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Fragility and compressibility at the glass transition

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Isothermal compressibilities and Brillouin sound velocities from the literature allow us to separate the compressibility at the glass transition into a high-frequency vibrational and a low-frequency relaxational part. Their ratio shows the linear fragility relation discovered by x-ray Brillouin scattering, though the data bend away from the line at higher fragilities. Using the concept of constrained degrees of freedom, one can show that the vibrational part follows the fragility-independent Lindemann criterion; the fragility dependence seems to stem from the relaxational part. The physical meaning of this finding is discussed.

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Very recently, Scopigno *et al.*[1] compiled x-ray Brillouin data in glasses, comparing the integrated Brillouin line intensity to the intensity of the central line. They found a linear relation between this ratio and the fragility $m = \partial \log \eta / \partial (T_g/T)$, defined in terms of the steep rise of the viscosity η towards the glass temperature T_g with decreasing temperature in the supercooled liquid.

This striking result poses two questions. The first is a more technical point: Does the momentum transfer range of the x-ray Brillouin technique still reflect the long-wavelength limit? The second is more fundamental: Is the fragility related to the Brillouin intensity or to the central line intensity? Scopigno *et al.* only demonstrate a linear relation to the *ratio* of these two quantities. The present paper intends to address these two questions by a comparison to literature data on the long-wavelength limit.

The total scattering of a supercooled liquid at low-momentum transfer is given by its isothermal compressibility χ_T:

$$\lim_{Q\to 0} S(Q) = \rho \frac{kT}{M}\chi_T, \tag{1}$$

where ρ is the density and M is the average atomic mass. Equation (1) has been found to be valid for several molecular and polymeric supercooled liquids[2] on the nm length scale of the x-ray Brillouin technique.

The x-ray Brillouin experiment splits the total scattering $S(Q)$ into an apparently elastic central component $S_{IS}(Q)$ and two Brillouin lines of summed intensity $S_{Brill}(Q)$. The longitudinal sound velocity $v_{l\infty}$ at the Brillouin line defines a high-frequency Brillouin compressibility $\chi_{Brill}=1/\rho v_{l\infty}^2$. The ratio $\alpha_{scatt}=S_{Brill}(Q)/S_{IS}(Q)$ at the glass temperature T_g reported by Scopigno *et al.*[1] should equal the ratio α_χ between vibrational and relaxational compressibility:

$$\alpha_\chi(T_g) = \frac{\chi_{Brill}(T_g)}{\chi_T(T_g) - \chi_{Brill}(T_g)}. \tag{2}$$

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Table I compiles literature data of the isothermal compressibility and the Brillouin sound velocity. Most of the Brillouin sound velocities in Table I were obtained by light scattering; at the glass transition, light and x-ray scattering sound velocities still agree.[10,14,18]

As shown in Fig. 1(a), the general tendency is the same and the three common cases of glycerol, OTP, and Se agree

TABLE I. Isothermal and Brillouin compressibility at the glass transition. Abbreviations: PIB=polyisobutylene, PB=polybutadiene, PET=polyethylenteraphtalate, OTP=orthoterphenyl, CKN=$K_3Ca_2(NO_3)_7$, PVAC=polyvinylacetate, BPA-PC=polycarbonate, PS=polystyrene, PMMA=polymethylmethacrylate, and PVC=polyvinylchloride.

Substance	T_g (K)	ρ (kg/m^3)	$v_{l\infty}$ (m/s)	$v_{t\infty}$ (m/s)	χ_{Brill} (GPa^{-1})	χ_T (GPa^{-1})
BeF_2	598[a]	1900[c]	4570[c]		0.0252	
SiO_2	1450[a]	2200[d]	6480[d]	3988[d]	0.0108	
B_2O_3	550[e]	1792[e]	3600[f]	1933[f]	0.0431	0.39[e]
PIB	201[b]	939[g]	2994[h]		0.119	
Glycerol	187[i]	1332[i]	3583[i]	1858[j]	0.0586	0.287[k]
Salol	218[a]	1268[l]	2382[l]		0.139	
1,4-PB	180[a]	940[g]	2500[m]		0.170	
PET	342[a]	1350[g]	2309[n]		0.139	0.324[o]
OTP	241[a]	1124[p]	2550[q]		0.137	0.39[p]
Se	308[a]	4262[r]	2000[s]		0.0587	0.16[r]
CKN	343[b]	2186[e]	3190[f]	1497[f]	0.0450	0.132[e]
PVAC	304[e]	1186[e]	2492[t]		0.136	0.498[e]
BPA-PC	418[b]	1180[u]	2176[v]	938[v]	0.179	0.511[o]
PS	375[b]	1028[u]	2219[w]		0.198	0.558[o]
PMMA	379[b]	1161[u]	2500[x]	1278[w]	0.138	0.473[o]
PVC	347[x]	1372[u]	2198[x]		0.151	0.385[o]

[a] Reference 1.
[b] Reference 3.
[c] Reference 4.
[d] Reference 5.
[e] Reference 6.
[f] Reference 7.
[g] Reference 8.
[h] Reference 9.
[i] Reference 10.
[j] Reference 11.
[k] Reference 12.
[l] Reference 13.
[m] Reference 14.
[n] Reference 15.
[o] Reference 16.
[p] Reference 17.
[q] Reference 18.
[r] Reference 19.
[s] Reference 20.
[t] Reference 21.
[u] Reference 22.
[v] Reference 23.
[w] Reference 24.
[x] Reference 25.

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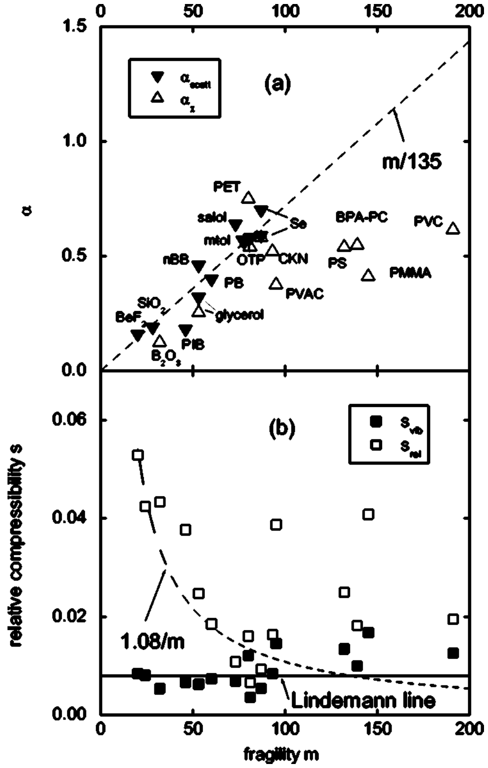

FIG. 1. (a) Comparison of α values from x-ray Brillouin scattering and from the long-wavelength limit. (b) Fragility dependence of normalized vibrational and relaxational compressibilities.

TABLE II. Ratio of vibrational and relaxational compressibility at the glass transition.

Substance	α_χ	α_{scatt}	f_s	M (10^{-27}kg)	B/B_0	m
BeF$_2$		0.16[a]	5/9	26.0		20[a]
SiO$_2$		0.191[a]	5/9	33.25		24[b]
B$_2$O$_3$	0.124		1/5	21.92	5.6	32[b]
PIB		0.182[c]	1/6	7.75		46[b]
Glycerol	0.253	0.32[a]	1/3	10.91	3.1	53[a]
Salol		0.64[a]	7/39	13.66		73[b]
1,4-PB		0.40[a]	1/6	8.96		60[a]
PET	0.751		13/66	14.49		80[d]
OTP	0.540	0.58[a]	1/12	11.93		81[b]
Se	0.579	0.7[a]	2/3	131.1		87[b]
CKN	0.516		19/33	31.76	2.1	93[b]
PVAC	0.375		1/4	11.9		95[b]
BPA-PC	0.539		14/99	12.78	2.1	132[b]
PS	0.548		5/48	10.97		139[b]
PMMA	0.411		2/9	11.07	2.2	145[b]
PVC	0.644		4/21	15.05		191[b]

[a] Reference 1.
[b] Reference 3.
[c] Reference 28.
[d] Reference 29.

reasonably well in both sets of data. The literature data go to much higher fragility and thus reveal a bending away from the postulated line: at higher fragilities, the compressibility ratio becomes fragility independent. But even so, the answer to our first question is clear: the relation discovered by x-ray Brillouin scattering[1] is a true property of the long-wavelength limit.

In order to answer the second question—namely, whether the Brillouin line or the central line provides the relation to the fragility—one needs to compare the vibrational or relaxational compressibility of different glass formers. This requires an appropriate normalization of the compressibility. It is reasonable to define a dimensionless ratio between the thermal energy at the glass transition and the vibrational and relaxational compression energy, respectively, by

$$s_{vib} = \frac{k_B T_g \chi_{Brill}}{v}, \quad s_{rel} = \frac{k_B T_g (\chi_T - \chi_{Brill})}{v}, \tag{3}$$

where v is an appropriate microscopic volume.

A priori, one would choose for v the atomic volume. However, this choice is not justified, because glass formers are complex solids, with a mixture of strong and weak nearest-neighbor bonds.[26,27] For instance, a polymer owes its material properties to a mixture of covalent and van der Waals bonds, very different in strength. Therefore one must take this difference in bonding strength into account.

Thus we define $v = v_{at}/f_s$, where v_{at} is the atomic volume and f_s is the fraction of soft degrees of freedom in the substance. The f_s values in Table II were calculated assuming the stretching of all covalent bonds (including the Be-F bond) as well as the bond bending at boron, nitrogen, and carbon to be hard. All other degrees of freedom were considered to be soft. The resulting s_{vib} and s_{rel} values are shown in Fig. 1(b). Though the scatter of points is even worse than in Fig. 1(a), one observes that the fragility rise is only weakly correlated with the vibrational softening, but strongly with a decrease of the relaxational compressibility.

The first part of this result is consistent with empirical knowledge: The glass temperature tends to be about a factor of 0.6 smaller than the melting temperature T_m, which in turn follows the empirical Lindemann criterion.[30] The Lindemann criterion states a mean-square vibrational displacement of the atoms in the crystal of 10% of the nearest-neighbor distance at the melting point. On the basis of a Debye model and a constant ratio of transverse and longitudinal sound velocity, one then expects the same vibrational compressibility in all glass formers at T_g, independent of the fragility m.

To quantify this Lindemann expectation, we assume a nearest-neighbor distance $d \approx v_{at}^{1/3}$ and an average ratio of longitudinal to transverse sound velocity, $v_{l\infty}/v_{t\infty} \approx 1.8$. The Lindemann criterion in the form improved by Gilvarry[31] reads

$$\langle u^2 \rangle (T_m) = \frac{3 k_B T_m}{M \omega_D^2} \equiv (0.083 d)^2. \tag{4}$$

Here $\langle u^2 \rangle$ is the mean-square displacement in *one* direction and ω_D is the Debye frequency

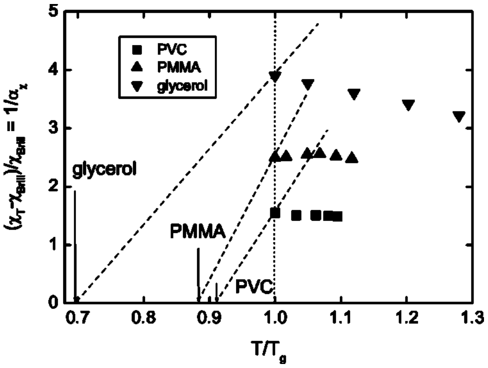

FIG. 2. Ratio of relaxational to vibrational compressibility for PVC, PMMA, and glycerol above T_g (the references are the same as in Table I). The arrows mark the Vogel-Fulcher temperatures of the three glass formers; the dashed lines show the free volume expectation.

$$\omega_D^3 = \frac{18\pi^2}{v_{at}(1/v_l^3 + 2/v_t^3)}. \tag{5}$$

With the above assumptions (including $T_g \approx 0.6T_m$), one finds

$$k_B T_g \approx 0.008 \frac{v_{at}}{\chi_{Brill}}. \tag{6}$$

This is the Lindemann line in Fig. 1(b), which is in reasonable agreement with the data points for the vibrational compressibility. Taking this Lindemann compressibility and the linear relation $\alpha = m/135$ of Scopigno *et al.* [the dashed line in Fig. 1(a)], one gets $s_{rel} = 1.08/m$, the dashed line in Fig. 1(b). We observe that this relation is only followed in the lower half of the fragility region, consistent with the bending away observed in Fig. 1(a).

The temperature dependence of the ratio between relaxational and vibrational compressibility $1/\alpha_\chi$ is shown in Fig. 2 for three of the glass formers of Table I. There is no strong decrease of the ratio towards T_g, so the relaxational compressibility is proportional neither to the free volume nor to the excess entropy of the glass former.[32] In the first case, it should extrapolate to zero at the Vogel-Fulcher temperature, in the second at the Kauzmann temperature (these two temperatures tend to lie close to each other[33–35]).

To clarify the physical meaning of the compressibility ratio, it is useful to rewrite it in terms of elastic moduli. Let B and G be the infinite-frequency bulk and shear modulus, respectively. $\chi_T = 1/B_0$, where B_0 is the zero-frequency bulk modulus (the zero-frequency shear modulus is zero above T_g). $1/\chi_{Brill} = B + 4G/3 \approx 1.7B$, where we used again the approximation $v_{l\infty}/v_{t\infty} \approx 1.8$ mentioned in the derivation of the Lindemann line. Thus

$$1/\alpha_\chi \approx 1.7\frac{B}{B_0} - 1, \tag{7}$$

so the ratio between relaxational and vibrational compressibility is a measure for the ratio between high-frequency and low-frequency bulk moduli. For strong glasses, this is high; for fragile glasses, it is low. In fact, for the five glasses where we know not only the isothermal compressibility, but also both the longitudinal and the transverse Brillouin sound velocity (see Table I), the calculated ratio B/B_0 in Table II decreases with increasing fragility (in those cases, it is possible to determine B/B_0 directly from experiment without any approximation).

The question is, what determines the ratio B/B_0 between long-time and short-time bulk moduli at the glass transition? This question can be translated into another question: What happens to the bulk modulus in the relaxation processes which bring the shear modulus down to zero? There are two extremes: (i) The bulk modulus is also brought down to zero. (ii) The bulk modulus is not affected at all. In the first case, B/B_0 is infinite and $\alpha_\chi = 0$; in the second case, $B/B_0 = 1$ and $\alpha_\chi \approx 1.43$. However, these extremes are never reached; in Table II, α_χ ranges from 0.124 to 0.751, so B/B_0 ranges from 1.35 to 5.6.

The consideration helps to understand the weakness of the temperature dependence in Fig. 2: B/B_0 changes only slowly with temperature (if it changes at all). One also understands the physical meaning of the relation found by Scopigno *et al.*[1]: In strong glass formers, B/B_0 is large, in fragile ones small. Strong glass formers show strong relaxational density fluctuations on the scale of their vibrational compressibility, a factor of 3–4 stronger than fragile ones.

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