Dynamics of Strong and Fragile Glass Formers: Differences and Correlation with Low-Temperature Properties

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Low-frequency Raman spectra of strong and fragile glass forming liquids were measured in a wide temperature range. From an analysis of the spectra and literature data it is found that the main difference in the dynamic structure factor is the ratio of vibrational to relaxational contributions: The stronger the glass former the higher this ratio. It is shown that this difference survives even at very low temperatures and determines the low-temperature anomalies of glasses. A possible way how the observed difference influences the fragility of a liquid is discussed.

During the past years new steps in the investigation of the glass transition were strongly stimulated by recent achievements of mode coupling theory (MCT) [1]. Results of neutron [2–5] and light [6] scattering experiments support the main predictions of the theory. The experimental studies were carried out on glass formers without directional bonds (mostly van der Waals or ionic systems), which show a similar high increase of viscosity η upon supercooling and usually are called fragile systems [7]. On the other hand, it is well known that in the presence of directional bonds the temperature variation of η is weaker [7]. These so-called strong and intermediate glass formers usually have covalent or hydrogen bonded networks with stable short and medium range structure, while fragile systems usually have less stable structure. But how this structural difference influences the fragility, i.e., the temperature dependence of viscosity, is still an open question. Or, to put it in another way, the differences of the dynamic structure factor $S(q,\omega)$ for the different glass formers have not yet been elaborated on in a systematic way.

In the framework of MCT two different relaxation processes are analyzed [1]: a slow α process and a fast β process. The latter usually covers frequencies in the range 10^{11}–10^{12} Hz. In the same frequency range low-energy vibrational excitations also contribute to $S(q,\omega)$ of supercooled liquids [2,5]. In the glassy state they can be described in terms of an excess (as compared to the Debye value) density of vibrational states, and are usually ascribed to some kind of localized vibrational excitations [8]. In the Raman spectra they appear in the form of the so-called boson peak, which has been observed even at temperatures close to the melting point T_m [9,10]. Thus the contribution of these vibrations is not negligible and may influence the dynamics of the glass transition. On the other hand, these vibrational peculiarities of the spectra are not explicitly taken into account by MCT, and in many analyses they are simply subtracted from $S(q,\omega)$ [3].

Starting from another experimental observation it is interesting to stress that the well known low-temperature anomalies of glasses are also situated in the same frequency range. In particular, all glasses have an excess (in comparison with the Debye value) specific heat C_p [11]: Around 5–10 K, C_p/T^3 has a maximum due to the same excess density of vibrational states which is seen as the boson peak in Raman spectra [12]. At $T \sim 1$–2 K, C_p/T^3 has a minimum and then increases with decreasing T, due to the linear term of C_p. The latter is usually ascribed to tunneling centers [11]. However, these anomalies have not yet been related to the dynamics of supercooled liquids, although some relation may naturally be expected.

The aim of this Letter is a systematic investigation of the differences in the dynamics of strong and fragile glass formers and how these differences are related to the degree of fragility and also to the low-temperature anomalies of glasses.

We measured Raman spectra of the glass forming liquids B_2O_3, glycerol, m-tricresyl phosphate (m-TCP), and $Ca_2K_3(NO_3)_7$ (CKN) with significantly different degrees of fragility F (Table I). There are several approaches to quantize F. Here we use the apparent activation energy E_η of viscous flow at T_g normalized by T_g:

$$F = \frac{E_\eta(T_g)}{T_g} = \frac{R}{T_g}\left[\frac{\partial \ln(\eta)}{\partial(1/T)}\right]_{T=T_g}, \qquad (1)$$

where R is the gas constant.

Right angle Raman spectra were measured using a U-1000 double monochromator. For the analysis of B_2O_3 a spectral slit width of 0.5 cm^{-1} and an Ar laser with wavelength 514.5 nm and power 200 mW were chosen. A Kr laser with wavelength 676 nm and power 100 mW was used for all other samples. Spectral slit widths were 0.5 cm^{-1} for glycerol and 0.25 cm^{-1} for m-TCP and CKN.

The obtained Raman spectra normalized by the temperature factor $\omega(n(\omega)+1) = \omega(1 - \exp(-\hbar\omega/kT))^{-1} \approx kT$

$$I_n = I/[\omega(\omega)+1)] \qquad (2)$$

are presented in Fig. 1. The spectra have, as usual, two

TABLE I. Degree of fragility F estimated from the temperature variation of viscosity or relaxational time at T_g: R_1 at T_g estimated from the Raman and neutron (η) scattering; R_2 from C_p for different glass formers (for explicit definition see text).

N	Substance	T_g (K)	F (kJ/mol K)	R_1	R_2
1	SiO_2	1446	0.44 (Ref. [7])	0.5(n) (Ref. [28])	0.28 (Ref. [13])
2	GeO_2	820	0.64 (Ref. [7])		0.43 (Ref. [11])
3	B_2O_3	526	0.76 (Ref. [14])	0.41	0.44 (Ref. [12])
4	$4SiO_2$-Na_2O	760	0.84 (Ref. [15])		0.56 (Ref. [16])
5	$3SiO_2$-Na_2O	735	0.84 (Ref. [15])		0.63 (Ref. [16])
6	Glycerol[a]	186	1.11 (Ref. [17])	0.39	0.63 (Ref. [11])
				0.6(n) (Ref. [29])	
7	PS[a] ($M=37\,000$)	370	1.12 (Ref. [18])		0.75 (Ref. [11])
8	Salol	218	1.2 (Ref. [19])	0.85 (Ref. [6])	
9	PB[a]	181	1.23 (Ref. [20])	0.95(n) (Ref. [2])	0.65 (Ref. [13])
10	m-TCP	206	1.45 (Ref. [21])	0.7	
11	o-terphenyl	243	1.55 (Ref. [19])	0.7	1 (Ref. [22])
				1(n) (Ref. [5])	
12	CKN	333	1.80 (Ref. [23])	1.3	
				1.7(n) (Ref. [2])	

[a]These substances have a high curvature of η at T_g; thus F depends strongly on the interpolation.

contributions: vibrational at $\omega > 1$ THz (boson peak, marked by arrows in Fig. 1) and relaxational (dominates at frequencies lower than the boson peak). It has been shown recently [6] that the latter corresponds to the β process analyzed within MCT. The boson peak, as shown in [12], is a reflection of the peculiarities of the vibrational density of states and not of the light-to-vibrations coupling coefficient. A criterion for the separation of vibrational from relaxational contributions is not evident, but in Fig. 1 the relaxational contribution decreases with ω, while the vibrational contribution increases with ω up to the maximum of the boson peak. Because of the overlap of these contributions some minimum appears in the spectra (Fig. 1). In first approximation and as a rather model-independent estimate one may take the ratio of the intensity at the minimum to the intensity of the boson peak maximum $R_1 = (I_n)_{min}/(I_n)_{max}$ for characterizing the relative contributions of relaxations and vibrations to the spectrum.

The value of this ratio is the main difference between the spectra of glasses under investigation (Fig. 1): The boson peak dominates in the spectra of B_2O_3 even at temperatures significantly higher than the melting point (725 K); in the spectrum of glycerol at T_m (300 K) it can be seen only as a shoulder; it disappears in the spectrum of m-TCP at $T \approx 230$ K, slightly above T_g; and it cannot be seen in the spectrum of CKN even at T_g. Here we want to stress that CKN is—at least to our knowledge—the first example of a glass which has no clear boson peak in Raman spectra at $T \sim T_g$.

This difference between the spectra strongly correlates with the degree of fragility F of the glasses: the higher the value of F, the higher the ratio R_1 (Table I). An analysis of literature data shows the same tendency for other glass forming substances: $LiCl \cdot 6H_2O$ has a pronounced boson peak in Raman spectra which disappears only at $T \gg T_q$ [24], but in $GeSBr_2$ [10] as in a number of organic glasses [6,9] it already disappears at T slightly above T_g. Moreover, this tendency is not specific for the Raman spectra only and may be also found in neutron data: $ZnCl_2$ [2] and $LiCl \cdot 6H_2O$ [25] have a pronounced low-energy vibrational peak in $S(q,\omega)$, which disappears at $T \gg T_g$; in polybutadiene there is only a weak peak which disappears at T slightly above T_g [2]; for o-
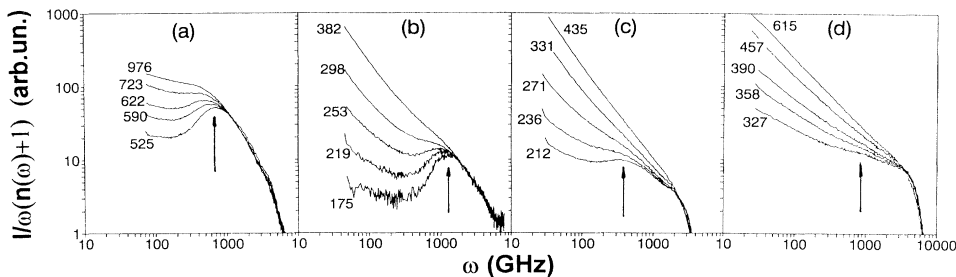

FIG. 1. Normalized Raman spectra of supercooled liquids (a) B_2O_3, (b) glycerol, (c) m-TCP, and (d) CKN at different temperatures. The arrows show the position of the boson peak at $T = T_g$.

terphenyl [5] and α-naphthylbenzene [2] at $T = T_g$ there is only a shoulder, but for CKN and $Ca(NO_3)_2 \cdot 4H_2O$ [2] not even a shoulder can be seen at $T = T_g$. Again, this difference correlates with the fragility of the systems. Some estimations of R_1 from $S(q,\omega)$ near T_g are also included in Table I. The above results show that for strong glasses even at $T > T_m$ the main contribution to the dynamical structure factor is given by low-energy vibrational excitations, while for fragile systems even at $T \sim T_g$ the main contribution is given by a fast β relaxation process.

The measured difference of the dynamic properties above T_g shows up also in low-temperature $(T < 20$ K$)$ anomalies of the heat capacity of glasses: The stronger the glass, the higher the ratio of the maximum of C_p/T^3 to the Debye value [Fig. 2(a)], i.e., the higher the excess density of vibrational states. The ratio of the minimum to the maximum of C_p/T^3, $R_2 = (C_p/T^3)_{min}/(C_p/T^3)_{max}$, depends also on the contribution of the linear term of C_p and may be used to characterize the relative contributions of tunneling systems and quasilocal vibrations to C_p. Here one finds again a correlation with fragility: For more fragile systems this ratio is higher (Fig. 2, Table I). Actually, for one of the most fragile glass formers, o-terphenyl, the maximum is not seen at all [Fig. 2(a)]. This means that more fragile systems have a larger linear term in C_p. For example, doping of SiO_2 by Na_2O and K_2O makes the system more fragile and leads to a strong increase of the linear term in C_p and to a decrease of the maximum of C_p/T^3 [16,26] [Fig. 2(b)].

The ratios R_1 at T_g and R_2 are collected in Table I and shown in Fig. 3 as a function of fragility F. Both values

correlate with F and, consequently, with each other. Thus, the peculiarities of the dynamic structure factor of glass forming liquids, i.e., the ratio of vibrational to relaxational contributions, are related to differences of the low-temperature anomalies of glasses. In particular, the relative intensity of the fast β relaxation process in the liquid correlates with the density of tunneling centers in the glassy state. From this correlation one can tentatively conclude that tunneling centers and the structures in which the fast β relaxation takes place have the same microscopic origin.

Now we come back to the question of how to relate the observed difference of $S(q,\omega)$ to the difference of the glass transition scenario for strong and fragile systems. Mode coupling theory focuses on the relaxation part of $S(q,\omega)$ [1]. Indeed the results obtained here (Fig. 1) show that the relaxational contribution dominates $S(q,\omega)$ of fragile systems. Thus, these glasses are ideal for testing MCT; its predictions were supported by many experimental studies on fragile systems [2-6]. In contrast, for strong and intermediate glass formers the vibrational contribution to $S(q,\omega)$ dominates, and the scenario of the glass transition changes significantly. In this case MCT analysis is hampered, unless the vibrational contributions will be included explicitly into the theory.

An interesting idea of calculating viscosity from $S(q,\omega)$ was recently published in [27]. The authors supposed that η may be related to the mean-square displacement of the atoms $\langle u^2 \rangle$: $\ln(\eta/\eta_0) \sim \langle u_0^2 \rangle/\langle u^2 \rangle$. From neutron scattering data in the frequency range 50-500 GHz they calculated the viscosity of selenium and obtained good agreement with experimental data using η_0 and $\langle u_0^2 \rangle$ as fit parameters. The physical background of linear relation between $\ln(\eta)$ and $1/\langle u^2 \rangle$ is not clear. Putting it in a more general way, one can write

$$\ln(\eta/\eta_0) \propto f(\langle u_0^2 \rangle/\langle u^2 \rangle), \tag{3}$$

where f is a not yet specified monotonic function. This approach recalls old ideas of free volume theory. Togeth-
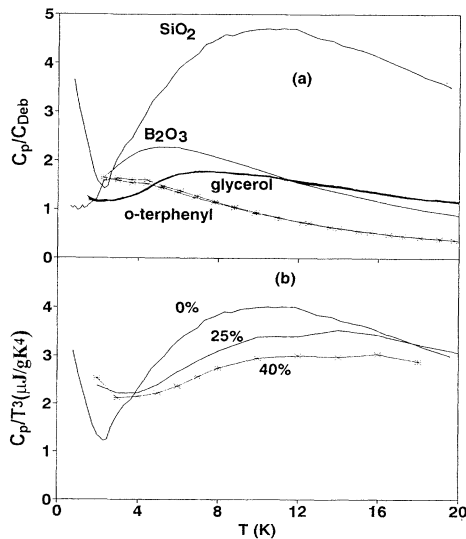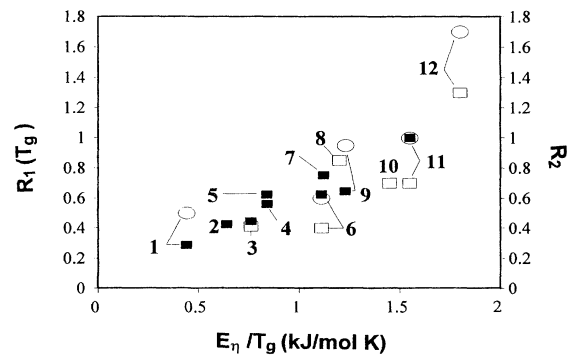

FIG. 2. Low-temperature heat capacity of different glasses: (a) for SiO_2 and Bi_2O_3 normalized to the Debye values [11], for glycerol and o-terphenyl, where c_{Deb} is not known, normalized to the crystalline values of C_p [11,22]; (b) for SiO_2 with different concentrations of Na_2O (data from [16]).

FIG. 3. Ratios of relaxational and vibrational contributions estimated from the Raman spectra ($\square$) and neutron data ($\bigcirc$) at T_g (R_1) and from the low-temperature heat capacity data (R_2) ($\blacksquare$) versus degree of fragility F for different glass formers. The numbers correspond to Table I.

er with our results it leads to some interesting conclusions. One can present $\langle u^2 \rangle$ as a sum of vibrational $\langle u^2 \rangle_{vib}$ and relaxational $\langle u^2 \rangle_{rel}$ terms: $\langle u^2 \rangle = \langle u^2 \rangle_{vib} + \langle u_2 \rangle_{rel}$. The first term has nearly harmonic behavior $\langle u^2 \rangle_{vib} \sim kT$, while the second term increases with temperatures much faster (Fig. 1). Since for fragile systems the second term is larger, $\langle u^2 \rangle$ for them will increase with T much faster and will have a higher value than for strong glass formers. This conclusion is supported by the $\langle u^2 \rangle$ values derived from neutron scattering [3,4]: In more fragile o-terphenyl $\langle u^2 \rangle$ increases much faster with T and has a larger value than in glycerol. As a result, the viscosity of strong glass formers, where $\langle u^2 \rangle_{vib}$ dominates, has a slow and smooth temperature variation, while an increase of the relaxational contribution $\langle u^2 \rangle_{rel}$ leads to a stronger temperature dependence of η for more fragile systems.

Using (1) and (3) we can express the degree of fragility in the following way:

$$F = RT_g \left[\frac{\partial f}{\partial \langle u^2 \rangle} \frac{\partial \langle u^2 \rangle}{\partial T} \right]_{T=T_g}$$

$$\propto \left[\frac{\partial \langle u^2 \rangle_{vib}}{\partial T} + \frac{\partial \langle u^2 \rangle_{rel}}{\partial T} \right]_{T=T_g}. \tag{4}$$

It explains why F increases with the increase of the relaxational contribution to $S(q,\omega)$ (Fig. 3). Moreover, it shows that F will depend on the temperature variation of $\langle u^2 \rangle_{rel}$. In particular, it may explain some deviation observed in Fig. 3 for glycerol, which has a comparatively small weight of relaxational contribution to the Raman spectra at T_g, but then strongly increases with temperature (Fig. 1). From these considerations we can speculate that for fragile systems the driving force of the glass transition, which determines temperature variations of $\langle u^2 \rangle$ and viscosity, is a local relaxational motion (fast β relaxation), while for strong glasses it is vibrational.

In summary, we have found a systematic difference in the dynamics between strong and fragile glass forming systems. They may be classified according to the dominant type of the low-frequency atomic (or molecular) motion: For fragile glass formers it is relaxation, while for strong glass formers it is vibration. And this difference determines the scenario of the glass transition. It was also shown that this difference in the dynamics of the liquids is conserved in glassy states down to very low temperature and determines the low-temperature anomalies of glasses. Thus one can tentatively conclude that the nature of the low-temperature anomalies of glasses has to be found in the melt.

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