Eur. Phys. J. B **17**, 667–671 (2000)

**THE EUROPEAN
PHYSICAL JOURNAL B**

EDP Sciences

Numerical studies of the vibrational isocoordinate rule in chalcogenide glasses

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Received 25 April 2000

Abstract. Many properties of alloyed chalcogenide glasses can be closely correlated with the average coordination of these compounds. This is the case, for example, of the ultrasonic constants, dilatometric softening temperature and the vibrational densities of states. What is striking, however, is that, at a given average coordination, these properties are nevertheless almost independent of the elemental composition. Here, we report on some numerical verification of this experimental rule as applied to the vibrational density of states. We find that this rule is not exact but holds qualitatively well over a wide range of compositions and local chemical correlations.

PACS. 63.50.+x Vibrational states in disordered systems – 61.43.Fs Glasses

1 Introduction

Establishing the microscopic properties of disordered materials based on macroscopic probes is a difficult endeavor: the characteristic isotropy of these materials limits measurements to mostly scalar, orientation-averaged properties, reducing significantly the amount of information accessible compared with, for example, what is available in crystals.

This is the case for scattering experiments. X-ray provides, after Fourier transform, only an isotropic radial distribution function. This smooth, structureless curve beyond medium-range order, can be reproduced numerically with a wide range of mutually inconsistent models as shown in reverse Monte-Carlo simulations [1]. Experimental scattering functions cannot provide, therefore, positive discrimination between models, they can only eliminate some of the bad models.

The experimental evidence for an isocoordinate rule in chalcogenide glasses provides yet another example of the difficulty of extracting microscopic information from these disordered materials. This rule states that for a given average coordination, samples with varying compositions will display identical properties. The isocoordinate rule has already been noted for a wealth of mechanical and thermal properties such as ultrasonic elastic constants[2], hole burning relaxation[3], and glass transition temperatures and hardness[4], and was found to hold for the more complex vibrational density of states [5–7]: systems as different as Se_8Ge_2 and Se_3As_2 with an average coordination of $\langle r\rangle = 2.4$ show a similar VDOS in the transverse acoustic (TA) region (see, for example, Ref. [5] Fig. 5).

The vibrational isocoordinate rule (VIR) has only been checked experimentally, until now, with the inherent limitations due to atomic species available and glass phase diagrams. This leaves some questions open regarding the range of validity of this rule as well as its accuracy. In this paper, we present the results of direct numerical simulations on a model system with simplified dynamics that provide a bound on a few of these points.

2 Details of the simulation

The simulations proceed as follows. We start with a 4 096-atom cell of Sillium – a perfectly tetravalent continuous-random network – constructed by Djordjevic *et al.* [8] following the prescription of Wooten, Winer and Weaire [9]; this network provides an idealized model with the appropriate initial topology. We then remove bonds at random in the network until we reach the desired concentration of 2-, 3- and 4-fold atoms. In the first stage of the simulation, we do not enforce any extra correlation and the final network corresponds to a perfectly random amorphous alloy. We then relax the network using a Kirkwood potential with interactions based on the table of neighbors, not on distance.

$$E = \frac{\alpha}{2}\sum_{\langle ij\rangle}(L_{ij}-L_0)^2 + \frac{\beta}{8}L_0^2\sum_{\langle ijk\rangle}\left(\cos\theta_{jik}+\frac{1}{3}\right)^2 \qquad (1)$$

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where α and β are taken to be the same for *all* bonds and L_0 is the ideal bond length. We take a ratio of three-body to two-body force, $\beta/\alpha = 0.2$, typical of tetrahedral semiconductors [13].

The resulting network is one of identical atoms except for the coordination. This is not too far from SeAsGe chalcogenides; because they sit side by side in the same row, these elements share very similar masses, elastic properties and Pauling electronegativities. As an additional simplification, we take the same tetrahedral angle for all triplets in the network. Real Se and As, in the respective 2- and 3-fold configuration, have angles that deviate from this value and tend towards 120 degrees. This simplification is less drastic than it appears because of the relatively low coordination, allowing a significant degree of flexibility in the network: angles can then be accommodated at very little elastic cost. A more serious concern is that although the 3 elements have very similar elastic constants in a 4-fold environment, the bonding gets stronger as the coordination decreases. Experimentally this effect shows up mostly in the high frequency TO peak [5]. Moreover, because of the square root scaling, the deviation becomes apparent only between samples at the extreme of the composition scale.

To verify the isocoordinate rule, we prepare 3 different compositions at each average coordination from $\langle r\rangle = 2.2$ to 3.0 (except at $\langle r\rangle = 2.2$, where only two different cells are created). We then proceed to distribute at random a desired proportion of 2-, 3- and 4-fold atoms. The three configurations typically correspond to (1) a configuration with a maximum of 3-fold atoms for the given average coordination, (2) one with a maximum of 4-fold, and (3) a composition between the two. For example, at $\langle r\rangle = 3.0$, we create a configuration with 50% of 2-fold and 50% of 4-fold atoms, one with 25, 50 and 25% of 2-, 3-, and 4-fold atoms, respectively, and one with 100% of 3-fold atoms. This gives us the widest composition range possible to study the VIR. Because we are not constrained by the glass forming diagram, this is also wider than what can be achieved experimentally.

After the topology is established, each sample is relaxed with the Kirkwood potential, using periodic boundary conditions. The 12 288 × 12 288 dynamical matrix is then computed numerically on the fully relaxed configuration and diagonalized exactly in order to obtain the full vibrational properties. The eigenvalues are binned and smoothed with a Gaussian of experimental width to provide the vibrational density of states presented in this paper.

We also introduce some chemical correlations to see how sensitive the VIR is to local fluctuations. We study two types of correlations: phase separation – introducing some kind of homopolar preference – and mixing, with heteropolar bonds. A cost function is introduced in the bond-distributing sub-routine and all other phases of simulation remain the same.

Table 1. Compositions used in this paper. All samples are created by removing bonds from a perfectly coordinated 4096-atom configuration while enforcing a certain proportion of 2-, 3- and 4-fold atoms.

Average composition	2-fold	3-fold	4-fold
2.2	0.80	0.20	0.00
	0.90	0.00	0.10
2.4	0.60	0.40	0.00
	0.70	0.20	0.10
	0.80	0.00	0.20
2.5	0.50	0.50	0.00
	0.65	0.20	0.15
	0.75	0.00	0.25
2.6	0.40	0.60	0.00
	0.55	0.30	0.15
	0.70	0.00	0.30
2.7	0.30	0.70	0.00
	0.45	0.40	0.15
	0.65	0.00	0.35
3.0	0.00	1.00	0.00
	0.25	0.50	0.25
	0.50	0.00	0.50

3 Results and discussion

3.1 The vibrational isocoordinate rule

As we decrease the average coordination of the networks, we go through the topological rigidity threshold, at $\langle r\rangle = 2.4$ [11]. Below this value, the network becomes floppy and its macroscopic elastic constants vanish; local rigidity remains, however, and the VDOS is mostly unaffected except for a shift in the position of the peaks and an accumulation of modes at low frequencies. The signature of these zero-frequency modes is reported here in the backward peak formed at low frequencies and the accumulation at the lower-end of the TO peak in networks with large fraction of 2-fold coordinated atoms. The backward peak corresponds to spurious imaginary frequencies associated with floppy modes. Based on the theory of topological rigidity, these modes are localized above the topological rigidity threshold, p_c, and span the whole network below this threshold.

Figure 1 shows the vibrational density of state as a function of average coordination from $\langle r\rangle = 2.2$ to 3.0. This distribution goes through the topological rigidity transition at $\langle r\rangle = 2.4$. First, we note that the VIR is approximately valid for two frequency bands: the transverse acoustic band – below $f = 0.7$ – and transverse optic band – above $f = 1.5$ – (here f is a reduced frequency). This holds for configurations with significant difference of composition, even configurations as different as the 100% 3-fold *vs.* 50-50 of 2- and 4-fold show fairly similar VDOS in these regions. This is a wider application range than what was measured experimentally; the data reported by

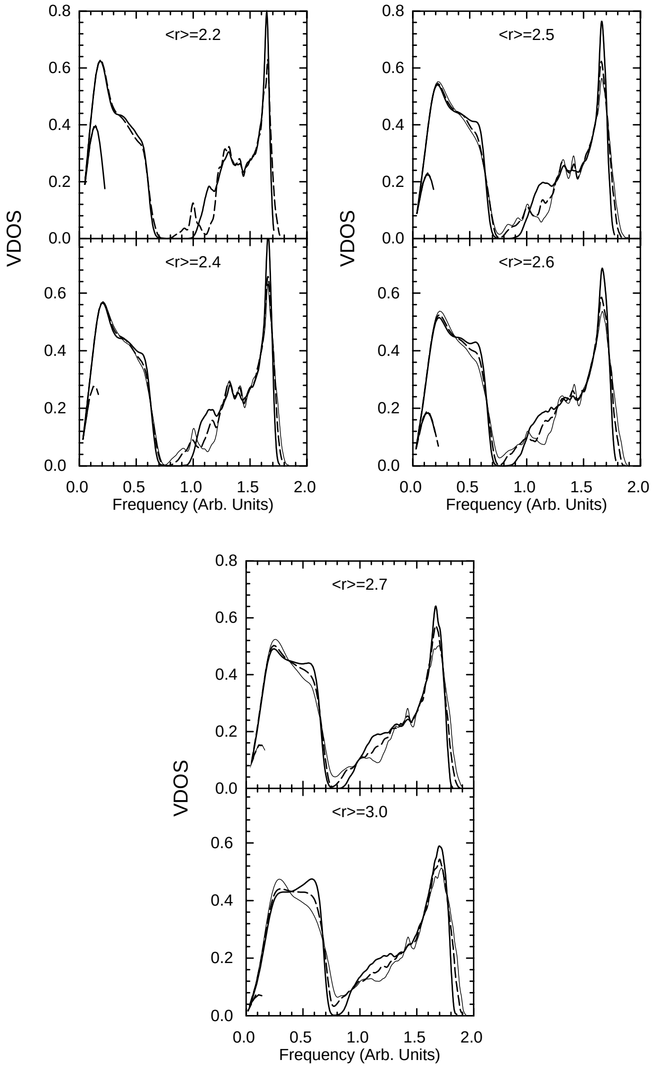

Fig. 1. Vibrational density of state (VDOS) as a function of frequency for a set of configurations of different composition and average coordination. Each plot shows the VDOS for two or three different compositions but identical average coordination. The compositions are given in Table 1. In each plot, the choice of line goes as a function of increasing percentage of 2-fold atoms: thick solid, dashed and thin solid. The additional peak at low energies in this and later figures is due to floppy modes.

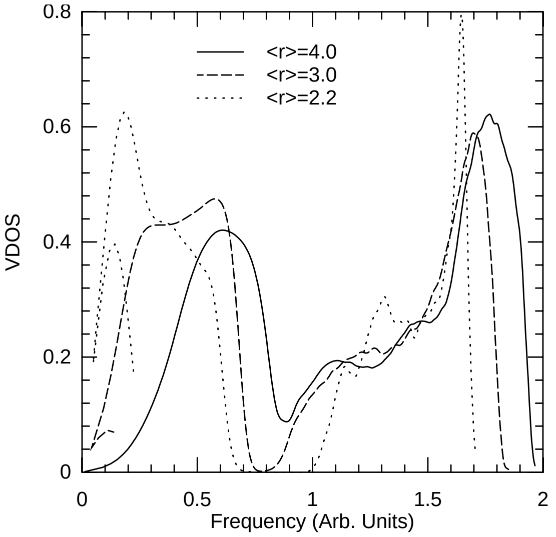

Fig. 2. Evolution of the VDOS as a function of average coordination for $\langle r \rangle = 2.2$, 3.0 and 4.0. The shift in the overall VDOS is explained by the significant decrease in the rigidity of the network as the number of bonds decreases.

Effey and Cappelletti shows that the isocoordinate rule applies to the TA band but is not consistent in the higher frequency region of the VDOS. This is especially true of samples with widely different composition. The shift in the TO peak seen in reference [5] seems to follow the concentration of Se, a result that is consistent with the expected increase in stiffness of the low coordinated atoms discussed above. (The assignments of the bands, TA, LA, LO and TO, is based on a comparison with the corresponding tetrahedral crystals [12].)

Taking this into account, a second look at the figures indicates clearly that the VIR is not an exact law. The structure of the TA peak in the configurations with $\langle r \rangle = 3.0$ shows significant variations as a function of the concentration of 3-fold coordinated atoms. The shoulder, slightly above $f = 0.5$ and present at other $\langle r \rangle$, decreases in importance as the average coordination goes down. This effect is not seen experimentally; the range of compositions for the real samples, however, is much narrower than that studied here.

Figure 1 also provides some indication about the relation between specific structures in the VDOS and the local environment. Of course, since the VIR holds well, signatures of the specific local bonding are weak except in the band between the TA and TO peaks, especially at low average coordination where more modes become localized. The structure around $f = 1$ consistently represents the four-fold coordinated atoms. We can compare these structures to a fully four-fold structure (Fig. 2).

The floppiness of the network is also reflected in the TO peak. Strikingly, the width of this peak is more related to the overall coordination of the network than to the local bonding environment. From the work of Alben *et al.* [10], the TA peak has been associated with the overall coordination while the TO peak had been ascribed to the local tetrahedral symmetry. The vibrational density of states of fully four-fold cells generally gives a much wider if somewhat lower TO peak with, in the case of ill-coordinated networks, a very flat structure [14]. Such a wide peak has generally been associated with non-tetrahedral environment but it is clear, based on the results obtained here, that the presence of strain is also necessary. Even at $\langle r \rangle = 3.0$ the network contains enough floppy modes to relax a good part of the strain: the optical modes become then more localized and emerge as a relatively sharp feature at the edge of the vibrational spectrum.

As the average coordination decreases the features in the longitudinal acoustic (LA) and longitudinal optic (LO) bands, around $f = 1.0$ and 1.4, respectively, also become

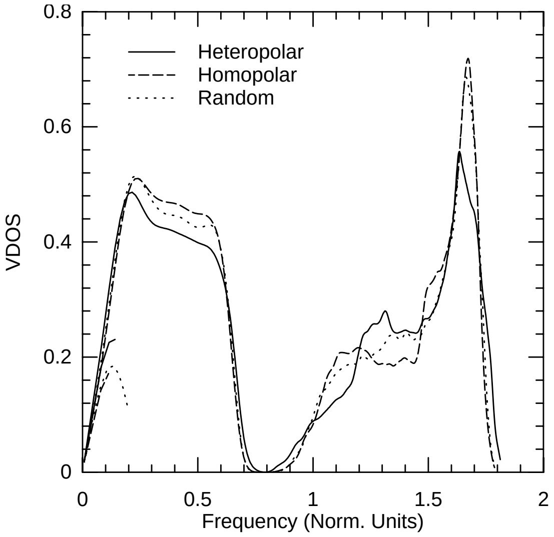

Fig. 3. Effect of short-range correlations on the vibrational density of state. We show here three samples at $\langle r \rangle = 2.6$ with 40% 2-fold and 60% 3-fold atoms but different local chemical order. Bonds between similar atoms are highly favored in the homopolar sample and highly penalized in the heteropolar sample. No account of chemical cost is introduced in the random case.

more prominent. The first is particularly sensitive to the concentration of 4-fold atoms. This is especially clear at the lowest average coordination where this feature is totally absent in the $Se_{80}As_{20}$ sample. At the same time, the LA peak is shifted upward to about $f = 1.15$ and can therefore be associated with the presence of 3-fold atoms. This interpretation is in full agreement with the experimental results reported by Effey and Cappelletti [5].

3.2 Correlations

The above results are all for non-correlated samples. It is likely however, that chemical ordering might take place in chalcogenide glasses. To address this question, we prepared, at $\langle r \rangle = 2.6$, two configurations of a 40-60 mixture of two-fold and three-fold atoms, one with full mixing, *i.e.*, heteropolar bonds strongly favored −and demixing− homopolar bonds preferred. In the first case, no 2-fold atom is bonded to another 2-fold atom. In the second case, clustering tends to take place.

Figure 3 shows the VDOS for these two cells as compared with the non-correlated case already described in the previous section. There is remarkably little difference between these three VDOS except in the gap between the TA and TO bands; the demixed states of the phase separated configuration splits the TO peak slightly. The major differences between the configurations is associated with the LA and LO bands, between $f = 1.0$ and 1.5. Mixed environment emphasize significantly the peak at 1.15 while the phase separation generates a peak at higher frequencies, around $f = 1.3$. The average of these two effects is clearly manifest in the non-correlated spectrum. These changes in the spectrum are subtle, however, and they cannot be checked experimentally at the moment.

The choice of $\langle r \rangle = 2.6$ was based on some peculiar spectra found experimentally for Se_2As_3 [5]. Although we have been unable to reproduce the experimental behavior, we can conclude from this section that simple two-body correlation is not sufficient to provide the type of structure in the VDOS seen experimentally. More striking local changes need to occur, such as pseudo-molecular constructions, which give rise to localized modes [5].

4 Conclusions

The present study focuses on the ideal case of a system with identical bonding and masses of constituent atoms. This establishes clearly the limits and generalities of the isocoordinate rule. However, these calculations are relevant to alloy systems for which the constituents are from adjacent columns of the periodic table (so that their electronegativities are similar) and from the same row (so that the bonding is close to covalent and masses are close). This assumption leaves only one parameter, β/α from equation (1), to characterize a specific system. We cannot, therefore, reproduce exactly the experimental data. In particular, the absence of polarization and the Si-like binding leads to less consistent behavior in the optical band. In spite of these limitations, it is possible to draw general conclusions about the applicability of the isocoordinate rule.

We have examined the isocoordinate rule at average concentrations varying from 2.2 to 3.0. This rule is not exact but it is accurate enough to serve as a general principle in the study of chalcogenide glasses: the variation in VDOS between samples of widely different concentrations but same average coordination is smaller than that between similar samples with average coordination differing by 0.1 or 0.2.

Moreover, it appears that the VDOS is not very sensitive either to the presence of correlations. Changing considerably the local correlations affects very little even the qualitative structure of the VDOS. This work also emphasizes the limited information in the low frequency band about the details of chemical bonding.

Without explicitly employing the correct choice for α, β for these chalcogenide glasses, we have reproduced the experimental observation of the dependence of the first peak only on $\langle r \rangle$. We have shown, moreover, that the breaking of the isocoordinate rule beyond the TA peak, in the experimental data, has two origins. Discrepancies in the high frequency region can be associated with a variation of mass and bonding between the species in the glass, while that in the middle of the VDOS reflect the topological correlations and local structure.

All these results, in parallel with the experimental results obtained recently point to the fact that it is difficult to obtain conclusive information simply from the VDOS: if two samples have a different VDOS, it is clear that they diverge; nothing can be said, however if they have the same VDOS.

We thank Drs. Ronald Cappelletti and Birgit Effey for many stimulating discussions. NM thanks the NSF for support under Grant DMR 9805848, DAD thanks NSF for support under grants DMR 0074624 and DMR 0081006.

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