

## **Diffusons, locons and propagons: character of atomic vibrations in amorphous Si**

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### **ABSTRACT**

Numerical studies of amorphous Si show that the lowest 4% of vibrational modes are plane wave like ('propagons') and the highest 3% of modes are localized ('locons'). The rest are neither plane wave like nor localized. We call them 'diffusons'. Since diffusons are by far the most numerous, we try to characterize them by calculating such properties as the wave-vector and polarization (which do not seem to be useful), 'phase quotient' (a measure of the change of vibrational phase between first-neighbour atoms), spatial polarization memory and diffusivity. Localized states are characterized by finding decay lengths, inverse participation ratios and coordination numbers of the participating atoms.

### **§ 1. INTRODUCTION**

Vibrational properties of disordered media have been reviewed by various workers and, in particular by Elliott and Leath (1975), Visscher and Gubernaitis (1980), Weaire and Taylor (1980), and Pohl (1998). Here we review and present new results in a program of numerical study of vibrations of amorphous Si. Among the new results not contained in earlier reviews are theoretical treatments of heat conductivity and thermalization rates in glasses.

Harmonic normal modes of vibration can be rigorously classified as extended (E) or localized (L). In three dimensions the vibrational spectrum has sharp E–L boundaries ('mobility edges') separating these two kinds of mode.

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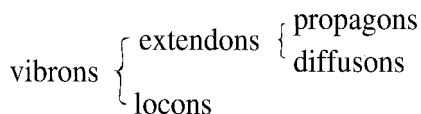


Figure 1. Taxonomy of vibrations in glasses.

There is another boundary, not sharp, which Mott called the ‘Ioffe–Regel limit’ and which we call the ‘Ioffe–Regel cross-over’. This P–D boundary separates the spectrum into a region with ballistic propagation (P) where the wave-vector is a reasonably good quantum number and a region with only diffusion (D) where the wave-vector cannot be defined but states are still extended. In region P, wave packets can travel at the sound velocity over distances of at least two or three interatomic spacings before scattering from disorder (Allen and Kellner 1998). The distance of ballistic propagation is the mean free-path  $\ell$ . In region D, only diffusive propagation occurs over any meaningful distance, and the concepts of mean free path and wave-vector lose usefulness. Although it may seem natural that the Ioffe–Regel cross-over should be close to the mobility edge (Alexander 1989), it is not true for the models that we have studied. Indeed, Mott and Davis (1971) emphasized the non-coincidence. Both region P and D lie in the extended (E) part of the spectrum.

The non-coincidence of the E–L boundary and the P–D boundary means that the spectrum has three kinds of states. We find useful the terminology ‘propagon’, ‘diffuson’ and ‘locon’ given in figure 1. The term ‘phonon’ is avoided because of disagreement about what it means in a glass.

We instinctively seek additional labels, to replace the detailed classification scheme by wave-vector and branch so useful in crystals. Here we attempt to characterize as completely as possible the dominant diffuson portion of the spectrum but fail to find useful subcategories. As already noted by Kamitakahara *et al.* (1987), all diffuson modes of a given frequency have essentially indistinguishable displacement patterns.

We study amorphous Si in harmonic approximation, using a model we believe to be very realistic. As shown in figure 2, the E–L boundary is near the top of the spectrum, with only 3% of the modes localized. The P–D boundary is near the bottom of the spectrum, with only 4% of the modes ballistically propagating. Diffusons fill 93% of the spectrum. We do not think that this is special either to our model or to amorphous Si. Other models for amorphous Si (Kamitakahara *et al.* 1987, Lee *et al.*, 1991, Nakhmanson and Drabold 1998) agree that the E–L boundary occurs near the top of the spectrum. Similar results are found for other glasses (Bouchard *et al.* 1988, Feldman and Kluge, 1995, Cobb *et al.* 1996, Taraskin and Elliott 1997, Carles *et al.*, 1998), and model systems (Sheng and Zhou, 1991, Sheng *et al.* 1994, Schirmacher *et al.* 1998), with localized states occurring only near the top of the spectrum or in tails near gaps in the vibrational densities of states. For three-dimensional systems with artificially large disorder, the mobility edge can be moved down to the middle of the spectrum (Canisius and van Hemmen 1985, Fabian and Allen 1996). The position of the P–D boundary near the bottom of the spectrum is widely accepted.

## § 2. LOW-FREQUENCY ANOMALIES

Our study of normal modes by exact diagonalization on finite-size systems inherently lacks information at low frequencies. For this reason, the present paper ignores

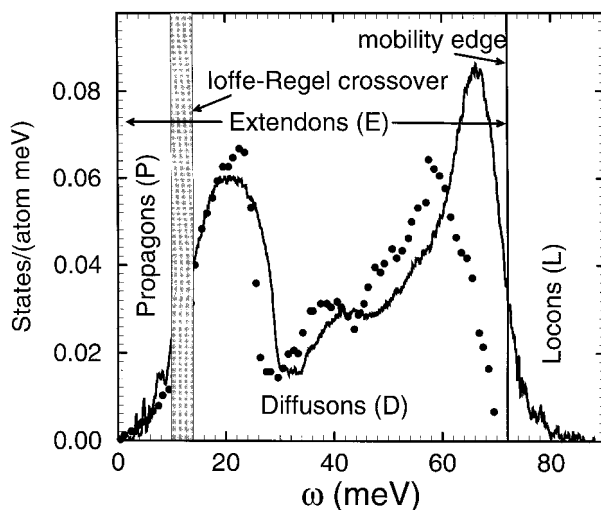


Figure 2. Density of vibrational states from the 4096-atom model compared with data from Kamitakahara *et al.* (1987).

the well known but only partially understood low-frequency anomalies in the vibrational properties of glasses. Our previous work (Feldman *et al.* 1999) argued that the homogeneous network models that we use probably contain no low-frequency anomalies. For completeness, we give here a brief catalogue and point to sources for further information.

‘Two-level’ or ‘tunnelling’ systems were introduced by Phillips (1972) and Anderson *et al.* (1972) motivated by experimental discoveries by Zeller and Pohl (1971). The predictive strength of this concept is beyond question, but the physical objects that the theory invokes remain elusive. A review was given by Phillips (1987).

The phrase ‘boson peak’ refers to a low-frequency feature seen by Raman scattering (Stolen 1970, Jäckle 1981) in many glasses, which is correlated with the occurrence of ‘excess modes’ in specific heat and other spectroscopies. There are many candidate explanations for these modes. One unified view, introduced by Karpov *et al.* (1983) is called the ‘soft-potential model’. This model holds that glasses generically have anharmonic regions, modelled as double-well potentials. These give rise to two-level systems, relaxational behaviour and quasilocalized or resonant harmonic normal modes. The last are a logical candidate for the excess modes. The subject was reviewed by Parshin (1994). Our models contain some quasilocalized modes at low frequencies, as is mentioned further in § 8.

‘Floppy modes’ (Phillips 1980, Thorpe 1983) and the daughter concept of ‘rigid unit modes’ (RUMs) (Dove *et al.* 1996, Trachenko *et al.* 1998) refer to low-frequency modes which have zero restoring force in nearest-neighbour central-force models. Constraint counting algorithms provide methods of estimating the numbers of such modes. They are expected to be quasilocalized in the harmonic approximation but intrinsically highly anharmonic. Such modes probably do not play any important role in amorphous Si because of the overconstrained coordination.

Finally, experimental evidence shows that amorphous Si contains usually fewer two-level-type excitations than most glasses, and that samples with essentially zero such excitations can be prepared by treatment with H<sub>2</sub> (Liu *et al.* 1997).

## § 3. THE MODEL

Amorphous Si is an over-constrained network glass. By one usual definition, it is not a glass since it is not produced by a glass transition upon cooling. Instead, thin films are condensed on cold substrates. When the film becomes too thick, crystallization cannot be prevented. The absence of a glass transition can be attributed to good kinetic properties of a single-component system with one strongly preferred bonding arrangement. To our mind, this just means that amorphous Si is simpler than most glasses, which for our purposes is more of an advantage than a disadvantage. With obvious caution required, we think that most of the properties that we shall discuss can be regarded as typical of most glasses.

For amorphous Si we use atomic coordinates generated using the algorithm of Wooten *et al.* (1985). We have studied models containing 216, 1000 and 4096 atoms, contained in cubic boxes of side 16.5, 28 and 44 Å respectively and continued periodically to infinity. All models are built using the Keating (1966) potential and then subsequently re-relaxed to a local minimum of the Stillinger–Weber (1985) potential. Different models differ in minor details, both for ordinary statistical reasons and because the algorithm was implemented slightly differently in each case. In this section we present structural properties of a 4096-atom model. This model has larger distortions from tetrahedral form than some of our other models, with 102 four-membered rings. Figure 3 shows neighbour distributions  $\mathcal{P}_n(\omega)$ . The distribution  $\mathcal{P}_1$  for the first neighbour is calculated by measuring the distance to the closest neighbour of each atom;  $\mathcal{P}_2$  is found from the distances to the second-closest neighbour. Note that the first four neighbours are distributed tightly within about 0.1 Å to the crystalline first-neighbour distance, 2.35 Å. The next 12 neighbours in crystalline Si are at 3.84 Å, a number fixed by the bond length (2.35 Å) and the tetrahedral bond angle (109.5°). In our model of amorphous Si, the closest of the next 12 (neighbour 5)

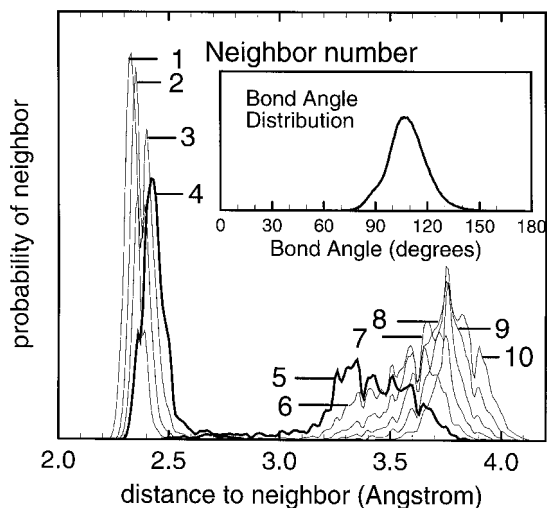


Figure 3. Distribution of  $n$ th neighbours in the 4096-atom model of amorphous Si. The fourth and fifth neighbours are shown in bolder lines. Note the small number of distant fourth or close fifth neighbours. The inset shows the distribution of bond angles averaged over all pairs of bonds with a common centre and distances less than 2.6 Å.

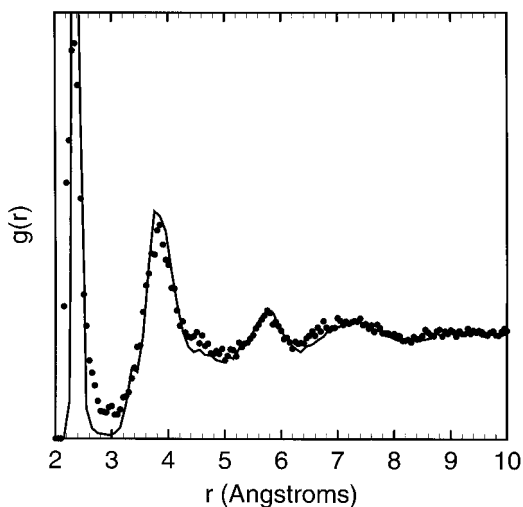


Figure 4. Radial distribution function obtained by summing the  $n$ th-neighbour distributions of figure 3 over all  $n$ , and dividing by a factor  $r^2$ . The data are from a neutron diffraction experiment by Kugler *et al.* (1993).

lies roughly between 3.2 and 3.7 Å, while the farthest of these 12 (neighbour 16, not shown) lies roughly between 3.9 and 4.4 Å. This reflects a flexibility in the bond angles, with values distributed between  $90^\circ$  and  $125^\circ$ , as shown in the inset of figure 3. The third set of neighbours in crystalline Si is 12 atoms at 4.50 Å. This is determined by the fact that the diamond structure has a dihedral angle of  $60^\circ$ , with all rings of the six-member 'chair' type. Rotation of the dihedral angle to  $0^\circ$  ('boat'-type rings) reduces the third-neighbour distance to 3.92 Å. Our model shows no gap at all between the second shell (neighbours 5–16) and the third shell (neighbours 17–28), consistent with random dihedral angles.

The sum  $\sum_n \mathcal{P}_n$  over all  $n$  gives the radial distribution function  $g(r)$ , plotted in figure 4 and compared with the experiments of Kugler *et al.* (1993). The close agreement is one measure of the realism of the model. However, much of the structure of  $g(r)$  seems only to reflect the atom density and nearest-neighbour distance; so it may not be a very stringent test.

#### § 4. VIBRATIONAL FREQUENCIES

The other aspect of the model is the interatomic forces. We chose the model of Stillinger and Weber (1985) which is designed to work for the liquid as well as the crystalline state. This required us to relax the coordinates from a Wooten *et al.* type to a minimum of the Stillinger–Weber potential. The stability of the minimum is proven by the positivity of all eigenvalues  $\omega^2$  of the dynamical matrix. The eigenfrequency distribution is shown in figure 2. Qualitatively satisfactory agreement is found with the neutron scattering data of Kamitakara *et al.* (1987). A similar overestimate of vibrational frequencies is made when Stillinger–Weber forces are applied to crystalline Si, so we think that the discrepancies should be attributed to the forces rather than to the atomic coordinates.

## § 5. LOCALIZED STATES

The definition of a localized state is exponential decay of the eigenvector with distance from some centre  $\mathbf{R}_0$ :

$$|\epsilon_i(\mathbf{R}_n)| \propto \exp\left(\frac{-|\mathbf{R}_n - \mathbf{R}_0|}{\xi_i}\right). \quad (1)$$

This defines the localization length  $\xi_i$  of the  $i$ th normal mode, if the decay is observed. Figure 5 shows selected modes, showing the very different characters of modes from the D and the L portions of the spectrum.

There is still controversy concerning the location of the mobility edge in glasses. Unfortunately, most experiments shed little light on this, since the measured spectral properties, being averages over a macroscopic region, do not differentiate between localized and delocalized states. The heat conductivity  $\kappa(T)$  is the property most strongly affected by localization. We think that the measured  $\kappa(T)$  strongly supports our placement of the P-D and E-L boundaries near the lower and upper edges of the spectrum. This will be discussed in the next section.

If eigenvectors are calculated, then no special tricks are needed to locate the theoretical mobility edge in models of amorphous silicon. A model with 216 atoms was large enough to locate the E-L boundary between 71 and 73 meV; the precise location varies somewhat from model to model. We have made some experiments with artificially enhanced disorder, randomly scaling half of the masses by a factor of five. This pushes the E-L boundary into the middle of the spectrum where it

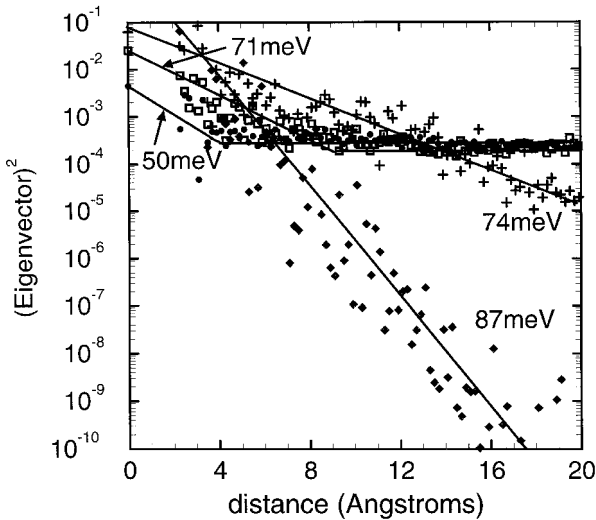


Figure 5. Spatial decay of vibrational eigenvectors  $\epsilon_i$ : (—), guides to the eye. For each mode  $i$  the atom with the largest  $|\epsilon_i|$  is located, and taken as the origin. The plot shows values of  $|\epsilon(\mathbf{R}_n)|^2$  averaged over spherical shells of  $|\mathbf{R}_n|$  of width  $\delta R = 0.2 \text{ \AA}$ . Results shown for  $\omega = 50, 71, 74$  and  $87 \text{ meV}$  are averages over three, four, two and two modes respectively. The modes at 50 and 71 meV have mean square eigenvector near  $1/(N = 4096)$  throughout the cubic cell of length  $44 \text{ \AA}$ , with enhanced values only in spatial regions of small measure. These modes are extended, as are all the modes below the mobility edge at  $73 \text{ meV}$ . The modes at 74 and  $87 \text{ meV}$  have mean values of  $|\epsilon(\mathbf{R}_n)|^2 \approx \exp(-2|\mathbf{R}_n|/\xi)$  with localization lengths  $\xi = 4.7$  and  $1.5 \text{ \AA}$  respectively.

becomes more blurred by size effects. Localized states of ‘pure’ amorphous Si are easily recognized. They are trapped in especially defective regions. This was discovered (Fabian 1997b) by defining a local coordination number  $Z_a$ , the number of neighbours of atom  $a$  at  $\mathbf{R}_a$ . The following arbitrary definition of neighbour suffices:

$$Z_a = \sum_b w(|\mathbf{R}_a - \mathbf{R}_b|), \quad (2)$$

where  $w(r) = 1$  for  $r < 2.35 \text{ \AA}$ ,  $w(r) = 0$  for  $r > 3.84 \text{ \AA}$  and  $w(r)$  is continuous and linear in between. This gives an average coordination of 4.7 neighbours. The ‘mode average coordination number’ is defined as

$$Z_i = \sum_a Z_a |\mathbf{e}_i(a)|^2. \quad (3)$$

Most modes have  $Z_i$  near average, but localized modes mostly collect at regions with a significantly higher coordination, as shown in figure 6.

We have seen the mobility edge in many independent calculations.

- (1) The participation ratio  $p_i$  (Bell and Dean 1970), plotted in figure 6, gives the number of atoms for which the mode has significant amplitude. For the  $E = P + D$  part of the spectrum, the value hovers near 500 for a model with 1000 atoms.
- (2) The diffusivity  $D_i$  drops to zero at the mobility edge. This is shown in the next section.
- (3) Sensitivity to boundary conditions is also discussed in the next section.
- (4) Level spacing distributions have been computed for diffusons and locons (Fabian, 1997b). As expected, diffusons obey Wigner–Dyson statistics, while locons obey Poisson statistics.
- (5) Eigenvector self-correlation functions were carefully studied in a 4096-atom model by Feldman *et al.* (1998).

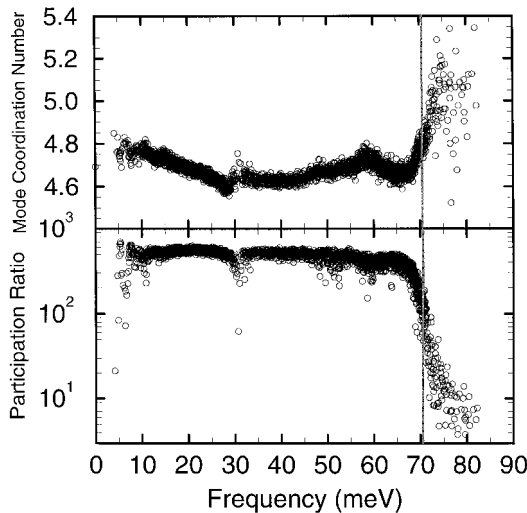


Figure 6. The mode average coordination number (equation (3)) and the participation ratio (on a logarithmic scale), calculated for a model with 1000 atoms.

(6) Many quantities  $q_i$  which can be evaluated for each mode  $i$  seem to depend only on  $\omega_i$  for diffusons, but become mode specific for locons. The quantities that we have looked at are as follows:

- (a) the mode-average coordination number, plotted in figure 6;
- (b) the phase-quotient parameter, discussed in § 9.3;
- (c) bond-stretching parameters (Fabian and Allen, 1997);
- (d) Grüneisen parameters for both volume and shear deformations (Fabian and Allen 1997, 1999).

## § 6. HEAT CONDUCTIVITY AND DIFFUSIVITY

Theoretical interpretation of heat conduction of glasses has been contentious. Below the 'plateau' region (typically 5–30 K) it is agreed that heat is carried by ballistically propagating low-frequency modes (the **P** region of the spectrum). Above the plateau,  $\kappa(T)$  rises, approaching at room temperature a constant value which is typically smaller than the crystalline value (a decreasing function of  $T$  at room temperature). A rigorous consequence (Allen and Feldman 1993) of the Kubo (1957) formula and the harmonic approximation is the relation

$$\kappa(T) = \frac{1}{V} \sum_i C\left(\frac{\hbar\omega_i}{2k_B T}\right) D_i, \quad (4)$$

where  $C(x)$  is the specific heat of a harmonic oscillator  $k_B(x/\sinh(x))^2$  and  $D_i$  is the 'diffusivity' of the  $i$ th normal mode of frequency  $\omega_i$ , given by

$$D_i = \frac{\pi V^2}{3\hbar^2 \omega_i^2} \sum_{j \neq i} |S_{ij}|^2 \delta(\omega_i - \omega_j), \quad (5)$$

where  $S_{ij} = \langle i|S|j \rangle$  is the intermode matrix element of the heat current operator. Equation (4) also emerges, with  $D_Q$  equal to  $v_Q^2 \tau_Q/3$ , from the Peierls–Boltzmann phonon-gas model (Gurevich 1986) of transport in crystals. The latter model is only justified if the mean free-path  $\ell_Q = v_Q \tau_Q$  is longer than a wavelength.

It was noted by Birch and Clark (1940) and by Kittel (1948) that, in glasses,  $\kappa(T)$  at  $T > 20$  K could be interpreted as the specific heat  $C(T)/V$  multiplied by a temperature-independent diffusivity  $D$  of order  $a^2 \omega_D/3$  where  $a$  is an interatomic distance. In the phonon-gas model, this would correspond to  $\ell \approx a$ , too small to justify use of the model. The success of this observation implies that the dominant normal modes in a glass are of the **D** variety and not **P**, because **P** implies that  $\ell \gg a$ , and not **L** because **L** implies that  $D = 0$  until anharmonic corrections are added which make  $D$  depend on  $T$ . This successful (and, we believe, essentially correct) interpretation lost favour after Anderson localization was understood, because a misconception arose that the **P**–**D** boundary (which certainly lies low in the spectrum of a glass) should lie close to the **E**–**L** boundary.

Our numerical calculations of  $D_i$  are shown in figure 7. Also shown are values of  $D_i$  from a formula of Edwards and Thouless (1972):

$$D_i = L^2 \Delta\omega_i, \quad (6)$$

where  $\Delta\omega_i$  is the sensitivity of the eigenenergy to a twist of the boundary condition. We have simply used for  $\Delta\omega_i$  the change in  $\omega_i$  when boundary conditions are



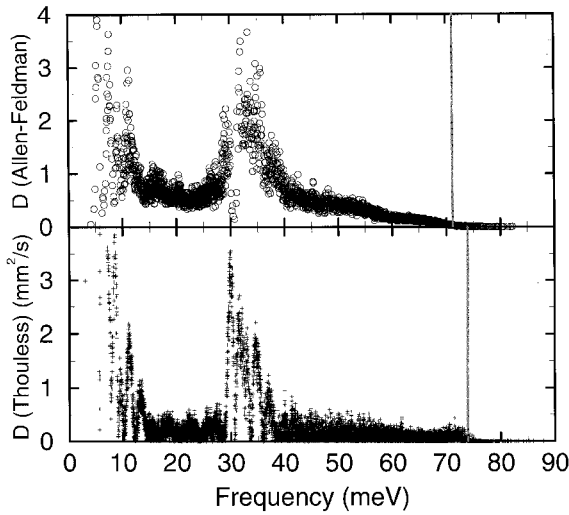


Figure 7. Diffusivity versus frequency (Feldman *et al.* 1993, Fabian 1997b) calculated for a 1000-atom model by equation (5), and for a 4096-atom model by equation (6). Mobility edges, shown as vertical lines, are slightly different in these two models.

changed from periodic to antiperiodic. The actual definition is probably

$$\Delta_{\omega_i} = \lim_{\phi \rightarrow 0} \left( \frac{\pi^2}{\phi^2} \Delta_{\omega_i(\phi)} \right) \quad (7)$$

where  $\Delta_{\omega_i(\phi)}$  is the shift when the phase is twisted by  $\phi$ . Antiperiodic boundary conditions correspond to  $\phi = \pi$ , while  $\phi = 2\pi$  returns to periodic boundary conditions with  $\Delta_{\omega_i(2\pi)} = 0$ . Therefore our calculation, which is the only one easily accessible for us, gives a probable lower bound to  $D_i$  for each mode  $i$ . Inspection of figure 7 shows that, with this interpretation, the two calculations agree reasonably well. Both go to zero at the mobility edge, and both become large and ragged in the P region below 10 meV. The raggedness comes from the sparseness of the eigenstates at low  $\omega$ , and the large values reflect the onset of ballistic propagation. In the D region above 12 meV, values have collapsed to the range of  $1 \text{ mm}^2 \text{ s}^{-1}$ , which corresponds to  $\omega_D a^2/3$ , with  $\omega_D$  set to 50 meV and  $a = 2 \text{ \AA}$ . This diffusivity is well below any value that could be allowed in a phonon-gas picture and agrees with the measured  $\kappa(T)$  (Allen and Feldman 1989, Feldman *et al.* 1993). The peak of  $D_i$  around 33 meV corresponds to a feature in the ‘phase quotient’ that will be discussed in § 9.3. Similar results for vitreous  $\text{SiO}_2$  have been reported by Feldman and Kluge (1995).

When  $\kappa(T)$  is calculated from equation (4), using the values of  $D_i$  from figure 7, the results, shown in figure 8, agree roughly with the data at higher temperatures. At low temperatures it is necessary to have an additional source of heat current, the ballistically propagating long-wavelength modes. In figure 8, this has been added in a thoroughly *ad hoc* fashion. We have simply assumed a Debye spectrum for the modes with  $\omega < \omega_0 = 3 \text{ meV}$ , and a temperature-independent diffusivity  $D(\omega) = D_0(\omega_0/\omega)^2$ . There is no theoretical justification for this. In principle, the temperature-independent diffusivity caused by glassy disorder should take the Rayleigh  $(\omega_0/\omega)^4$  form at low  $\omega$ , and one needs a stronger type of scattering, inelastic, and

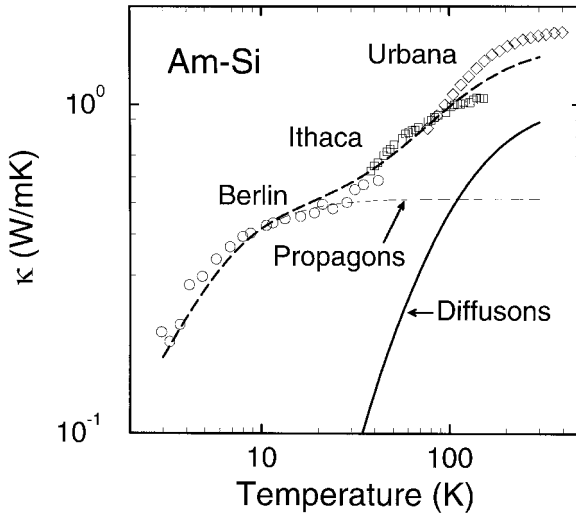


Figure 8. Thermal conductivity  $\kappa$  versus temperature  $T$  measured for amorphous Si: ( $\circ$ ), from Pompe and Hegenbarth (1988); ( $\square$ ), from Cahill *et al.* (1989); ( $\diamond$ ), from Cahill *et al.* (1994); (—), a calculation from the diffusivity values shown in figure 7 for a 1000-atom model using equation (4); (---), calculation from modes at low energy assuming that their diffusivity obeys an  $\omega^{-2}$  law; (- - -), sum of the two contributions from calculations.

therefore  $T$ -dependent, to match the data. However, the  $(\omega_0/\omega)^2$  behaviour has been seen at intermediate frequencies, both experimentally (Sette *et al.* 1998) and numerically (Dell'Anna *et al.* 1998, Feldman *et al.* 1999); so we have used this simpler fitting procedure to match the data.

Our most important conclusion is that the 're-increase' in thermal conductivity above the plateau region is attributable to heat carried by 'diffuson' modes in much the way imagined by Birch and Clark and by Kittel, and that the plateau is a simple cross-over region, not requiring any new physics to explain. In particular, we believe that 'excess modes' (also known as a 'boson peak') is not a necessary ingredient to explain the plateau. Amorphous Si seems to lack these 'excess modes' but still has a plateau.

## § 7. THERMAL EQUILIBRATION

There is some evidence suggesting that vibrations in glasses, if disturbed from equilibrium, may return very slowly. For amorphous Si, experiments were reported by Scholten and Dijkhuis (1996) and by Scholten *et al.* (1996). Our investigations show that, if the disturbance is not too large and is purely vibrational, then the rate of return to equilibrium should be as fast as, if not faster than, in a corresponding crystal. Surprisingly, we find that this is true both in the locon and in the diffuson portion of the spectrum, contradicting a view (Orbach 1996) supported by fracton theory (Alexander 1989, Orbach and Jagannathan 1993) that localized vibrations must equilibrate slowly.

In thermal equilibrium, the harmonic vibrational eigenstates have average populations given by the Bose-Einstein distribution. Fabian and Allen (1996) used anharmonic perturbation theory to calculate the inverse lifetime or equilibration rate

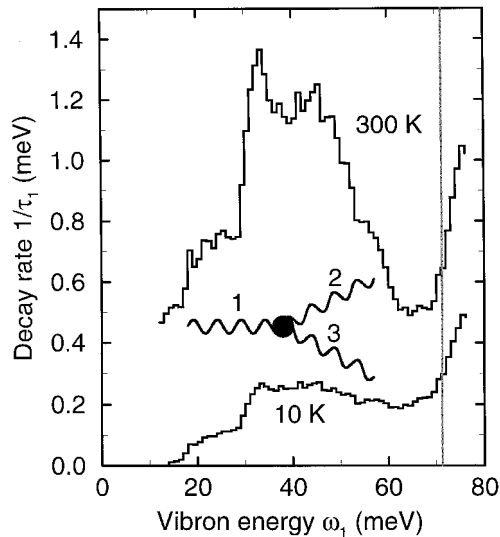


Figure 9. Decay rates calculated by anharmonic perturbation theory for amorphous Si. The inset shows the process diagrammatically.

$1/\tau$  by which a vibrational state returns to the Bose–Einstein distribution if driven out of equilibrium. Their results are shown in figure 9. The validity of the perturbation theory is confirmed both by the smallness of the ratio  $1/\omega\tau$  and by a direct test in the classical regime using molecular dynamics by Bickham and Feldman (1998a,b) and Bickham (1999).

It can be seen in figure 9 that no change occurs in the size of  $1/\tau$  at the mobility edge. A careful treatment of locons does not support the idea that they thermalize slowly. Their anharmonic thermalization rates (Fabian 1997a) are as fast as, or even faster than, those of diffusons, and also comparable with, or faster than, the corresponding thermalization rates of vibrations in crystals. The source of the misconception of slow equilibration is the idea that direct decay of a locon into two locons should be negligible. This idea fails because, unlike, for example, band-tail electronic states in amorphous Si, the vibrational states are not at all dilute. Slow thermalization rates (forbidden by all theories that we understand) could be tested by looking for a contribution from thermal vibrations to attenuation of very high-frequency sound (Fabian and Allen 1999). If the thermalization rate is extremely slow, this contribution to the attenuation would be greatly enhanced.

### § 8. RESONANT MODES

Inspection of figure 6 shows that a few modes in the D region and somewhat more in the P region have anomalously small participation ratios, of the order of 100 out of the 1000 atoms available. These states are not exponentially localized (Fabian, 1997b; Feldman *et al.*, 1999) but are temporarily trapped in regions of peculiar coordination, from which they can tunnel into the continuum of extended states. Such states were first reported by Biswas *et al.* (1988) in a small model similar to ours; a model with larger numbers of threefold- and fivefold-coordinated atoms had more such modes, which were speculated to bear some relation to the ‘floppy modes’

of Phillips and of Thorpe. Such modes were studied in detail by Schober and Laird (1991), Schober and Oligschleger (1996) and Oligschleger and Schober (1999).

We have recently argued (Feldman *et al.*, 1999) that, in our (mostly fourfold-coordinated) models of amorphous Si, such states tend to disappear as the size of the model becomes larger, presumably because each such mode is trapped only in a very specific peculiar region. As the number of atoms in the model increases, so does the number of peculiar regions but, if each resonant mode is trapped in only one region, the fraction of time spent outside that region increases because the volume outside that region has increased. On the other hand, such modes, especially those in the P region, may be more pronounced in real amorphous Si and other real glasses than they are in the models that we study. This is because our models are spatially homogeneous on scales greater than 4 Å, while real glasses may have mesoscopic defects such as voids which would attract more such modes.

Fabian and Allen (1997, 1999) found that the resonant modes have giant (approximately - 40) Grüneisen parameters  $\gamma_i$ . These parameters measure the sensitivity of  $\omega_i$  to macroscopic strain. In a glass (just as in a crystal where the positions of atoms are not all fixed by crystallographic symmetry) strains cause not just a homogeneous shift of atomic coordinates but also an additional local relaxation, which turns out to be particularly large in just those peculiar regions where the resonant modes are temporarily trapped. Anomalously large values of  $\gamma_i$  play an important role in explaining the anomalously large and sample-dependent measured low-T thermal expansion of glasses and also should show up in enhanced contributions to the attenuation of high- $\omega$  sound waves at higher T.

## § 9. CHARACTER OF DIFFUSONS

The most important property that distinguishes diffusons is their intrinsic diffusivity  $D_i$  with values of order  $\omega_D a^2/3$ . If wave packets were constructed in such a way as to be approximately monochromatic and simultaneously localized at the centre of a cell in a reasonably small radius (perhaps 6-8 Å), then we believe that, no matter how well directed such a pulse was at  $t = 0$ , the centre of the pulse would hardly move, and the radius would evolve as  $\langle r^2 \rangle = 6Dt$  for all times until reaching the cell boundary where it would interfere with its periodic image. Unfortunately, a 44 Å cell is only marginally large enough, and computational difficulties have so far prevented us from performing this experiment. Here we describe our efforts to find other ways to characterize diffusons.

### 9.1. Wave-vector

At the P-D boundary, wave-vectors become ill defined. Figure 10 shows a test. The squared Fourier weight is defined as

$$w_i(\mathbf{Q}) = \left| \sum_{\ell} \exp[i\mathbf{Q} \cdot \mathbf{R}(\ell)] \varepsilon_i(\mathbf{R}(\ell)) \right|^2 \quad (8)$$

where  $\mathbf{Q}$  is chosen as  $(2\pi/L)(h, k, l)$  with integer  $h, k, l$  so that the periodic images interfere constructively. We define  $w_i(\mathbf{Q})$  as  $w_i(\mathbf{Q})$  averaged over spherical shells with a wave-vector of width  $0.2 \times 2\pi/L$ . The value  $Q = 9.2 \times 2\pi/L$  corresponds to when neighbouring atoms are completely out of phase. The 51 meV diffusons show a peak Fourier content near  $8 \times 2\pi/L$ , but the peak height is less than twice a 'background'

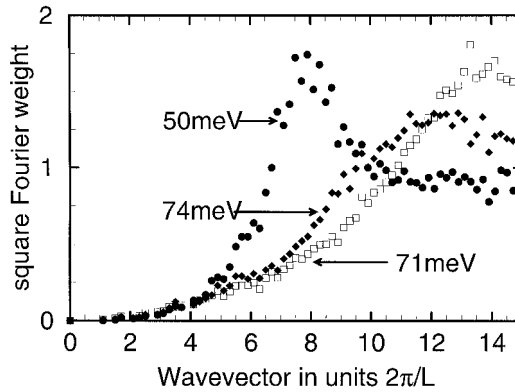


Figure 10. Fourier weights calculated from equation (8) for diffusons at 50 and 71 meV, and locons at 74 meV, averaged over three, four and two modes respectively.

value found at larger  $Q$  which dominates the behaviour. There is no ballistic character to these modes.

### 9.2. Polarization

Diffusons have no wave vector. Not surprisingly, they also lack a polarization as is shown in figure 11. Propagons, by definition, have a wave-vector. The nature of the propagons in the 4096-atom model was examined by Feldman *et al.* (1999). As shown there, the modes near  $\omega = 3.5$  meV have well defined transverse acoustic (TA) character, with the smallest possible wave-vector  $Q = 2\pi/L$ . Figure 11 shows that

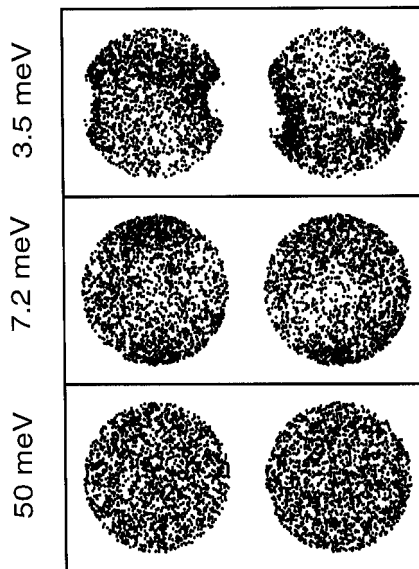


Figure 11. Area-preserving projection normalized unit polarizations  $\hat{\epsilon}_i(\mathbf{R}(\ell))$  onto circles (one circle for each hemisphere). Three modes  $i$  are shown, with each of the 4096 components showing as a dot.

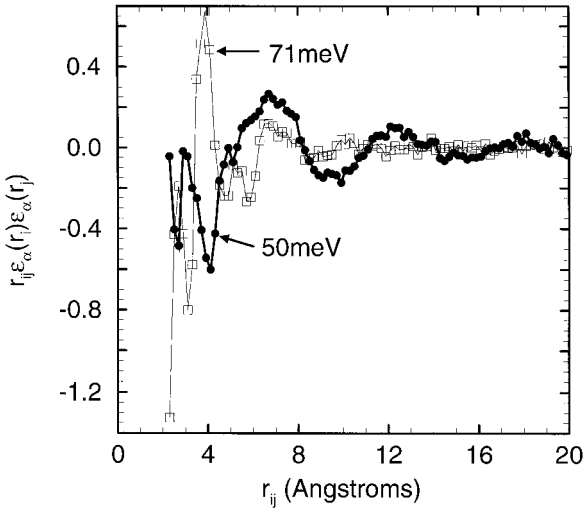


Figure 12. The spatial fall-off of  $\epsilon(\mathbf{r}_i) \cdot \epsilon(\mathbf{r}_j)$  weighted by  $r_{ij}$  and averaged for the same three modes at 50 meV and four modes at 71 meV as in figure 5.

these modes have only a limited preference for a direction of polarization. Similarly, the mode at 7.2 meV has  $Q = 2\pi/L$  and longitudinal acoustic (LA) character, but not much polarization.

Polarization directions of diffusons wander uniformly over the unit sphere, and one may ask what is the spatial range of decay of polarization memory in a mode. This is shown in figure 12. In a crystal, one has surfaces in  $Q$  space where modes have constant frequency,  $\omega(\mathbf{Q}) = \text{constant}$ . A single eigenstate is some arbitrary linear combination of the degenerate Bloch waves on this surface. If the surfaces were spherical and the linear combinations random, we would expect that  $\epsilon(\mathbf{r}_i) \cdot \epsilon(\mathbf{r}_j)$  would fall off spatially as  $[\cos(Qr_{ij})]/r_{ij}$ . Figure 12 shows that, for diffusons at 50 meV, some polarization memory, but much less than expected for a crystal, persists out to 12 Å, while higher- $\omega$  diffusons lose polarization memory more rapidly.

### 9.3. Phase quotient

The ‘phase quotient’  $\phi_i$  was defined by Bell and Hibbins-Butler (1975) as

$$\phi_i = \frac{\sum_{(a,b)} \epsilon_i(a) \cdot \epsilon_j(b)}{\sum_{(a,b)} |\epsilon_i(a) \cdot \epsilon_j(b)|}, \quad (9)$$

and is plotted in figure 13. For low  $\omega_i$ , values near 1 indicate that nearest-neighbour atoms (the only ones summed in equation (9)) vibrate mostly in phase, while, for high  $\omega_i$ , values near -1 indicate that nearest neighbours vibrate mostly out of phase. Like so many other properties, this depends only on  $\omega_i$  until the E-L boundary is crossed but is very mode specific for locons. The sharp rise at  $\omega_i \approx 29$  meV is interesting and may help to explain why, at the same frequency,  $D_i$  (figure 7) has a sudden rise. In crystalline Si, at approximately the same point in the spectrum, the TA branch ends and the density of states has a local minimum. Thus 29 meV marks a

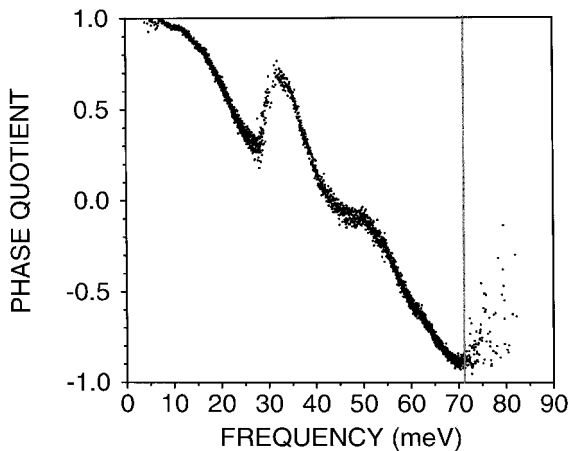


Figure 13. Phase quotient versus energy for a 1000-atom model.

point in the spectrum where diffusons change character from bond bending (somewhat TA like) with relatively high frequency because of large phase difference from atom to atom, to bond stretching (somewhat LA like) with not such a large phase difference but an equally high frequency because the bond-stretching forces are larger than the bond-bending forces. Apparently the latter kind of mode has greater diffusivity by a factor 2 or more. In a crystal we attribute this to a larger group velocity of the LA branch and a smaller density of states for decay by elastic scattering. Neither of these properties can be properly invoked for diffuson modes in a glass, but apparently similar physics is somehow at work.

#### § 10. SUMMARY

Since 95% of the states in amorphous Si, and probably many other glasses as well, are diffusons, we should understand their properties. All diffusons at a given frequency  $\omega$  seem essentially identical. As  $\omega$  changes, their properties evolve, mostly smoothly, but the sudden jump in diffusivity and in phase quotient at 29 meV shows that not all variability is lost.

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