

A Unified Model for the Low-Energy Vibrational Behaviour of Amorphous Solids

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1992 Europhys. Lett. 19 201

(<http://iopscience.iop.org/0295-5075/19/3/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 142.66.3.42

This content was downloaded on 05/09/2015 at 23:41

Please note that [terms and conditions apply](#).

A Unified Model for the Low-Energy Vibrational Behaviour of Amorphous Solids.

S. R. ELLIOTT(*)

*Laboratoire de Science des Matériaux Vitreux, Université de Montpellier II
Place Eugene Bataillon, 34095 Montpellier Cedex 5, France*

(received 18 December 1991; accepted in final form 24 April 1992)

PACS. 63.50 – Vibrational states in disordered systems.

PACS. 66.70 – Nonelectronic thermal conduction and heat-pulse propagation in nonmetallic solids.

Abstract. – The anomalous low-energy vibrational behaviour exhibited by amorphous solids (a peak in the vibrational density of states, in C_v/T^3 and in the Raman spectrum—the boson peak—and a plateau in the thermal conductivity) is ascribed to the phonon scattering caused by intrinsic density fluctuation domains in the structure, within which short- and medium-range order is maintained and beyond which the material is structurally isotropic and homogeneous. Phonon localization occurs when the mean-free path is comparable to the size of the domains. This model can also explain the correlation between the boson-peak frequency and the position of the first sharp diffraction peak in the structure factor observed in a number of inorganic and polymeric amorphous solids.

The dynamical behaviour of amorphous solids at low excitation energies appears to be universal [1] and is substantially different from that exhibited by crystalline solids [2]. In the energy range, say $E = (2 \div 10)$ meV, the vibrational density of states (VDOS) as measured by inelastic neutron scattering [3], or inferred from heat-capacity data in the temperature range $(5 \div 30)$ K [4], is considerably larger than the Debye value calculated using sound-velocity data. In addition, the so-called «boson peak» at low energies in the Raman scattering spectra of amorphous materials [5] is also a manifestation of such excess modes.

The origin of these «excess» vibrational states has long been controversial. Rather detailed, but material-specific, models have been proposed, *e.g.* the coupled rotation of SiO_4 tetrahedra in $v\text{-SiO}_2$ [3], but the observation of these modes in disordered solids appears to be so widespread (in metals as well as nonmetals [1]) that a more general explanation seems to be needed. Thus, the involvement of «soft» anharmonic potentials has been invoked [6, 7], as has the existence of fractal structures with fractonlike dynamics above a certain critical frequency [8]. More recently, it has been proposed [9, 10] that (frustrated) dipolar interactions between (ill-defined) defects are responsible both for the non-Debye-like

(*) Permanent address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

behaviour in the specific heat (C_v) and the anomalies in the thermal conductivity (κ) at $T \sim (5 \div 30)$ K. Finally, the role played by the inhomogeneous nature of the structure of amorphous solids has been stressed, and the involvement of (ill-defined) «clusters» or structural correlations has been proposed by a number of authors [1, 11-14]. The «clusters» discussed in ref. [13] are defined energetically as the size of regions supporting local modes whose lifetime is greater than their inverse frequency; resonant scattering of phonons by such local excitations is proposed to give a peak in the VDOS and the plateau in κ .

We start by noting that, in general, *two* length scales characterise the structure of an amorphous solid: one is the nearest-neighbour atom-atom bond length, a , and the other is the correlation length, R , over which short-range order (SRO) and medium-range order (MRO) are maintained. The correlation length can be defined in a number of ways. For example, R can be taken as the distance at which atomic-correlation features (peaks) in the radial distribution function (RDF) are no longer discernible; this length therefore marks the point, with respect to an arbitrary-origin atom, beyond which the material appears structurally homogeneous and isotropic. Alternatively, the structure can be regarded as a packing of atoms and interstitial voids, in which case R marks the point at which the partial atom-void RDF becomes featureless since, at smaller distances, SRO and MRO of *atomic* sites can be regarded equivalently as arising from correlations in the positions of the *voids*. For the case of v -SiO₂, the correlation length estimated directly from the experimental total atom-atom RDF [15] and also from the partial atom-void RDF calculated for a structural model [16] is $R \approx (12 \div 15)$ Å.

Thus, our picture of the structure of amorphous solids involves intrinsic structural inhomogeneities associated with density fluctuation domains of diameter $2R$. It should be noted that *each* atom can be regarded as being at the centre of such a domain. The size of such domains is expected to be larger for more «open» (covalently bonded) structures than for more densely packed structures.

Obviously, such density fluctuations can strongly scatter phonons, resulting in a reduction in the mean-free path. In the limit of very strong scattering, the low-energy vibrational excitations can become *localized* and this may lead to an enhancement of the VDOS. (This density fluctuation model is similar to that in ref. [17], but there the variations in density were associated with free volume, and not the much larger fluctuations associated with SRO and MRO, considered here.)

The atomic-density fluctuations will lead to elastic scattering of phonons, for which the relaxation time $\tau(\omega)$ (and hence the mean-free path $l(\omega)$) is given by [18] the Rayleigh law, *viz.* $\tau(\omega) \propto \omega^{-4}$. It has been argued [19] that this very strong frequency dependence will cause a vanishing of the diffusivity of phonon-density fluctuations («second sound») at some critical frequency ω_0 and hence, through anharmonicity effects, to localization of the phonons themselves at $\omega = \omega_0$. Although these arguments are based on weak-localization theory (*i.e.* for $\omega \ll \omega_0$) and consequently are not strictly valid close to the localization threshold, nevertheless the finding that the scattering-induced reduction in phonon lifetime, presaging the onset of localization, is accompanied by an *enhancement* of the VDOS at $\omega = \omega_0$ is likely to remain true. A similar enhancement of the VDOS was found in a study based on an analogy between particle hopping in a random medium and the phonon problem [20]; the enhancement coincides with the frequency at which the phonons become very strongly damped.

Another, equivalent, point of view of this phonon localization behaviour is in terms of the Ioffe-Regel condition, *viz.* the limiting value of the mean-free path l in the strong-scattering limit, corresponding to the onset of localization, is given by

$$ql \approx 2\pi, \quad (1)$$

where the wave vector $q = 2\pi/\lambda$ and where λ is the phonon wavelength. In this picture, the minimum value for the mean-free path, l , is determined by the size of the «particles» causing the scattering [21] or, in the present case, by the diameter, $2R$, of the density fluctuation domains in amorphous solids. By means of an extrapolation procedure, using the Ioffe-Regel postulate, values of l in the range $(20 \div 30)$ Å for various inorganic glasses have been obtained from thermal conductivity data [22]. These values agree to within a factor of 2 or so with the values of $2R$ (estimated from the RDF).

This phonon localization model would be expected to be associated with a sound-wave structure factor, $Q^2 S(Q)$ for the coherent inelastic neutron scattering (INS) intensity. Buchenau *et al.* [3] had previously rejected this possibility for the case of v -SiO₂ on the basis of their INS data which do *not* show the peak at $Q \approx 1.5$ Å⁻¹ observed in $S(Q)$ [15]. However, our interpretation [23] of the origin of the first sharp diffraction peak (FSDP) of $S(Q)$ as a chemical-order pre-peak (associated with interstitial voids) would imply that, in fact, no such peak should be observed in the INS intensity.

If the low-energy peak in the VDOS is due to phonon localization, there is no need to invoke the Martin-Brenig model [24] for the origin of the boson peak in the Raman spectrum of glasses; the boson peak is thus due to the peak in the VDOS and *not* to a peak in the Raman coupling constant [4]. The peak in the VDOS, and hence approximately that of the boson peak, lies at a frequency ν_0 which is determined by a characteristic length scale of the amorphous solid, the diameter of the density-fluctuation domains $2R$, via the Ioffe-Regel relation (eq. (1)). If we use the dispersion relation $q = \omega/v_s$ for propagating phonons in the Debye approximation (where v_s is the sound velocity), then

$$\nu_0 \approx v_s/2R. \quad (2)$$

This expression is obviously only approximate since the linear phonon dispersion law must break down at high frequencies and particularly as the phonon localization transition at $\nu = \nu_0$ is approached. Nevertheless, use of eq. (2) with experimental data for ν_0 and v_s for a variety of amorphous solids [25] gives estimates for R in the range $(10 \div 15)$ Å (see table I), in agreement with estimates from the RDF. (It is interesting to note that Duval *et al.* [14] obtain a similar expression for ν_0 , but by assuming instead that it is the fundamental vibrational mode of discrete clusters or «blobs». However, there is no experimental evidence for the existence in normal glasses of the type of clusters that they envisage.)

We can now understand the previously puzzling correlation found between the boson peak frequency, ω_0 , and the position, Q_1 , of the FSDP of the structure factor of inorganic glasses and amorphous solids [25]. If we choose to define R in terms of the atom-void partial RDF

TABLE I. - *Experimental values of boson peak frequency ν_0 and velocity of sound v_s and correlation length R derived using eq. (2) for a variety of amorphous solids.*

Material	ν_0 (cm ⁻¹)	v (m s ⁻¹)	R (Å)
SiO ₂	40/60 (*)	4100/3764 (*)	17.1/10.5
SiSe ₂	9	800	14.8
As ₂ S ₃	26	1650	10.6
As ₂ Se ₃	24	1440	10.0
GeS ₂	22	2030	15.4
GeSe ₂	20	1820	15.2
Ge	80	3600	7.5
Se	18	1050	9.7

All values of ν_0 and v_s from ref. [5], except for those marked (*) which are from ref. [26].

(where the atom is chosen to be the cation, *e.g.*, Si in SiO₂), then

$$R \approx \alpha b, \quad (3)$$

where b is the nearest-neighbour atom-void separation and $\alpha \approx 3 \div 4$. Now, b is comparable to the nearest-neighbour cation-cation distance, d (at least for v -SiO₂ where the analysis has been performed [16]) and, in our recent interpretation of the origin of the FSDP as a pre-peak associated with the chemical ordering of interstitial voids around cation-centred structural units [23], the FSDP position is given approximately by the relation

$$Q_1 \approx 3\pi/2d. \quad (4)$$

Thus, combining eqs. (2)-(4), we obtain finally

$$Q_1 \approx 3\pi\alpha v_0/v_s. \quad (5)$$

In fig. 1, we show a plot [25] of experimental data of Q_1 vs. $\Omega = v_0 c/v_s$; lines with the predicted gradient of $3\pi\alpha \approx 30 \div 40$ agree very well with the overall observed behaviour.

The present model also allows the behaviour of the boson peak as a function of density and composition to be understood. Generally, it appears that v_0 increases with increasing density of the material. For example, this behaviour has been observed in α -As₂S₃ at high pressures [27], in irreversibly pressure-compacted v -SiO₂ [26] and in fast-neutron-irradiated v -SiO₂ [28]. Although some of the frequency shift can be accounted for by concomitant increases in the sound velocity v_s (see eq. (2)), nevertheless this cause by itself is not completely sufficient; in addition, there must be a corresponding *decrease* by $\sim (20 \div 30)\%$ in the correlation length R . Such a decrease in R with increasing density is entirely reasonable.

Large changes in v_0 are also found when network modifiers are added to glasses; *e.g.*, for (Li₂O) _{x} (B₂O₃)_{1- x} it is found that v_0 increases as x increases [29]. Again, although (compositional) changes in v_s play a role, the magnitude of the frequency shift can only be fully accounted for if the correlation length R decreases with x . This can be understood if the modified glass is more close-packed than is the unmodified glass.

We turn now to a discussion of the temperature dependence of the thermal conductivity of glasses, in the range (10 \div 100) K, where a plateau is ubiquitously observed. There has been considerable discussion concerning the origin of this plateau [2, 9, 10, 12, 13, 22, 30-35]. It is

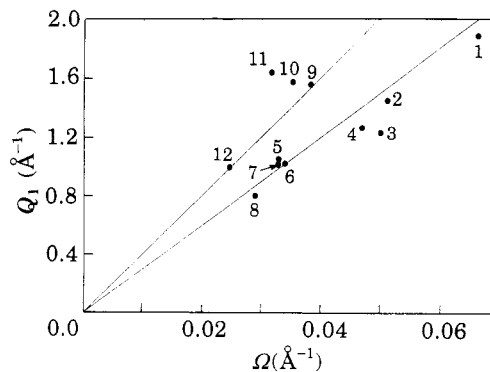


Fig. 1. - Plot of experimental values (points) for the FSDP position, Q_1 , vs. normalized boson peak frequency, $\Omega = v_0 c/v_s$ (v_0 in cm^{-1}) for a number of amorphous solids [25]; the straight lines are theoretical predictions of the model with gradients of 30 and 40. 1) Ge; 2) Se; 3) As₂Se₃; 4) As₂S₃; 5) GeS₂; 6) SiSe₂; 7) GeSe₂; 8) AgI-AgO-B₂O₃; 9) SiO₂; 10) BeF₂; 11) B₂O₃; 12) PMMA.

now widely accepted that the plateau is associated with a sharp fall in the value of the phonon mean-free path (to atomic dimensions) with increasing frequency. The origin of this very strong frequency dependence of l has long been ascribed to Rayleigh-Klemens scattering [30-35], but the origin of the scattering centres has been uncertain and it has been doubted whether the strength of such scattering could be sufficient to account for the observed values of κ . We show here that our model of density fluctuation domains can produce scattering of the required order of magnitude.

The frequency dependence of the phonon mean-free path can be written as [33, 34]:

$$l = [D^{-1}(k_B/\hbar\omega)^4 + l_0], \quad (6)$$

where D is the Rayleigh-Klemens scattering strength and l_0 is a limiting constant mean-free path ($\approx a$). If isotropic density fluctuations are responsible for the phonon scattering, then we can show that the expression due to Jäckle [33] can be written approximately in the simplified form

$$D = \frac{(1 + \gamma^2/2)}{3v_s^4} \langle(\Delta\rho/\rho)^2\rangle R^3 \left(\frac{k_B}{\hbar}\right)^4, \quad (7)$$

where γ is an appropriate Grüneisen parameter. (Note that eq. (10) of ref. [34] appears to be in error by a factor of 1/4.) For v -SiO₂, for example, the parameter values are $\gamma = -2.15$ [34], $v_s = 4.1 \text{ km s}^{-1}$ and $R \approx 15 \text{ \AA}$, and $\langle(\Delta\rho/\rho)^2\rangle$ can be estimated from the experimental RDF [15] by assuming that it is the volume-weighted average over the domain size, *viz.*

$$\langle(\Delta\rho/\rho)^2\rangle = \frac{1}{V\rho^2} \int_0^R 4\pi r^2 |\Delta\rho|^2 dr, \quad (8)$$

where $V \equiv 4\pi R^3/3$. A rough evaluation of eq. (8) from the data using a discrete summation procedure leads to the value $\langle(\Delta\rho/\rho)^2\rangle \approx 35/R^3 = 0.01$ for $R \approx 15 \text{ \AA}$.

Evaluation of eq. (7) then yields $D \approx 40 \text{ m}^{-1} \text{ K}^{-4}$, compared with the value necessary to fit the experimental data [33], *viz.* $D \approx 167 \text{ m}^{-1} \text{ K}^{-4}$. This agreement between theoretical and experimental values is satisfactory, since previous estimations [31-34] have been too small by 1-2 orders of magnitude. The reason that our model gives a larger scattering contribution is that the correlation length R is larger than those assumed previously (of the order of molecular dimensions, *viz.* $(2 \div 4) \text{ \AA}$), and also that the magnitude of the density fluctuations is appreciably larger, than those previously considered, associated either with free volume [17], bond length fluctuations [32] or the hydrodynamic density fluctuations frozen in a glass on melt-quenching [33]. It has been claimed recently [36] that the Rayleigh scattering from oxygen bond-angle force constant fluctuations in v -SiO₂ is sufficiently large to account for the plateau in κ in this material; a formula for the scattering, due originally to Pekeris [37] and subsequently simplified [34], was used for the estimation of D . However, it should be noted that this equation contains a numerical factor that is 24 times larger than that in the equivalent relation given by Jäckle [33] and used here (eq. (7)); as a result, it is likely that the Pekeris [37] formula leads to a considerable over-estimate for D [34], although the origin of this numerical discrepancy is not clear and this warrants further theoretical consideration.

* * *

I am grateful to Prof. J. PELOUS for bringing ref. [28] and [36] to my attention, to the Nuffield Foundation for a Science Research Fellowship and to the C.N.R.S. for financial support. The hospitality of Prof. R. VACHER is gratefully acknowledged.

REFERENCES

- [1] MALINOVSKY V. K., NOVIKOV V. N., PARSHIN P. P., SOKOLOV A. P. and ZEMLYANOV M. G., *Europhys. Lett.*, **11** (1990) 43.
- [2] For a review, see e.g., PHILLIPS W. A. (Editor), *Amorphous Solids: Low-Temperature Properties* (Springer-Verlag, Berlin) 1981.
- [3] BUCHENAU U., PRAGER M., NÜCKER N., DIANOUX A. J., AHMAD N. and PHILLIPS W. A., *Phys. Rev. B*, **34** (1986) 5665.
- [4] AHMAD N., HUTT K. W. and PHILLIPS W. A., *J. Phys. C*, **19** (1986) 3765.
- [5] JÄCKLE J., in ref. [2], p. 135.
- [6] KARPOV V. G., KLINGER M. I. and IGNATIEV F. N., *Sov. Phys. JETP*, **57** (1983) 439.
- [7] BUCHENAU U., GALPERIN YU. M., GUREVICH V. L. and SCHÖBER H. R., *Phys. Rev. B*, **43** (1991) 5039.
- [8] ORBACH R., *Science*, **231** (1986) 814.
- [9] YU C. C., *Phys. Rev. Lett.*, **63** (1989) 1160.
- [10] COPPERSMITH S. N., *Phys. Rev. Lett.*, **67** (1991) 2315.
- [11] MALINOVSKY V. K. and SOKOLOV A. P., *Solid State Commun.*, **57** (1986) 757.
- [12] GRAEBNER J. E., GOLDING B. and ALLEN L. C., *Phys. Rev. B*, **34** (1986) 5696.
- [13] YU C. C. and FREEMAN J. J., *Phys. Rev. B*, **36** (1987) 7620.
- [14] DUVAL E., BOUKENTER A. and ACHIBAT T., *J. Phys. Condensed Matter*, **2** (1990) 10227.
- [15] WRIGHT A. C. and SINCLAIR R. N., *J. Non-Cryst. Solids*, **76** (1985) 351.
- [16] CHAN S. L. and ELLIOTT S. R., *Phys. Rev. B*, **43** (1991) 4423.
- [17] WALTON D., *Solid State Commun.*, **14** (1974) 335.
- [18] KLEMENS P. G., *Proc. R. Soc. London, Ser. A*, **208** (1951) 108.
- [19] AKKERMANS E. and MAYNARD R., *Phys. Rev. B*, **32** (1985) 7850.
- [20] SCHIRMACHER W. and WAGENER M., in *Dynamics of Disordered Materials*, edited by D. RICHTER, A. J. DIANOUX, W. PETRY and J. TEIXERA., *Springer Proc. Phys.*, Vol. 37 (Springer Verlag, Berlin) 1989, p. 231.
- [21] GRAEBNER J. E. and GOLDING B., *Phys. Rev. B*, **34** (1986) 5788.
- [22] GRAEBNER J. E., GOLDING B. and ALLEN L. C., *Phys. Rev. B*, **34** (1986) 5696.
- [23] ELLIOTT S. R., *Phys. Rev. Lett.*, **76** (1991) 711.
- [24] MARTIN A. J. and BREINIG W., *Phys. Status Solidi B*, **64** (1974) 163.
- [25] NOVIKOV V. N. and SOKOLOV A. P., *Solid State Commun.*, **77** (1991) 243.
- [26] WALRAFEN G. E., CHU Y. C. and HOKMABADI M. S., *J. Chem. Phys.*, **92** (1990) 6987.
- [27] ARAI T., KATAURA H., YASUOKA H. and ONARI S., *J. Non-Cryst. Solids*, **77-78** (1985) 1149.
- [28] KONSTANTINOV A. V., MAKSIMOV L. V., SILIN A. R. and YANUSH O. V., *J. Non-Cryst. Solids*, **123** (1990) 286.
- [29] LOROSCH J., COUZI M., PELOUS J., VACHER R. and LEVASSEUR A., *J. Non-Cryst. Solids*, **69** (1984) 1.
- [30] ZELLER R. C. and POHL R. O., *Phys. Rev. B*, **4** (1971) 2029.
- [31] ZAITLIN M. P. and ANDERSON A. C., *Phys. Rev. B*, **12** (1975) 4475.
- [32] WALTON D., *Phys. Rev. B*, **16** (1977) 3723.
- [33] JÄCKLE J., *Proceedings of the IV International Conference on Physics of Non-Crystalline Solids*, edited by G. H. FRISCHAT (Trans. Tech.) 1977, p. 568.
- [34] JONES D. P., THOMAS N. and PHILLIPS W. A., *Philos. Mag. B*, **38** (1978) 271.
- [35] FREEMAN J. J. and ANDERSON A. C., *Phys. Rev. B*, **34** (1986) 5684.
- [36] RAYCHAUDHURI A. K., *Phys. Rev. B*, **39** (1989) 1927.
- [37] PEKERIS C. L., *Phys. Rev.*, **71** (1947) 268.