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Vibrational dynamics and the structure of glasses

E Duval†, A Boukenter‡ and T Achibat†

† Laboratoire de Physico-Chimie des Matériaux Luminescents, URA 442 du CNRS, Université Lyon I, 43 Boulevard du 11 Novembre, 69622 Villeurbanne, France

‡ Laboratoire du Traitement du signal et Instrumentation, UA CNRS 842, 23, rue du Dr Paul Michelon, 42023 St Etienne, France

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Abstract. A model assuming a non-continuous structure of glasses is established to interpret the inelastic neutron scattering and Raman scattering. The ‘boson’ peak in Raman scattering is related to the vibrational density of states ‘excess’. These two related features are a result of vibrations localized in the blobs that compose the glass. Size distributions of the blobs are deduced from neutron and Raman scatterings.

1. Introduction

The low-frequency vibrational dynamics in glasses or liquids depend strongly on the static or transient organization, respectively, or on the disordered structure. In the frequency domain from about 1 cm^{-1} to 100 cm^{-1} , universal features appear in the different responses, which are functions of the density of vibrational states (DVS). In particular the inelastic neutron scattering (Buchenaü *et al* 1984, 1986, Malinovsky *et al* 1990) and the heat capacity (Pohl 1981) manifest a DVS excess.

The low-frequency broad band in the Raman scattering spectrum, called the ‘boson peak’, is another universal characteristic of glasses. It is also present in numerous liquids.

However, until recently it was not clear that the ‘boson peak’ is related to an excess in the DVS. The low-frequency Raman scattering of light is due to vibrational modes which are localized by the disorder. The Raman intensity $I(\omega)$ is usually written in the form (Jäckle 1981)

$$I(\omega) = C(\omega)R(\omega)(n(\omega) + 1)/\omega \quad (1)$$

where $n(\omega) + 1$ is the Bose factor for Stokes scattering, $R(\omega)$ is the Raman DVS and $C(\omega)$ describes the coupling between the light wave and the vibration. The derivation of $C(\omega)$ from the model of Martin and Brenig (1974), which is a modification of an earlier theory of Whalley and Bertie (1967), has been extensively used for the interpretation of Raman scattering from glasses. From this model

$$C(\omega) \propto \omega^2 \exp(-\omega\sigma/v)^2 \quad (2)$$

where v is the sound velocity and 2σ the structural correlation length. A continuous disordered network, characterized by the correlation length 2σ , is assumed for glasses.

The expression (2) for the coupling constant $C(\omega)$ has a maximum for $\omega \approx v/\sigma$ and, consequently, the boson peak in Raman scattering was interpreted as being the maximum of $C(\omega)$. However, this interpretation is questionable following the results of the comparison of Raman scattering with inelastic neutron scattering and heat capacity for several glasses (Ahmad *et al* 1986, Malinovsky *et al* 1990). Ahmad *et al* (1986), using the DVS deduced from heat capacity, interpreted the Raman scattering of vitreous As_2S_3 using expression (1) and showed that $C(\omega)$ has no maximum but rises monotonically with the frequency. This behaviour is confirmed for vitreous silica using the vibrational density of states deduced from the inelastic neutron scattering measurements of Buchenaü *et al* (1984, 1986): $C(\omega)$ does not yield a maximum and the variation of the Raman scattering is close to the variation of the 'neutron' DVS. Very recently Malinovsky *et al* (1990) compared their measurements of Raman and neutron scatterings from different glasses, in particular from SiO_2 and As_2S_3 . They reached the same conclusion: the maximum of the low-frequency Raman scattering (boson peak) does not result from a maximum of the coupling constant but rather from a maximum of the DVS excess with respect to the Debye density of states.

Buchenaü *et al* (1984, 1986) identified the additional low-frequency modes as coupled rotations of SiO_4 tetrahedra. In so far as the apparent density of states excess is universal for glasses, the interpretation of Buchenaü *et al* seems to us to be incomplete. In our opinion the shape of the DVS, and of the low-frequency Raman scattering spectrum, is related to the universal structure of glasses. The aim of this paper is to discuss the relation between low-frequency vibrational dynamics and the structure of glasses and to suggest an interpretation.

2. Model

In figure 1 the reduced intensity of Raman scattering $I(\omega)/(n(\omega) + 1)$ of vitreous As_2S_3 , deduced from the measurements of Nemanich (1977) is compared with the neutron DVS, $N(\omega)$, determined by Malinovsky *et al* (1990) from inelastic neutron scattering. The similarity of the two curves in logarithmic coordinates is remarkable, apart from a slight translation of $I(\omega)/(n(\omega) + 1)$ towards the low frequencies. One obtains, after comparison:

$$I(\omega)/(n(\omega) + 1) = N(\omega)\omega^b \quad (3)$$

with $b = 0.4 \pm 0.1$. Comparing (1) and (3), and assuming that $R(\omega)$ is equal to $N(\omega)$, we obtain $C(\omega) \propto \omega^c$ with $c = 1.4 \pm 0.1$. Malinovsky *et al* (1990) found a similar value of c . It is now clear that the curvature of $I(\omega)/(n(\omega) + 1)$ does not arise from $C(\omega)$, but rather from the density of states $R(\omega)$ or $N(\omega)$. Furthermore the DVS and the coupling constant $C(\omega)$ do not reflect the Debye model where both vary as ω^2 (Jäckle 1981).

In figure 2 the reduced intensity of vitreous SiO_2 is compared with the neutron DVS determined by Buchenaü *et al* (1986).

The features of figure 2 for SiO_2 are the same as those of figure 1 for As_2S_3 . The value of the coefficient c is 0.25 ± 0.1 . However, in the domain $60\text{--}120 \text{ cm}^{-1}$ c varies between 1 and 1.5.

From these experimental results and their comparison, three points have to be emphasized:

- (i) The Debye model fails to interpret the DVS and the Raman scattering.

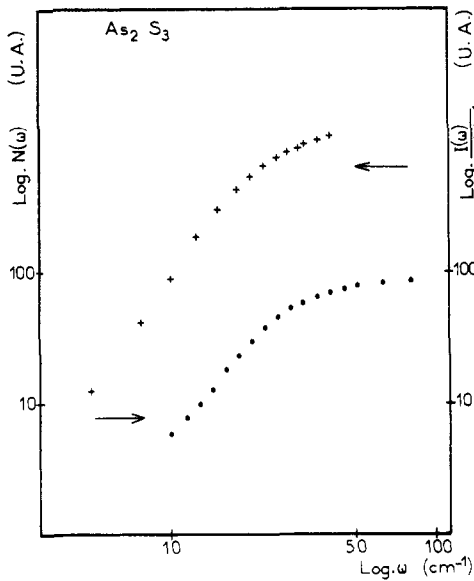


Figure 1. Neutron density of vibrational states, $N(\omega)$ (Malinovsky *et al* 1990) and Raman reduced intensity (Nemanich 1977) of As_2S_3 glass.

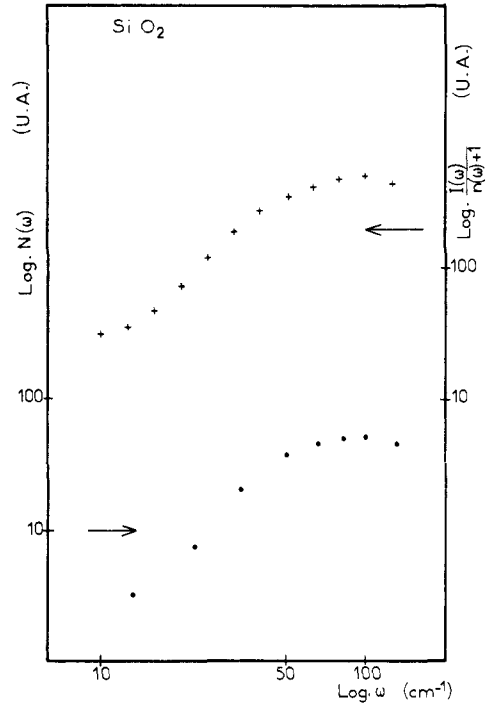


Figure 2. Neutron density of vibrational states, $N(\omega)$ (Buchenaü *et al* 1986), and Raman reduced intensity (our measurements) of SiO_2 glass.

- (ii) At low frequencies $N(\omega)$ varies more rapidly than ω^{d-1} with $d = 3$. This means that $N(\omega)$ does not correspond to the vibrations of a continuous network.
- (iii) $C(\omega)$ is not related to the correlation length of a disordered lattice.

As emphasized before $N(\omega)$ cannot be interpreted as additional vibrations specific to a particular glass but is related to the glass structure itself. Novikov (1989) assumes that the density of states excess results from the vibrations of disclination defects. The existence of such defects is implied by the curved space model of Mosseri and Sadoc (1984). Like Buchenaü *et al*, Novikov believes that the defect vibrations add to the Debye vibrations of the rest of the glass.

In the model presented in this paper it is assumed that the network is not continuous, but composed of blocks or blobs, of size 10–20 Å. In contrast to the well known models (Randall *et al* 1930, Evstropyev *et al* 1972) the blobs are not considered to be microcrystalline, but disordered. The disordered glass network is disrupted by defects which segregate the structure into blobs. The bonding between atoms of nearest-neighbour blobs is certainly weaker than the bonding inside the blobs. Consequently the vibrational dynamics can be divided into two regimes:

- (i) the low-energy regime which concerns the motion of blobs with respect to each other;
- (ii) the high-energy regime that accounts for the vibrations in blobs.

There is a gap between these regimes, but it is probably in this gap that defect excitations appear, like the well known two-level systems (TLS) (Anderson *et al* 1972). Nevertheless we expect that the effective density of states in the high-energy regime increases as the number of blobs able to accommodate the vibrations increases.

The size distribution of blobs is symbolized by the function $f(a)$. The lowest-energy vibrational mode localized in a blob has a frequency ω_0 such that (Duval *et al* 1986, Boukenter *et al* 1989)

$$\omega_0 = S(v/2a) \quad (4)$$

where v is the velocity of sound in a blob, $2a$ is the size of the blob, and S is a shape factor. Therefore the size distribution corresponds to a frequency distribution of the blob fundamental modes. We define a distribution $F(\omega_0)$ which is such that $F(\omega_0) d\omega_0$ is the ratio of the volume occupied in the glass by the blobs whose fundamental mode frequencies lie between ω_0 and $\omega_0 + d\omega_0$ to the glass sample volume.

If the vibrations have a wavelength much longer than the mean value of $2a$, they are delocalized in the glass. At the other extreme the vibrations with a wavelength smaller than about $4a$ are localized in the blobs. There is a crossover between delocalized long-wavelength vibrations and vibrations localized in blobs. For the delocalized vibrations the density of states is a Debye density of vibrational states $D(\omega) \propto \omega^2$.

The vibrations localize more and more as the number of blobs of size $2a$ greater than about two wavelengths increases. If $g(\omega)$ is the real DVS inside the blobs, the observed effective DVS $g_{\text{eff}}(\omega)$ of vibrations localized in blobs is

$$g_{\text{eff}}(\omega) = g(\omega) \int_0^\omega F(\omega_0) d\omega_0. \quad (5)$$

If ω_1 is the upper limit for the frequency ω_0 , which corresponds to the smallest size of blob, then for $\omega > \omega_1$,

$$g_{\text{eff}}(\omega) \propto g(\omega). \quad (6)$$

Therefore the DVS inside the blobs is given by the variation in $g_{\text{eff}}(\omega)$ for $\omega > \omega_1$. The curves of $N(\omega)$ in figures 1 and 2 are in accordance with equation (5). Assuming that $N(\omega)$ is equal to $g_{\text{eff}}(\omega)$, obtained from the high-frequency linear part of the curves, we obtain $g(\omega) \propto \omega^n$ with $n = 0.35 \pm 0.1$ for As_2S_3 and $n = 0.2 \pm 0.1$ for SiO_2 .

Dividing $g_{\text{eff}}(\omega)$ by ω^n and taking the derivative, we obtain bell-shaped curves (figures 3 and 4) for the distributions $F(\omega_0)$. The maximum is situated at $20 \pm 3 \text{ cm}^{-1}$ for As_2S_3 and 37 cm^{-1} for SiO_2 .

It is interesting to compare the inelastic neutron scattering with the Raman scattering. If we assume that the Raman DVS, $R(\omega)$, like the neutron DVS, $N(\omega)$, is equal to the effective DVS, $g_{\text{eff}}(\omega)$, then from the expression (1) the reduced Raman intensity becomes:

$$I(\omega)/(n(\omega) + 1) = C(\omega)/\omega g_{\text{eff}}(\omega). \quad (7)$$

We have seen before that $C(\omega) \propto \omega^c$ with $c = 1.4 \pm 0.1$ for As_2S_3 , and $c = 0.25 \pm 0.1$ in the major part of the Raman spectrum of SiO_2 . Then, taking the derivative of the ratio $I(\omega)\omega^{1-c}/(n(\omega) + 1)$, from (5) and (7), we obtain again $F(\omega_0)$. The distributions $F(\omega_0)$ obtained from Raman and neutron scatterings are compared in figures 3 and 4. The maximum of the Raman bell-shaped curve is situated at $15 \pm 2 \text{ cm}^{-1}$ for As_2S_3 and at $43 \pm 3 \text{ cm}^{-1}$ for SiO_2 . These values are very close to those obtained from neutron

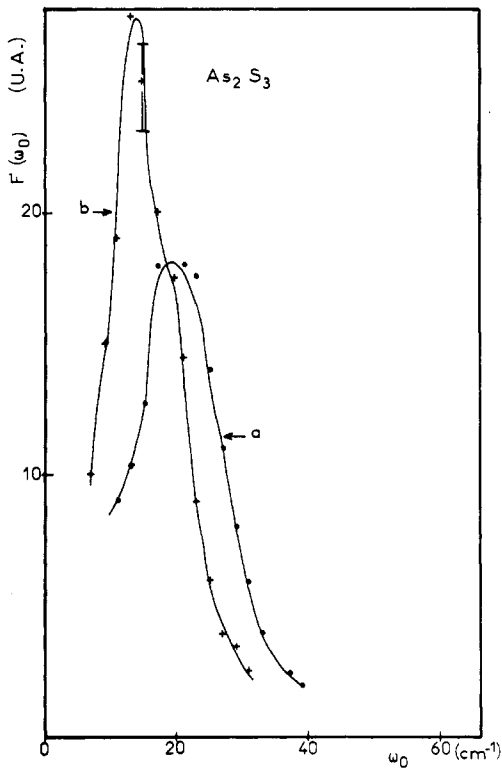


Figure 3. Distribution functions $F(\omega_0)$ deduced from: (a) neutron scattering (Malinovsky *et al* 1990); (b) Raman scattering (Nemanich 1977) for As_2S_3 glass.

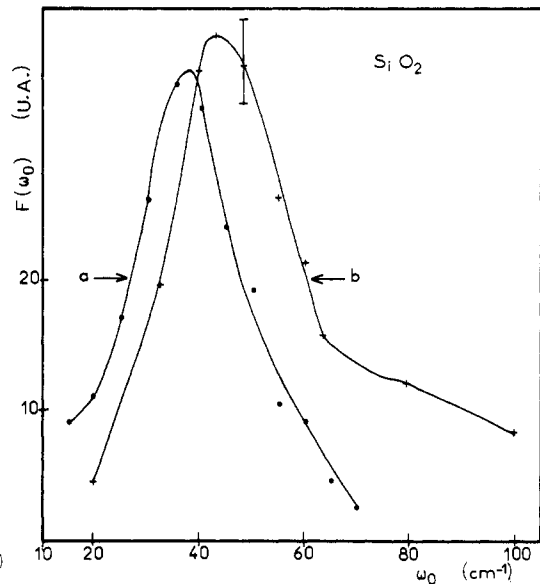


Figure 4. Distribution functions $F(\omega_0)$ deduced from (a) neutron scattering (Buchenäü *et al* 1986); (b) Raman scattering (our measurements) for SiO_2 glass.

scattering. For SiO_2 there is a supplementary bump between 60 and 120 cm^{-1} . This anomaly was noted above and merits a specific study which will be published later.

From expression (4) it is possible to deduce the most probable size of blob if we know the shape factor S . From Raman spectroscopy, however, it is difficult to deduce their shape. For spherical particles S is close to 0.8 (Duval *et al* 1986) and for linear objects $S = 0.5$. Certainly blobs are not exactly spherical and provisionally we choose an intermediate value, $S = 0.65$. Taking $v = 1690 \text{ m s}^{-1}$ for As_2S_3 and 4100 m s^{-1} for SiO_2 (Graebner and Golding 1986), with $\omega_0 = 17 \text{ cm}^{-1}$ for As_2S_3 and 40 cm^{-1} for SiO_2 , we find for the maximum of the size distribution that $2a = 21 \text{ \AA}$ and 22 \AA , respectively. These values are not surprising and are in agreement with the size estimated from the width of the first sharp diffraction peak of As_2S_3 , which is about 20 \AA (de Neufville *et al* 1973/74, Nemanich 1977).

The DVS inside the blobs is approximately $g(\omega) \approx \omega^{0.35}$ for As_2S_3 and $g(\omega) \approx \omega^{0.2}$ for SiO_2 . Assuming $g(\omega) \approx \omega^{d-1}$, the dimensionality d would be 1.35 and 1.2 respectively. It is tempting to treat d as a fractal dimensionality. More simply these dimensionalities, close to one, can reflect the chain-like shape of blobs.

There is a clear difference between the values of the coupling coefficient $C(\omega)$ of As_2S_3 and SiO_2 . The ω -dependencies are, respectively, $\omega^{1.4}$ and $\omega^{0.25}$. This difference

can be interpreted as being due to the presence of supplementary fluctuations, in the As_2S_3 blobs, with a correlation length smaller than the blob size: fluctuations that would not exist in SiO_2 . It was shown (Rousset *et al* 1990) that the effect of these fluctuations or of a supplementary disorder on $C(\omega)$ is to add a term that is equal to the dimensionality d in the ω -exponent.

3. Discussion and conclusion

In the model presented in this paper, the structure of glass is treated as an aggregation of blobs of size $\approx 20 \text{ \AA}$. In the case of As_2S_3 and SiO_2 the blobs are not microcrystallites. For As_2S_3 this conclusion is in agreement with the work of Phillips (1981). But this characteristic is probably not universal. For example, in amorphous Si the blobs would be crystalline (Ourmazd *et al* 1985).

Our model is reminiscent of the cellular model of Baltes (1973). However, in this early model only one size of cell was considered, and a Debye density of states was assumed inside the cells. The cellular model of Baltes was discussed by Tait (1975) and this was reported by Pohl (1981). Both authors showed the deficiency of Baltes model which is the result of a well defined cell shape.

Until recently it was generally agreed (Jäckle 1981) that the low-frequency Raman scattering $I(\omega)/(n(\omega) + 1)$, which has a ω^3 -dependence (Nemanich 1977), was in agreement with the Debye model and the Raman scattering of phonons. The comparison of inelastic neutron scattering and Raman scattering shows that this interpretation is wrong, since the DVS does not obey the Debye law. The deviation from the ω^3 -behaviour was interpreted as a deficiency of the Debye model, which was related to the fact that the acoustic phonon branches of the corresponding crystal showed strong dispersion in the same frequency region as the deviation (Jäckle 1981). We think that this deviation is due, instead, to the specific structure of glass and is a general feature. The non-deviation appears accidental.

Novikov (1989) interprets the inelastic neutron scattering as being due to the presence of vibrations localized in disclination defects, which add to normal Debye vibrations. He shows that the number of 'defect' atoms that form disclinations amounts to 10–15% of the total number of atoms. We did not observe the Debye density of states for the experimental neutron density of vibrational states (Buchenaü *et al* 1984, Malinovsky *et al* 1990) at $\omega > 20 \text{ cm}^{-1}$ and $\omega > 40 \text{ cm}^{-1}$ for As_2S_3 and SiO_2 , respectively. In consequence we do not think that non-Debye vibrations concern only the defects vibrations. Nevertheless the question remains open.

Two objections can be raised against our model. The first is the following: until now no direct and clear observation of the assumed cluster structure of glasses has been achieved, by e.g. electron microscopy nor by small-angle neutron or x-ray scattering. However, it is likely that the non-continuous structure, which can be observed in vibrational dynamics, does not show a corresponding well resolved fluctuation density. As indicated above, blobs exist because of a bonding that is weaker between atoms in different nearest-neighbour blobs than between atoms inside a blob. Certainly the blobs do not have a simple shape and probably consist of chains that are more or less ramified.

The second objection is explicit in the papers of Buchenaü *et al* (1984, 1986) and concerns silica-glass especially. Neutron elastic scattering shows a relatively strong first peak at the momentum transfer value $Q \approx 1.6 \text{ \AA}^{-1}$. However, the corresponding first peak in the inelastic structure factor $S(Q)$ is relatively weak for the frequency domain

considered here. It was mainly because of this that Buchenaü *et al* deduced that the excess density of states results from coupled rotation of bonded SiO_4 tetrahedra, since the scattering from such excitations does not have a first peak at 1.6 \AA^{-1} . *A priori* this peak would appear clearly for sound waves.

In fact this first peak is related to the distance between atoms in different nearest-neighbour tetrahedra. Therefore, vibrations would give rise to the first peak in $S(Q)$ if the atoms of both nearest-neighbour tetrahedra had equivalent displacements or oscillated approximately in phase (Buchenaü *et al* 1985, 1986). Now our blobs can be considered as more or less ramified and tortuous chains of tetrahedra connected by shared corners. The distribution of shared (or non-shared) corners is certainly random. On the other hand, the angle of rotation about the Si–Si axis of a tetrahedron relative to the nearest neighbour varies along the chain (Guttman and Rahman 1986). Consequently the tetrahedra in a blob are non-equivalent in the chain, and the vibrational displacements of atoms in the different nearest-neighbour tetrahedra are non-equivalent too, so the vibrations are not in phase with the oscillations of the structure factor. This can explain the weakness of the 1.6 \AA^{-1} peak in the inelastic structure factor. Without knowing the precise structure of the blobs it is difficult to imagine the vibrational motion although it is possible that this motion partially consists of relative rotations of tetrahedra.

This model seems to us to be consistent since it allows us to deduce the low-frequency Raman scattering precisely from the inelastic neutron scattering, apart from a slight anomaly for SiO_2 . Furthermore, to a first approximation, it interprets the thermal measurements. From the DVs deduced from the heat capacity of Ahmad *et al* (1986) a similar variation of the distribution of $F(\omega_0)$ is found with a maximum at 15 cm^{-1} . On the other hand it is clear that the plateau in the thermal conductivity corresponds to the localization of vibrational modes in the blobs. The limits of the plateau (Graebner and Golding 1986) are in agreement with the distribution $F(\omega_0)$.

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