicity parameter) and the latter influences the strength of the boson peak. These observations might explain the puzzling correlation observed between the fragility and fast dynamics in glass-forming systems.

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I. INTRODUCTION

Significant progress in understanding the complex behavior of supercooled liquids has been achieved during the last two decades. The most prominent feature exhibited by the supercooled liquids—the glass transition—is currently one of the central issues in the condensed matter physics [1–6], which has influenced many other fields including biology [7]. At the glass transition, the structural relaxation time τ_α of supercooled liquid increases rapidly with decreasing temperature and becomes longer than the conventional laboratory time. However, despite the long history of investigations, the nature of the glass transition is still not well understood. In particular, it is not clear why the rate of thermal variations of viscosity (or τ_α) near the glass transition temperature T_g is different in various glass formers, even after scaling temperature by T_g (Fig. 1). This property classifies glass formers by the so-called fragility that was introduced by Angell [8]. A different mode of data representation (the entropy of activation of viscous flow near glass transition), which essentially reflects the same property of viscosity, was also suggested by Nemilov in 1964 [9]. There are various quantitative definitions of fragility [2,10,11]. The most commonly used is the slope of the logarithm of viscosity in the fragility plot (Fig. 1) at T_g :

$$m = \left. \frac{\partial \log_{10} \eta}{\partial (T_g/T)} \right|_{T=T_g}. \quad (1)$$

According to this classification, there are strong glass formers, like silica, that exhibit slow decrease of the viscosity or structural relaxation time τ_α , with T/T_g described by nearly Arrhenius dependence, and fragile ones, like van der Waals and ionic liquids or some polymers. Fragile glass formers

have strongly non-Arrhenius behavior of viscosity with steeper temperature dependence near T_g . The deviation from Arrhenius behavior increases with increasing fragility. Typically, fragility is higher in materials with larger anharmonicity, as is shown in Refs. [12,13].

One of the unexplained observations is the correlation of fragility and the fast dynamics in glasses [12,14–16]. It was observed that the so-called boson peak—i.e., excess vibrations in the THz frequency range—has a larger amplitude (in comparison to the Debye density of vibrational states) in strong glass formers than in fragile ones [15]. Also, the intensity of the fast relaxation relative to that of the boson peak at T_g is an increasing function of fragility [12,14,16]. More recently, it was shown that fragility correlates with another parameter that characterizes vibrations in the THz range: the ratio of the integral over the Brillouin line to the integral over the central peak at T_g in the inelastic x-ray scattering spectrum of glasses [17]. Thus, as is stressed in Ref. [17], the fragility of a liquid may be embedded in the properties of the glassy state.

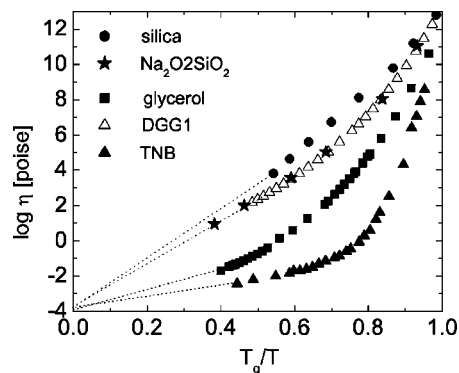


FIG. 1. An example of a fragility plot. DGG1 is a soda-lime silica glass; see Table II for details. The viscosity data for silica and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ are taken from Ref. [2], for DGG1, glycerol, and TNB from Ref. [28].

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TABLE I. Parameters for polymeric samples with different molecular weight M_n . The number after PS and PIB presents the molecular weight. The parameter M_w/M_n shows the molecular weight distribution, and ν_l and ν_t are Brillouin frequencies corresponding to the longitudinal and transversal acoustic vibrations. Data for fragility m are taken from Ref. [29].

M_n	PS197	PS550	PS990	PS8000	PS200600	PIB51000
M_w/M_n	1.02	1.07	1.12	1.05	1.11	1.80
T_g , K	152	240	292	362	373	200
ν_l , GHz	12.09	11.5	10.75	9.78	9.12	20.26
ν_t , GHz	5.30	5.13	5.15	4.84	4.61	10.78
ν_l/ν_t	2.28	2.17	2.09	2.02	1.98	1.88
m	—	72	94	133	162	46

In this paper we present a detailed analysis of the correlations of various properties of glasses to the fragility of the liquid. We show that the fragility of simple glass formers is controlled by a very basic property: the ratio of the instantaneous shear and bulk elastic moduli that can be expressed through the Poisson ratio. This observation, first reported in Ref. [18], helps to shed some light on the nature of the correlation between the fragility and fast dynamics in glasses. On the other hand, we show that the activation energy of the viscous flow in the normal high-temperature liquid state is also an indicator of the fragility of the liquid in the supercooled state. So fragility is embedded also in the properties of high-temperature liquid. We discuss the correlation of the nonergodicity parameter with the fragility. Using some approximations, we show that this correlation follows from the connection between the nonergodicity parameter and the ratio of the bulk and shear moduli of the glass. Deviations from the general correlations (e.g., for some polymers) are discussed in detail.

Section II describes the light scattering measurements of the sound velocities and the fast dynamics spectra in some polymers important for our analysis. Section III considers the relationship between the low- and the high-temperature regimes of viscosity on the fragility plot. It suggests the expression of the fragility on the basis of the high-temperature behavior of the viscosity. Section IV uses the results of Sec. III and some additional suggestions in order to predict the correlation between the fragility and Poisson's ratio of glasses. It considers also deviations from this correlation. Section V presents an analysis of the correlation between the fast dynamics and fragility on the basis of the findings of Secs. III and IV. Section VI summarizes the results and conclusions of the paper.

II. EXPERIMENT

Monodisperse polystyrene (PS) samples with molecular weight M_n from 197 to 200 600 were purchased from Scientific Polymers. The number average molecular weights and molecular weight distributions are listed in Table I. A polyisobutylene (PIB) sample with molecular weight 51 000 was purchased from Polymer Source (Canada), with a glass transition temperature 200 K. Depolarized light scattering (DLS) spectra were measured using a Raman spectrometer (Jobin

Yvon T64000) and a tandem Fabry-Perot interferometer (Sandercock model) with free spectral range (FSR) ~ 360 GHz (~ 12 cm $^{-1}$). All DLS measurements were done in backscattering geometry. Brillouin spectra were measured in right-angle scattering geometry (scattering angle 90°) using an interferometer with a FSR ≈ 20 GHz. In order to obtain the transverse and longitudinal modes at the same time, we measured the so-called H0 spectra (the polarization of the incoming beam is parallel to the scattering plane, and no analyzer was used in the measurements of scattering light intensity). The samples were placed in optical vials and sealed vacuum tight. An optical cryostat (Janis ST-100 model) was used for temperature variations. For all the measurements, a laser power 100 mW (Ar $^{++}$, $\lambda_0=514.5$ nm) was used. Results obtained for ν_l and ν_t are presented in the Table I.

III. HIGH-TEMPERATURE ESTIMATE OF FRAGILITY

We begin our analysis with a simple observation: the fragility that is usually defined in the glass transition region can be estimated also on the basis of the high-temperature viscosity or the α -relaxation time data [18]. It means that the behavior of a normal liquid above its melting temperature contains information on the fragility. Indeed, by the construction of the fragility plot, all viscosity or relaxation time curves intersect at two points: (i) at T_g , where by definition $\log \eta(T_g)=13$ (η in Poise) or $\log \tau_\alpha(T_g)\sim 3$ (τ in sec), and (ii) at very high temperatures, $T_g/T\rightarrow 0$, where basically all liquids have $\log \eta\equiv \log \eta_0\sim -4$ [19] or the relaxation time is of the order of the microscopic time, $\log \tau_\alpha\sim \log \tau_0\sim -14$. It means that, if a supercooled liquid has a steeper slope of $\log \eta$ in fragility plot near T_g , it inevitably has a smaller slope of $\log \eta$ at high temperatures in the normal liquid state. Thus, the high-temperature slope of viscosity determines fragility. In other words, the steepness of the temperature variations of the relaxation time or viscosity near T_g is determined by the high-temperature behavior of the liquid.

In the limit of high temperatures, relaxation in most of the liquids shows an Arrhenius temperature dependence $\eta = \eta_0 \exp(E/T)$, with temperature-independent activation energy E . In this regime, the high-temperature slope of $\log \eta$ in the fragility plot (Fig. 1) is equal to E/T_g and should be the smaller the higher is the fragility. Experimental data, taken

TABLE II. The value of parameters used in the paper. V_t and V_l are the transversal and longitudinal sound velocities in the glassy state; E is the high-temperature activation energy of the shear viscosity, taken at the temperature range where the viscosity exhibits Arrhenius behavior; m is the fragility index defined in the text; A_{bp} is the amplitude of the boson peak; T_g is glass transition temperature, T_m is melting temperature. Abbreviations mean the following: (a) o-terphenyl; (b) 1,3,5-tri-a-naphthyl benzene; (c) m-tricresyl phosphate; (d) 40 Ca₂(NO₃)₂ 60KNO₃ mol %; (e) polybutadiene; (f) polyisobutylene; (g) soda-lime silica glass, 71.72SiO₂, 1.23Al₂O₃, 0.191Fe₂O₃, 0.137TiO₃, 0.436SO₃, 6.73CaO, 4.18MgO, 14.95Na₂O, 0.38K₂O wt %; (h) borosilicate glass; (i) lead silica glass, 46SiO₂, 45.32PbO, 5.62K₂O, 2.5Na₂O, 0.56R₂O₃ wt %; (j) borosilicate crown glass, 70SiO₂, 11B₂O₃, 9Na₂O, 7K₂O, 3BaO wt %.

	V_l (km/s)	V_t (km/s)	E/T_g	m	A_{bp}	T_g (K)	T_m (K)
Glycerol	3.71[57]	1.89[57]	18.4[28]	48[28],53[58,59]	2.9[60]	186	292
Salol	2.40[61]	1.15[62]	10.2[63]	63[64,65] 66[28], 73[59]		218	315
m-toluidine	2.40[66]	1.10[66]		77[59],79[67]		187	
OTPa	2.94[68]	1.37[68]	9.22[69]	81[59], 82[28]	2.3[68]	243	329
Toluene			6.68[2]	59[64],105[65] 107[59],122[70]		126	178
Propylene carbonate			11.5[69]	77[28],104[59]		158	218
TNB ^b			9.91[28]	69[28], 86[71]		345	472
ethanol			16.4[2]	55[64]		97	361
Propanol			22.6[69]	40[59]		98	
m-TCP ^c	2.50[72]	1.15[72]		76[14], 87[59]		205	
Se	1.90[73]	0.94[74]		71[28], 87[59,67]	2.6[75]	305	
CKN ^d	3.30[76]	1.53[76]		93[59], 94[14] 102[28]	1.6[15]	333	
PB ^e	2.76[53]	1.37[53]			2.3[77]	180	
PIB ^f		$v_l/v_t=1.88$			3.5[78]	200	317
BeF ₂	4.57[79]	2.94[79]	48.0[80]	20[81], 24[64]		598	
SiO ₂	5.90[33]	3.80[33]	39.2[28]	20[59], 25[28], 28[17]	6.0[82]	1450	
GeO ₂	3.77[79]	2.36[79]		20[59], 24[64]		818	
As ₂ S ₃	2.65[79]	1.44[79]		39[83]		454	
B ₂ O ₃	3.39[57]	1.87[57]	16.5[28]	32[59], 40[14] 44[28]	3.0[84,85]	526	
DGG1 ^g			27.0[28]	35[28]		811	
NBS717 ^h			27.0[28]	26[28]		795	
NBS711 ⁱ			25.1[28]	32[28]		710	
BSC ^j			24.6[28]	32[64], 35[28]		840	
(Na ₂ O)4(SiO ₂)	K/G=1.54[26]			37[59]			
(Na ₂ O)2(SiO ₂)	K/G=1.72[26]						

from the literature (Table II), show that E/T_g indeed correlates well with the inverse fragility m (Fig. 2), with the best fit given by the equation [18]

$$\frac{E}{T_g} = \frac{19.2^2 \ln 10}{m}. \quad (2)$$

We note that such a relationship with a slightly different coefficient $(17)^2 \ln 10$ follows also from the Vogel-Fulcher-Tammanh (VFT) ansatz for viscosity, $\eta = \eta_0 \exp[B/(T-T_0)]$, if one assumes that the latter is valid in the entire temperature range. The VFT function effectively has a temperature-

dependent activation energy in the glass transition region; however, it exhibits Arrhenius behavior at high temperature with activation energy $E=B$, while $m = (\log \eta_g / \eta_0)^2 / (1-T_0/T_g)$. By definition, $B = \log(\eta_g / \eta_0)(T_g - T_0) \ln 10$, so that $m = 17^2 \ln 10 T_g / B$; i.e., it predicts the relationship (2) with a slightly different coefficient. The quantitative disagreement can be related to the well-known fact that a single VFT function cannot accurately describe η at all temperatures [20].

The observation that the fragility can be found on the basis of the high-temperature viscosity data may be helpful because the high-temperature behavior of the normal liquid

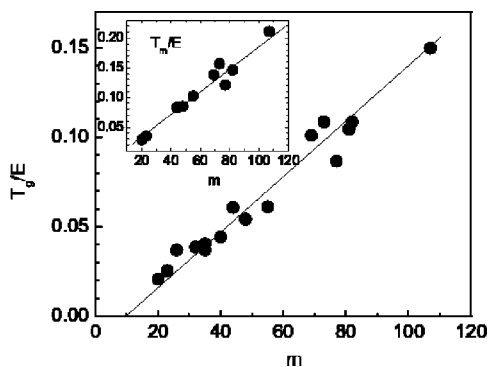


FIG. 2. Correlation between fragility m and the ratio of the high-temperature activation energy E to the glass transition temperature T_g . Materials are listed in ascending fragility order: BeF_2 , SiO_2 , NBS715, NBS711, DGG1, BSC, propanol, B_2O_3 , glycerol, ethanol, salol, propylene carbonate, OTP, TNB, toluene, ZBLAN20. The inset shows the correlation of m to T_m/E for BeF_2 , SiO_2 , B_2O_3 , glycerol, ethanol, salol, propylene carbonate, OTP, TNB, toluene. Literature data for parameters, explanation of abbreviations, and respective references are given in Table II.

is simpler than that of the supercooled liquid. It may lead to some new results regarding fragility that can be difficult to obtain from consideration of the supercooled regime alone. We note that since T_g normally is $\sim 2/3$ of the melting temperature T_m , one can expect that the ratio T_m/E should also correlate with fragility. Indeed, the inset in Fig. 2 demonstrates a good linear correlation between fragility and T_m/E . This means that fragility can be expressed via equilibrium parameters of a normal liquid and its melting temperature—i.e., without any reference to the glass transition or supercooled regime of the liquid state.

IV. CORRELATION BETWEEN THE POISSON'S RATIO OF GLASS AND FRAGILITY OF LIQUID

A. Derivation of the correlation

The relation $m \propto T_g/E$ that follows from Eq. (2) leads to some simple correlations between the fragility and instantaneous elastic moduli. Various authors [21–23] suggested that the activation energy of viscosity in liquids is proportional to the instantaneous shear modulus G_∞ , $E \propto G_\infty V_c$, where V_c is some volume that does not show significant temperature variations at high T .

Also, it is known that T_g correlates with the elastic constants of glass [24]; e.g., correlations of T_g with Young modulus [25], shear modulus [22], bulk modulus [25], and longitudinal modulus [26] were found. However, it is not obvious which combination of shear and bulk moduli actually should be taken, because these correlations usually are considered inside a class of materials with similar chemical structure and, thus, with similar Poisson's ratio. One of the simplest rationalizations of the correlation between T_g and elastic constants comes easily from combination of two phenomenological observations: the connection between T_g and the melting temperature T_m , $T_g \approx (2/3)T_m$, and the Lindemann criteria of melting. The latter states that the mean-

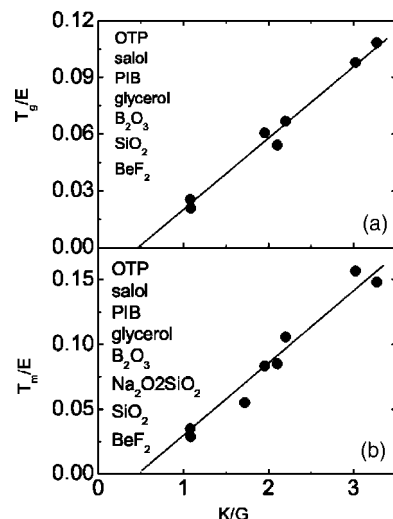


FIG. 3. Correlations between the ratio of the instantaneous bulk to shear modulus, K_∞/G_∞ and T_g/E (a) or T_m/E (b). The solid line in (a) corresponds to Eq. (4). Materials are listed in decreasing K_∞/G_∞ order. The values of parameters are given in Table II.

square atomic displacement at $T=T_m$, x_m^2 , is a universal portion of the average interatomic distance. In the Einstein model, $kx_m^2 \sim T_m$, where k is an effective elastic modulus. Thus, the possibility of a correlation between the elastic constants and T_g becomes clear. In the Debye model of vibrations, T_m is proportional to the Debye sound velocity—i.e., to a combination of the shear and bulk moduli in an isotropic solid. The free volume model of the glass transition predicts $T_g \propto K_\infty$, where K_∞ is the instantaneous bulk modulus [25]. In this model, T_g is defined in terms of a kinetic process involving volume contraction at a convenient time interval of about 10^3 sec, and thus the bulk modulus is relevant.

Since in an isotropic glass former there are only two independent instantaneous elastic moduli, bulk, K_∞ , and shear, G_∞ , one can assume that, generally,

$$T_g \propto K_\infty + xG_\infty, \quad (3)$$

where x is some constant. Respectively, one can expect that the ratio T_g/E is proportional to $K_\infty/G_\infty + x$. Analysis of published experimental data for a few glass formers indeed reveals a correlation of T_g/E with the parameter K_∞/G_∞ , estimated for the respective glass (Fig. 3). It can be fitted by the expression

$$T_g/E \sim 0.037(K_\infty/G_\infty - 0.41). \quad (4)$$

Because of quasiharmonic softening and relaxation, the elastic constants of glasses depend on temperature and frequency. We consider the parameter K/G in the glassy state at high enough frequencies in order to neglect the effects of relaxation; i.e., we take instantaneous elastic moduli K_∞ and G_∞ . The ratio of shear and bulk moduli of glasses can be estimated from the ratio of longitudinal ($V_l = \sqrt{M/\rho}$) and transverse ($V_t = \sqrt{G/\rho}$) sound velocities,

$$K/G = (V_l/V_t)^2 - 4/3, \quad (5)$$

where ρ is the mass density and

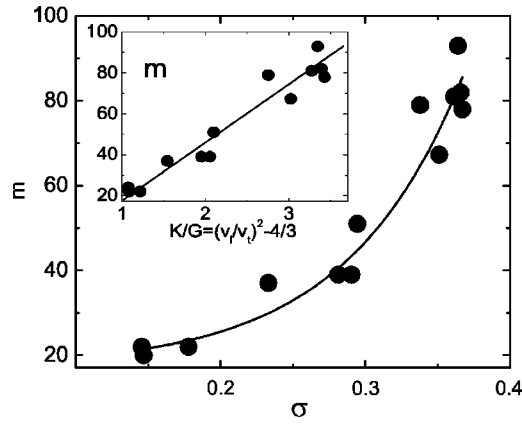


FIG. 4. The correlation between Poisson's ratio at T_g and fragility. Inset: correlation of fragility with the ratio of the bulk and shear moduli K_∞/G_∞ . The straight line shows the relationship from Eq. (7). Materials (in decreasing fragility order): CKN, m-TCP, OTP, Se, m-toluidine, salol, glycerol, B_2O_3 , As_2S_3 , $20Na_2O80SiO_2$, SiO_2 , GeO_2 , BeF_2 . In those cases where more than one value of fragility is known, we use here the average value. The ratio K_∞/G_∞ is estimated using the values of the longitudinal and transversal sound velocities. Literature data for fragility, V_l and V_t , and respective references are given in Table II.

$$M = K + (4/3)G \quad (6)$$

is the longitudinal elastic modulus. We note that the high-frequency sound velocity in glasses is connected to the adiabatic bulk modulus, although the difference between the isothermal and adiabatic bulk moduli in the glassy state is very small. Thus, in what follows we use adiabatic elastic constants, except for a few cases that are clearly indicated.

Equations (2) and (4) show that fragility should correlate with the ratio of the elastic constants K_∞/G_∞ or sound velocities V_l/V_t . Analysis of a large number of glasses, including covalent and hydrogen-bonded, van der Waals, and ionic ones, indeed shows a correlation between the ratio K_∞/G_∞ and fragility m (inset in Fig. 4): the weaker the system resists the shear stress in comparison with the bulk one in the glassy state (higher K_∞/G_∞), the more fragile appears its behavior in the melt [18]. The scattering of points in Fig. 4 is comparable to the scattering of the values of m for a particular glass-forming liquid in the literature.

The correlation between m and K_∞/G_∞ of the respective glass can be well described by the relationship given in Ref. [18]:

$$m = 29(K_\infty/G_\infty - 0.41) \quad \text{or} \quad m - 17 = 29(K_\infty/G_\infty - 1), \quad (7)$$

where 17 is the lowest value expected for m , because it corresponds to the Arrhenius temperature dependence, and K_∞/G_∞ in glasses is not expected to be lower than 1 (for strong glasses like silica and BeF_2 , $K_\infty/G_\infty \sim 1.1$ and this ratio increases with fragility). This correlation corresponds well to the observation first made by Nemilov [9,22] that strong glass formers are materials with covalent bonding and fragile ones with van der Waals or ionic intermolecular forces. Obviously, the transversal displacements of atoms re-

quire a change of the angles between directed bonds in the case of covalent bonding. As a result, the ratio of shear to bulk moduli is higher in covalent systems than in the case of van der Waals interactions which have no directed bonds. Thus, typically in strong glass formers the ratio V_l/V_t is lower than in fragile ones.

We note that correlation (7) means also that fragility of a liquid correlates to the Poisson ratio of its glass, σ , which is connected to the ratio K_∞/G_∞ by the equation

$$\sigma = \frac{3K_\infty/2G_\infty - 1}{3K_\infty/G_\infty + 1}. \quad (8)$$

The correlation between fragility and Poisson's ratio is shown in Fig. 4. Poisson's ratio increases with fragility. Since it has an upper limit 0.5, this dependence is nonlinear and shows a tendency to grow up to ∞ at $\sigma \rightarrow 0.5$. Thus, this correlation emphasizes a very simple rule: the stronger the glass can resist shear deformation rather than dilatation, the stronger (more Arrhenius-like) behavior exhibits its structural relaxation.

B. Deviations from the correlation

Although the majority of glass formers are in agreement with the correlation between m and K_∞/G_∞ , there are systems that demonstrate deviations. Finding such examples may help to understand better the nature of this correlation and, more generally, of fragility. Below we consider a few such examples we were able to find.

The first of them is related to polymers. Polymers are not shown in Fig. 4 because they require special consideration. It is known that the fragility of some polymers depends strongly on the molecular weight M_w . For example, the fragility of polystyrene (PS) varies from ~ 70 at low M_w (~ 500) up to ~ 160 at high M_w (10^5) [27]. In order to check the correlation of fragility with V_l/V_t for PS we investigated five PS samples with the molecular mass from 197 to 200 600 (Table I). The ratio of sound velocities, V_l/V_t , was found by measuring the frequencies of the longitudinal (ν_l) and transversal (ν_t) Brillouin lines in a light scattering experiment. The frequency of the Brillouin lines is related to the sound velocity by the relation

$$\nu_{l,t} = \frac{2\pi n V_{l,t}}{\lambda} \sin \theta/2, \quad (9)$$

where θ is the scattering angle, n is refractive index, and λ is the wavelength of the light. Thus the ratio of Brillouin frequencies measured at the same angle gives the ratio of the sound velocities, $V_l/V_t = \nu_l/\nu_t$. Brillouin frequencies for PS samples with different molecular weight, their ratio ν_l/ν_t , and respective fragilities are presented in Table I. The ratio of sound velocities in samples with the smallest and largest molecular weights differs by $\sim 10\%$ only, while the fragility increases by more than a factor of ~ 2 . Moreover, the fragility of PS decreases with increasing ratio V_l/V_t , in contrast to the general trend of Fig. 4.

In Fig. 5 we compare the dependence of the fragility on the ratio V_l/V_t in nonpolymeric glass formers ("elementary

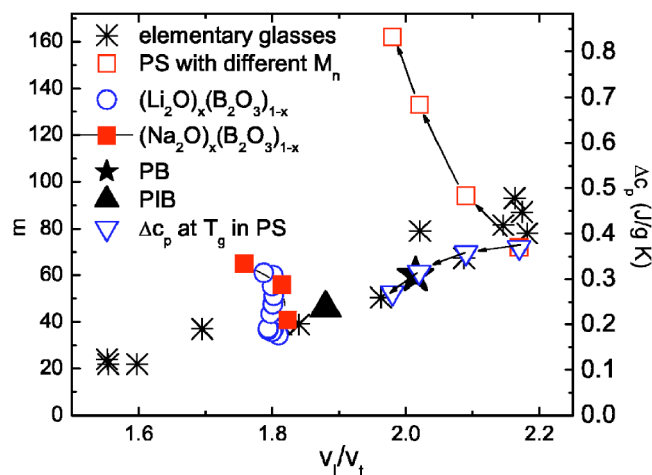


FIG. 5. Correlation between fragility and the ratio of the longitudinal and transverse sound velocities in polymers polystyrene (PS, \square), polybutadiene (PB, \star), polyisobutylene (PIB, \blacktriangle), and lithium (\bullet) and sodium (\blacksquare) borate glasses. For comparison, the data for elementary glasses from Fig. 4 are shown by stars (\star). The molecular weight of PS samples changes from $M_n=500$ to $\sim 10^5$; arrows show the direction of increasing of M_n . Fragility data for PS with different M_n are from Ref. [29], jumps of the specific heat ΔC_p at the glass transition for the same PS samples (data from Ref. [30]) are shown by ∇ . The concentration of the alkali oxide x varies from 0 to 0.28 in lithium borate glass (data from Ref. [31]) and from 0 to 0.35 in sodium borate glass (data from Ref. [32]).

glasses” in the terminology of Ref. [28]) and some polymers: PS with different molecular weights and polymers with intermediate fragility, polybutadiene (PB) and polyisobutylene (PIB). In the case of PIB, the V_l/V_t ratio was measured by Brillouin light scattering in the present paper (Table I). The data for low-fragility polymers, PB and PIB, agree nicely with the correlation of m and V_l/V_t (Fig. 5), even at high molecular weights. The agreement of PIB and PB behavior with general correlation might be related to the fact that fragility does not change strongly with M_n in these polymers. The data for low-weight PS ($M_n \sim 550$) with $m \sim 70$ also agree with the general correlation of Fig. 4. However, the fragility of PS increases significantly (up to ~ 160) with an increase in M_n , showing a tendency to saturate at $M_n \sim 10^5$, similar to the behavior of T_g [27]. We note another unusual behavior of PS: contrary to the general tendency for elementary glasses, T_g in PS increases while the elastic moduli decrease (with increasing M_n). Thus, one of the assumptions used to rationalize the correlation between m and K_∞/G_∞ —namely, Eq. (3)—is not fulfilled for PS samples with different molecular weight. This might be the reason why the correlation between m and K_∞/G_∞ does not work for high-molecular-weight PS. We want to emphasize that these deviations are not specific for PS only. Other high-fragility polymers—e.g., poly(methyl methacrylate) (PMMA)—will also deviate from the general trend, at least at high M_n . They have similar ratio $V_l/V_t \sim 2$ while fragility can be $m \sim 130$ and even higher. We know that in the case of PMMA and poly(propylene glycol) fragility also decreases with decrease in molecular weight [29]. That suggests that the deviation observed for PS (Fig. 5) might be general for other high-fragility polymers.

It is known that there is also another measure of the fragility: namely, thermodynamic fragility. It is connected to the change of the specific heat at the glass transition, Δc_p : more fragile systems usually show higher $\Delta c_p/c_p$. Although in many cases $\Delta c_p/c_p$ correlates with fragility [2], in some liquids, especially with hydrogen bonding, this correlation is violated. It is interesting to note that contrary to the dynamical fragility m , the thermodynamic fragility in PS decreases with an increase in molecular weight. This tendency is in agreement with the correlation of Fig. 4. Figure 5 shows the correlation between Δc_p (data from Ref. [30]) and V_l/V_t for PS samples with different M_n (Δc_p corresponds to the right axis). The arrows show the direction in which M_n increases. Both Δc_p and V_l/V_t decrease with increasing molecular weight following the correlation observed for elementary glass formers. Thus, in PS the thermodynamic fragility correlates with Poisson’s ratio while dynamic fragility does not.

Another exception from the general correlation between m and V_l/V_t is a sequence of lithium borate $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ and sodium borate $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ glasses with different x . In lithium borate glass, the ratio V_l/V_t changes insignificantly with increasing x from 0 to 0.28, while m increases from 35 to 60 [31]. In sodium borate glasses, when x changes from 0.15 to 0.35 the ratio V_l/V_t decreases by 3%, while fragility increases from 41 to 65 [32]. The structure of borate glass can be described as a random three-dimensional network of BO_3 triangles with a large fraction of almost planar B_3O_6 boroxol rings. Alkali-metal atoms modify the network structure in such a way that the fraction of boroxol rings decreases and there appear other structural units: i.e., pentaborate, triborate, diborate, and metaborate groups. Probably, the influence of the complicated topology of this covalent network on the viscosity with changing x leads to a violation of the basic correlation between the Poisson’s ratio and fragility m characteristic for glasses with simpler network topology. It would be interesting to check if the thermodynamic fragility, measured by the jump of the specific heat at the glass transition, correlates with the Poisson’s ratio, as it does in the case of PS.

V. FRAGILITY AND FAST DYNAMICS

A. Nonergodicity parameter and fragility

The relationship between the fragility and ratio of the instantaneous bulk and shear moduli found in the previous sections allows one to rationalize the correlation of the fragility with fast dynamics in glasses [12,14,15,17]. We suggest that the key element here is the so-called nonergodicity parameter f_0 . It characterizes the amplitude of the α -relaxation process: f_0 is the height of the plateau of the time-dependent density-density correlation function in glass formers at times shorter than the α -relaxation time, but longer than the fast-relaxation time. It shows what portion of the density fluctuations is frozen in a glass. It is known that

$$f_0 = 1 - \frac{V_0^2}{V_\infty^2}, \quad (10)$$

where V_0 and V_∞ are longitudinal sound velocities at frequencies below and above the α -relaxation peak, respec-

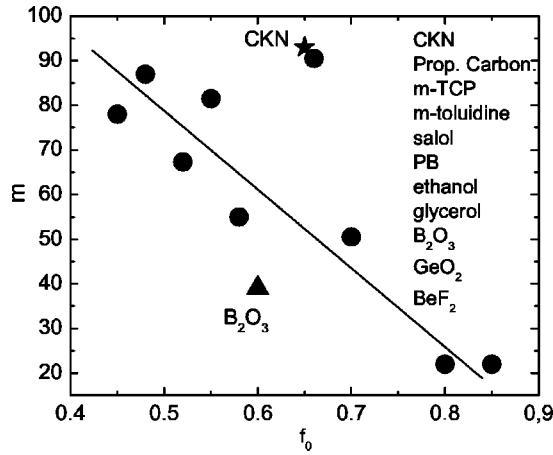


FIG. 6. Correlation between the fragility m and nonergodicity parameter f_0 at T_g . Materials are listed in the decreasing m order.

tively [6]. In other words, V_0 is the sound velocity in the case when structural correlations relaxed and V_∞ is the sound velocity in a frozen structure. A sizable part of the difference between V_0 and V_∞ is due to relaxation of shear modulus. Since $M=K+(4/3)G$, a crude approximation gives [18]

$$f_0 \sim \frac{4}{3} \frac{V_t^2}{V_l^2} = G_\infty / [K_\infty + (3/4)G_\infty]. \quad (11)$$

Thus, the ratio G_∞/K_∞ in this approximation also determines the amplitude of the nonergodicity parameter. So the latter should be connected to fragility: higher fragility corresponds to smaller f_0 . Experimental data for f_0 and m basically support these expectations (Fig. 6). However, there are glass formers—namely, $K_3Ca_2(NO_3)_7$ (CKN), propylene carbonate, and B_2O_3 —that show significant deviations. We attribute the deviation of the B_2O_3 and CKN data from the general trend in the correlation between f_0 and m to the roughness of the approximation in Eq. (11). In particular, in ionic glass CKN, the charge fluctuations may enhance structural fluctuations and, respectively, the nonergodicity parameter f_0 , without significant influence on the V_l/V_t ratio.

In Ref. [17] the parameter α , defined as

$$\alpha = R_{LP}^{-1}(T)T_g/T$$

(here $R_{LP}(T) = I_c/2I_{Br}$ is the Landau-Placzek ratio, and $2I_{Br}$ and I_c are the integrated intensities of the combined Brillouin doublet and the central line of the dynamic structure factor $S(q, \omega)$, respectively), was found for a few glasses at temperatures $T < T_g$ using inelastic x-ray scattering data. This parameter resembles the Landau-Placzek ratio at T_g if $R_{LP}^{-1}(T)$ increases linearly with temperature below T_g (as was observed in these experiments). It has been shown in Ref. [17] that α and m correlate, $\alpha \propto m$. It is difficult to estimate theoretically $R_{LP}(T)$ in the x-ray scattering experiment [17] because the Brillouin line in this case is determined by vibrations in the boson peak frequency range, which themselves are not well understood. However, since in Ref. [17] α does not depend on scattering wave vector q and the boson peak is in acoustic region of the vibrational spectrum, it has a sense

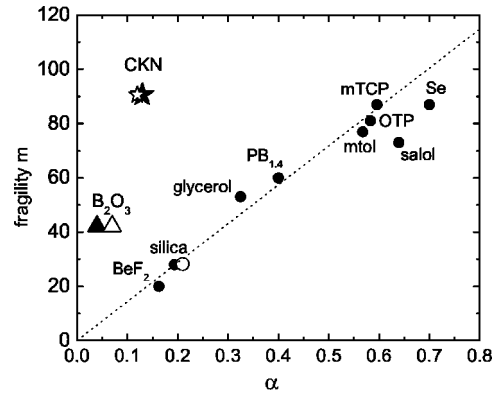


FIG. 7. Correlation between the parameter α (taken from Ref. [17]) and fragility m (solid circles). X-ray and light scattering data for B_2O_3 (solid and open triangle, respectively) and CKN (solid and open star, respectively) and light scattering data for SiO_2 (open circle) are added. X-ray data for B_2O_3 and CKN are from Ref. [35], and light scattering data for B_2O_3 are from Ref. [36], for CKN are from Ref. [37], and for SiO_2 are from Ref. [38].

to estimate α in the case of the plane-wave phonons. In this case,

$$R_{LP}(T) = \kappa_T M - 1, \quad (12)$$

where κ_T is the isothermal compressibility and M is the adiabatic longitudinal modulus at Brillouin frequency [33,34]. Using the relationships $V_0^2 \approx 1/\rho\kappa_T$ and $V_\infty^2 \approx M_\infty/\rho$, α can be expressed via the nonergodicity parameter f_0 at T_g :

$$\alpha = (1 - f_0)/f_0. \quad (13)$$

As was shown in Ref. [34], the right-hand side of Eq. (13) indeed correlates well with the fragility.

The correlation of the fragility with the Landau-Placzek ratio at T_g can be explained if one takes into account the relations (7) and (13). Substituting Eq. (11) into Eq. (13) gives

$$\alpha \propto K_\infty/G_\infty. \quad (14)$$

This provides a clear microscopic interpretation of the correlation between α and m reported in Ref. [17]: K_∞/G_∞ controls both the relative amplitude of the structural relaxation in a glass and the fragility of a supercooled liquid.

We note that in addition to the data presented in Ref. [17], x-ray scattering data for the Brillouin line and the central peak are published also for B_2O_3 and CKN glasses [35]. These literature data give possibility to obtain an estimate of the parameter α . Assuming that the central peak can be described by a Lorentzian, we estimate $\alpha=0.04$ for B_2O_3 and $\alpha=0.13$ for CKN, in both cases for $q=2 \text{ nm}^{-1}$. It is interesting that estimates of the parameter α from light scattering data for the Landau-Placzek ratio at T_g give $\alpha=0.07$ for B_2O_3 [36] and $\alpha=0.12$ for CKN [37], in reasonable agreement with the x-ray data. A good agreement between x-ray and light scattering data for α is also observed for SiO_2 : α (x-ray) = 0.19 [17] and α (light scattering) = 0.21 [38]. The data (Fig. 7) show clearly that both B_2O_3 and CKN glasses violate the correlation of α and fragility found in Ref. [17].

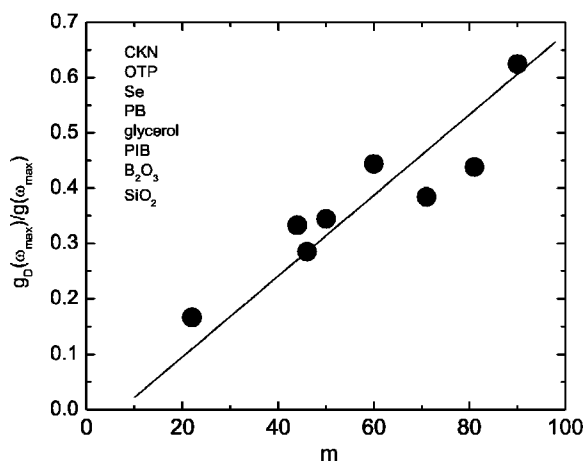


FIG. 8. Correlation between the inverse amplitude of the boson peak, $1/A_{bp} = g_D(\omega_{max})/g(\omega_{max})$, and fragility. Glasses are listed in the order of increasing A_{bp} .

This agrees with the above-shown deviations for B_2O_3 and CKN from the correlation between m and f_0 characteristic of many other glasses (Fig. 6). On the other hand, we want to emphasize that B_2O_3 and CKN do not show any anomalies in the correlation plot between m and K_∞/G_∞ (Fig. 4).

B. Correlation of fragility and the amplitude of the boson peak

Now we switch to an analysis of another puzzling correlation that was found a decade ago: the correlation of fragility with some peculiarities of the vibrational spectra in glassy state [14,15]. Most (if not all) disordered materials have an excess density of vibrational states, $g(\nu)$, in the THz frequency range [39]. This excess vibrational density is best visible in the $g(\nu)/\nu^2$ presentation and is called the boson peak. Homogeneous materials are expected to show Debye-like behavior, $g_D(\nu)/\nu^2 = \text{const}$, in that presentation. However, $g(\nu)/\nu^2$ in disordered materials exhibits a peak in the THz frequency range where most of the crystals still have a Debye density of states. The nature of the boson peak remains a subject of active debate [15,40–47]. It was found that the amplitude of the boson peak, A_{bp} , measured as the maximum of the ratio of $g(\nu)$ to $g_D(\nu)$,

$$A_{bp} = |g(\nu)/g_D(\nu)|_{\max}, \quad (15)$$

correlates well with the inverse fragility of the respective glass former [15]. In Ref. [15] this was concluded on the basis of low-temperature specific heat data. Direct comparison of the neutron scattering data for the density of states in glasses confirms this correlation (Fig. 8). The data in Fig. 8 can basically be described by a simple dependence

$$A_{bp} \propto m^{-1}. \quad (16)$$

The relation between A_{bp} and the fragility still remains unexplained. Here we show that it can be connected to the correlation between the fragility and nonergodicity parameter.

Indeed, according to various models [15,47–49], A_{bp} is related to the amplitude of the frozen structural fluctuations.

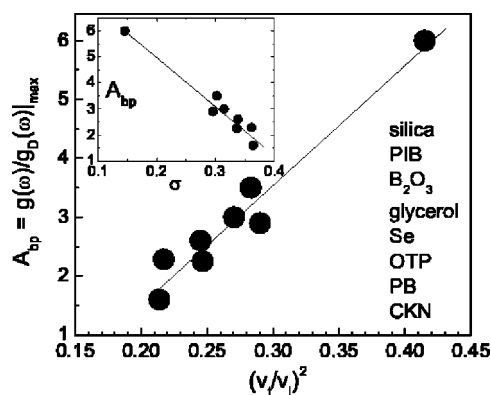


FIG. 9. Correlation between the amplitude of the boson peak, $A_{bp} = g(\omega)/g_D(\omega)|_{\max}$, and the ratio of the transversal and longitudinal sound velocities. Glasses are listed in the order of decreasing A_{bp} . The inset shows the correlation between A_{bp} and Poisson's ratio σ .

So one would expect higher A_{bp} in materials with higher $f_0(T_g)$. It can be checked by comparing f_0 and A_{bp} in materials for which both parameters are available. There are only a few of such glasses; more literature data can be found for the correlation between A_{bp} and the ratio V_t/V_l . The latter, according to Eq. (11), may represent f_0 . Comparison of $(V_t/V_l)^2$ and A_{bp} (Fig. 9) indeed shows a very good correlation. The amplitude of the boson peak also correlates with the Poisson ratio (inset in Fig. 9): the boson peak is stronger in glasses with smaller Poisson ratio. Thus, the correlation of the boson peak amplitude to fragility suggested in Ref. [15] seems to be related to the same role of the nonergodicity parameter. In other words, the capability of structure to resist shear deformation in comparison to bulk deformation also determines the boson peak amplitude through the amplitude of the frozen fluctuations, $f_0(T_g)$.

C. Fast relaxation and fragility

The low-frequency tail of the boson peak overlaps with the quasielastic scattering spectrum—i.e., with the fast relaxation contribution—even at temperatures much below T_g . Contrary to the α relaxation, the characteristic time of the fast relaxation, $\tau \sim 10^{-12}$ sec, depends weakly on temperature while the amplitude increases with increasing T [50]. It has been observed [14] that the intensity of the fast relaxation spectrum normalized to the boson peak intensity is high in fragile glass formers and low in strong ones. To quantify this correlation without using any model assumptions, the authors introduced a parameter $R_1 = I_{min}/I_{max}$, which is the ratio of the intensity at the minimum between the fast relaxation and the boson peak, I_{min} , to the amplitude of the boson peak, I_{max} (see Fig. 10). I_{min} and I_{max} in that case present a spectral density. It was shown that this parameter measured at T_g correlates with the fragility m [14]: higher $R_1(T_g)$ corresponds to higher m .

We note that deviations from the correlation between R_1 and m have been presented recently in Ref. [51] for As_2S_3 and As_2O_3 glasses. According to the data presented in Ref. [51] R_1 in As_2S_3 and As_2O_3 glasses is much higher than the

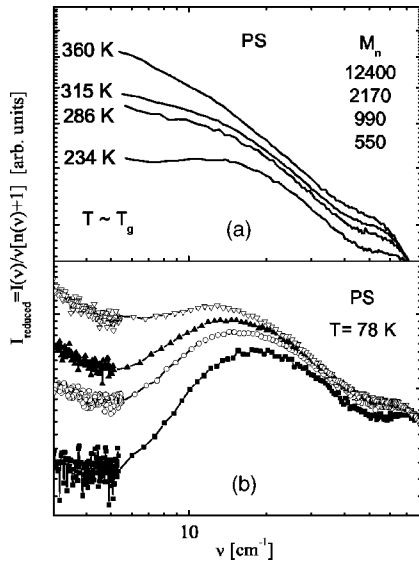


FIG. 10. Low-frequency light scattering spectra of polystyrene samples with different molecular weight M_n . (a) Spectra at temperatures near the respective glass transition; (b) spectra at $T=78$ K.

value expected from this correlation. However, the experimental data of Ref. [51] disagree with three previous investigations of As_2S_3 glasses [52] and one reported recently [53]. It is shown in Ref. [53] that the instrumental tail of the elastic line was not properly taken into account in the experimental spectra of Ref. [51] and this lead to overestimates of R_1 . Accurate data of Ref. [53] provide an estimate of $R_1 \sim 0.42$ in As_2S_3 (Fig. 11), in good agreement with the correlation in other glasses. So the deviations from correlations between R_1 and m reported in [51] are questionable and are clearly wrong for the case of As_2S_3 .

It is interesting to check the relative strength of the fast relaxation in a series of polystyrene samples with different molecular weight M_n . As was discussed in Sec. V B, fragility m in PS increases with M_n . The low-frequency Raman spectra of PS with different M_n (Fig. 10) show that the quasielas-

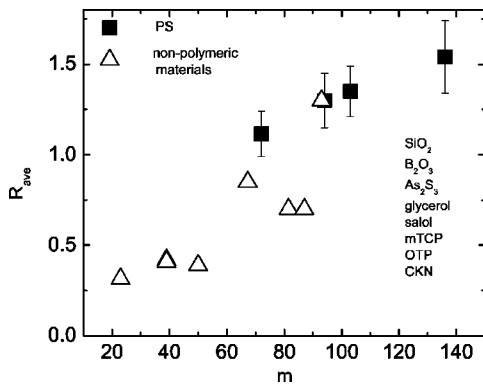


FIG. 11. Correlation between the parameter R_{ave} and fragility for polystyrene samples with different molecular weight $M_n=550, 990, 2370, 12\,400$. Fragility increases with M_n . For comparison, the parameter R_1 for some other glasses is shown (data from Ref. [86]). R_1 for As_2S_3 is from Ref. [53]. Materials are listed in increasing fragility order.

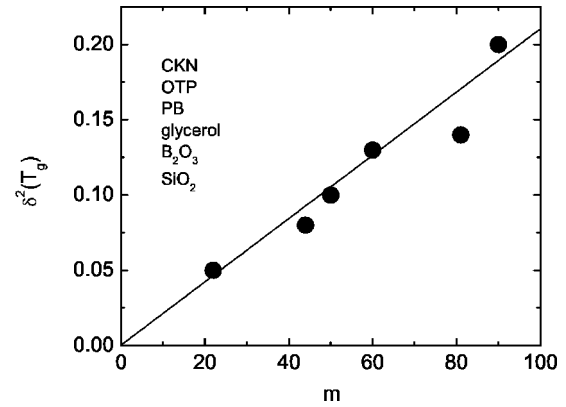


FIG. 12. Correlation between fragility and the strength of the fast relaxation $\delta^2(T_g)$ in the light scattering spectra. Light scattering data are from Ref. [12] (PB, glycerol, B_2O_3), [87] (CKN, SiO_2), and [88] (OTP). Materials are listed in decreasing fragility order.

tic contribution increases with molecular weight. So, qualitatively, it changes in the same direction as the fragility does and in that respect it follows the general trend. The simplest model-independent way to quantify the molecular weight dependence of the fast relaxation intensity is to estimate the parameter R_1 . At $T=T_g$ the minimum between the quasielastic part of the spectrum and the boson peak is seen only for the lowest-molecular-weight sample, $M_n=550$. The tail of the fast relaxation covers the boson peak at higher molecular weights [Fig. 10(a)]. That makes the parameter R_1 not well defined at $T=T_g$. For a rough estimate of R_1 we took for the position of the minimum of the spectrum and the maximum of the boson peak the same frequencies as they have at lower temperatures where these frequencies are well defined [Fig. 10(b)]. This estimate gives a value that is lower than the actual one because the intensity at the frequency of the boson peak has a contribution from the quasielastic scattering, so we denote it R_{1low} . To obtain the upper limit for R_1 and R_{1up} we took the amplitude of the boson peak at $T=77$ K after fitting the low-frequency spectra by a combination of a Lorentzian for the quasielastic part of the spectrum and log-normal function for the boson peak [29]. We take the average value $R_{1ave}=(R_{1low}+R_{1up})/2$ as an estimate of R_1 , and R_{1low} and R_{1up} provide estimates of the error bars. Indeed, R_1 in PS with different molecular weights shows good correlation with fragility m (Fig. 11). Thus, the fast dynamics in PS samples with different molecular weights correlates to fragility. Moreover, the correlation follows well to the general trend observed for other glass forming systems (Fig. 11). This is in contrast to the deviations observed for PS in the case of fragility and Poisson's ratio (Fig. 5).

The relative strength of the fast relaxation may be characterized also by the parameter $\delta^2(T_g)$, which is the ratio of the integral over the fast relaxation spectral density to that of the boson peak [12,16,54] at the glass transition temperature. This approach assumes that the spectrum of the fast dynamics can be decomposed on the sum of the relaxation spectrum and the boson peak. Figure 12 shows that this parameter, found from an analysis of the light scattering spectra in glasses in the GHz-THz frequency range, correlates well with fragility,

$$\delta^2(T_g) \propto m. \quad (17)$$

There are a few mechanisms of the fast relaxation in glasses that are discussed in the literature: namely the mode coupling theory [6], the thermally activated relaxation in double-well potentials (DWP's) [16,55], and fast fluctuations of the free volume [54]. It is shown that the thermal activation in DWP's with the typical barrier heights of the order of a few hundred K dominates the fast relaxation at $T \leq T_g$ in both very fragile (CKN [16], polystyrene [50], PMMA [56]) and strong glass formers (silica [16]). This mechanism, as well as other models, says nothing about the possible correlation of the fast relaxation with fragility. There is a correlation between the anharmonicity and fragility [12,13] and also it is shown that the anharmonicity contributes to the fast relaxation [12]. However, it seems that this contribution in the glassy state is in most cases weaker than that of the thermally activated jumps in DWP's and may become significant only above T_g . Thus, the correlation $\delta^2(T_g) \propto m$ (Fig. 12) in various glass formers remains unexplained. The correlation between R_1 or $\delta^2(T_g)$ and m means that either the strength of the boson peak or the intensity of the fast relaxation, or both, correlates to fragility.

The origin of the correlation between the fragility and parameters R_1 and $\delta^2(T_g)$ can be understood if one takes into account the results of the previous section. Indeed, both R_1 and δ^2 characterize the strength of the fast relaxation relative to the intensity of the boson peak. The latter, if normalized to the Debye density of states, correlates to fragility: it decreases roughly as m^{-1} (Fig. 8). Thus, the definition of the R_1 and δ^2 includes the fragility-dependent factor, which is not related to the fast relaxation. In order to remove this factor, it would be reasonable to normalize the intensity of the fast relaxation by the Debye level of vibrational density of states instead of the boson peak. The resulting parameter will show a "true" dependence of the fast relaxation on fragility; i.e., it will be independent of the boson peak intensity, but will be normalized by the expected Debye level. To find such parameter, we multiply $\delta^2(T_g)$ by A_{bp} , the ratio of the boson peak amplitude to the Debye level in the inelastic neutron scattering data, thus substituting the boson peak by the Debye level in the product. As a result, this parameter

$$\delta_D^2(T_g) = \delta^2(T_g)A_{bp} \quad (18)$$

measures effectively the integrated intensity of the fast relaxation with respect to the Debye level.

We were able to collect a few data points for $\delta_D^2(T_g)$ from literature. These data show that $\delta_D^2(T_g)$ is essentially independent of fragility (Fig. 13). This suggests that the entire dependence of the parameters R_1 and $\delta^2(T_g)$ on fragility comes from that of the boson peak and not from the fast relaxation. The fast relaxation at T_g , normalized to a proper Debye level (determined by the mass density and sound velocities), appears to be independent of fragility.

Indirectly this conclusion is supported by an earlier analysis of low-temperature specific heat data of glasses c_p made in Ref. [15]. After normalization to the Debye level, c_p exhibits two characteristic features at low temperatures: the excess specific heat at 2–10 K, which corresponds to the boson

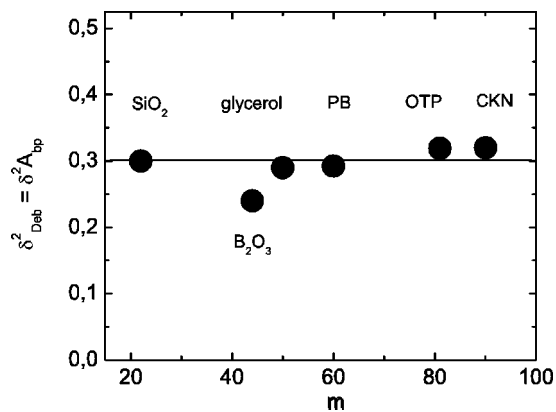


FIG. 13. The parameter $\delta^2(T_g)A_{bp}$ vs fragility. The data show that the intensity of the fast relaxation normalized to the vibrational Debye level is essentially independent of fragility.

peak vibrations, and the additional contribution to the specific heat at $T \leq 1$ K, ascribed to tunneling systems. In Ref. [15] it was found that the amplitude of the excess c_p related to the boson peak decreases with increasing fragility m , while the contribution of tunneling systems is very similar even in glass formers with very different fragility such as silica and CKN. This was rather an unexpected observation. It might become more clear now: the amplitude of the tunneling contribution normalized to the Debye level is more or less independent of fragility, the same as the amplitude of the fast relaxation at higher temperatures.

VI. CONCLUSIONS

We present a detailed analysis of the proposed in the literature correlations between fragility and various properties of glass-forming systems. We emphasize that the fragility parameter m measured close to T_g correlates linearly with the ratio of T_g to the high-temperature activation energy E (Fig. 2). Moreover, the fragility correlates with the parameters of the normal liquid: namely, with the ratio of the melting temperature to E (inset in Fig. 2). Thus, fragility is embedded in equilibrium properties of high-temperature liquid.

We show that the ratio of instantaneous shear to bulk moduli in glass-forming systems, or, alternatively, Poisson's ratio, appears to be an important parameter for both slow and fast dynamics. In particular, it controls the fragility of liquids and the amplitude of the boson peak in glasses [18]. Glass formers with a higher ratio of shear to bulk modulus in the glassy state are less fragile in a supercooled liquid state and have stronger boson peak. Thus, by measuring the ratio of transversal and longitudinal sound velocities of a material in the glassy state one can predict its fragility in the supercooled liquid state (Fig. 4). We show that the influence of the instantaneous shear modulus on both the high-temperature activation energy and the amplitude of the structural relaxation (nonergodicity parameter f_0) explains these observations.

However, the correlation of fragility with the ratio of elastic moduli does not always hold. Some high-fragility polymers and alkali borate glasses with different concentrations

of alkali-metal atoms demonstrate strong deviations from the correlation. It is shown that fragility changes in the direction opposite to the one expected from the correlation with Poisson's ratio in polystyrene samples with different molecular weight. The deviation from the general trend may be connected to the influence of the topology of the molecular structure on viscosity or structural relaxation time or to particular entropic contribution. More specific studies of these systems might help to understand better the nature of fragility in supercooled liquids.

The ratio of elastic moduli in glasses also controls the nonergodicity parameter f_0 , and consequently, f_0 in most cases correlates with fragility. The correlation of f_0 with fragility rationalizes a recent finding—the correlation of the Landau-Placzek ratio in glasses with fragility [17]. We present two examples CKN and B_2O_3 , which show strong deviations from this general trend. The reason for these deviations remains unclear. CKN and B_2O_3 do not deviate from general correlations of fragility with other parameters, suggesting that there might be a specific contribution to the experimentally measured values of f_0 in these materials.

We propose that the same nonergodicity parameter is connected to the vibrational anomaly of glasses, the boson peak, through the amplitude of the structural relaxation frozen at T_g . We show that the strength of the boson peak also correlates with the ratio of the elastic constants in the glassy state: the higher is the ratio of the shear to the bulk moduli, the stronger is the boson peak. This explains the previously

found correlations between the fast dynamics and fragility of glass formers. It is shown that the intensity of the fast relaxation, normalized to the Debye density of vibrational states, appears to be essentially independent of fragility. This result is very surprising and deserves further investigation.

The analysis presented here emphasizes the importance of the ratio of the instantaneous shear and bulk moduli for dynamics of glass-forming systems. It controls the high-temperature activation energy of the structural relaxation. The latter defines the fragility estimated around T_g . The ratio K_∞/G_∞ also affects the amplitude of the structural relaxation and in this way influences the fast dynamics in glasses. These findings provide an explanation for puzzling observations of correlations between the fast dynamics and fragility. Example of high-fragility polymers deserves particular attention. Our data show that the correlation of m with V_f/V_t breaks down for PS with higher M_n , although the correlation of m with the fast dynamics characterized by the parameter R_1 remains valid. Does that imply a stronger connection of fragility to the fast dynamics than to the ratio of the moduli? Further studies of this system might help to understand various factors that control fragility and the fast dynamics in glass forming systems.

ACKNOWLEDGMENTS

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