Vibrational Localization in Amorphous Silicon

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Localized vibrational modes have been identified in a number of computer-generated models of amorphous silicon. Networks containing coordination defects give rise to extra resonant states at low frequencies. The densities of states, and dynamic structure factors for localized, resonant, and extented modes, are discussed and compared with recent neutron-scattering data.

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The disorder-induced localization of electronic states is one of the most interesting properties of amorphous solids. It also has a considerable practical importance, since the existence of a mobility edge separating localized and extended states is crucial to the usefulness of amorphous semiconductors for device applications. That vibrational excitations can exhibit similar behavior near a band edge may not be particularly surprising, but the relative ease with which the factors affecting vibrational localization in a simple amorphous solid can be visualized offers some useful insights. In this Letter we present computer simulations of *a*-Si showing that vibrational localization phenomena are not confined to the vicinity of the high-frequency band edge, but can also occur at low frequencies, if atoms of low coordination number are present. We believe that the appearance of the low-frequency localized vibrational states is closely associated with ideas of underconstraint versus overconstraint in glasses, and with the two-level states that occur in most amorphous solids. We have calculated dynamic structure factors for both modes at several frequencies, in order to assess the observability of localization effects in neutron-scattering experiments[1] on *a*-Si.

We have considered *a*-Si models generated by two methods. In the first, Wooten, Winer, and Weaire[2] (W3) disordered a diamond structure by means of Monte Carlo (MC) bond switching, so that distorted tetrahedral coordination was preserved for all atoms, but fivefold and sevenfold rings were introduced. In the second method, due to Biswas, Grest, and Soukoulis[3] (BGS), rapid quenching from the melt to low temperature was simulated by molecular-dynamics (MD) methods, with use of the separable two- and three-body Si interatomic potentials recently developed by Biswas and Hamann.[4] This classical model, which accounts well for the energies of various defect configurations within a tetrahedral structure, was employed by BGS[3] to produce *a*-Si networks with structural features in good agreement with experiment. Similar molecular-dynamics schemes were used by Ding and Andersen[5] for *a*-Ge, and by Luedtke and Landman[6] for *a*-Si. Vibrational properties of the BGS *a*-Si models were examined[3] with Keating[7] models and agreed well with experiment. In both the BGS and W3 methods, periodic boundary conditions were imposed, producing cubic supercells of N atoms, with $N=216$, 512, and 2000 for the former, and $N=216$ for the latter. Both methods produce networks which have minimum structural energies at densities somewhat greater than crystalline, about 9.6% larger for BGS, and 3.1% for W3.

The key difference between the BGS models and that of W3, or other continuous random-network models,[8] is the presence in the former of coordination defects, consisting mainly of three- and five-coordinated atoms. The numbers (r_n) of two-, three- and, five-coordinated sites were (0,14,18), (1,34,52), and (0,186,61) for our $N=216$-, 512-, and 2000-atom glasses. In contrast, all sites in the W3 network have four-coordination. Clearly the BGS glasses have defect concentrations that exceed experimental estimates for bulk *a*-Si of device quality. However, it is much easier to understand the properties of such defects when they are present in our calculation at high concentrations, and we expect that their characteristics would be similar at small concentrations, incorporating some properties that pertain to real *a*-Si films produced under various nonequilibrium conditions. As we shall see, the coordination defects lead to new localized vibrational modes at low frequencies, and also enhance the localization at high frequencies. It has recently been proposed[9] that five-coordinated atoms are important native defects in *a*-Si. Networks produced[6,10] with the Stillinger-Weber potential[11] also give five-coordinated sites, i.e., such defects are not specific to the potential employed.

To compare consistently the spectra of W3 and BGS networks, we used the same Keating potential[7] for the structural relaxation and subsequent vibrational properties of both. For each network, the dynamical matrix was diagonalized to yield the normal-mode frequencies, eigenvectors, and densities of states $g(\omega)$. Keating parameters $\alpha=42.1$ N/m and $\beta/\alpha=0.16$ give good agreement with the experimental $g(\omega)$ for both the BGS and W3 models (Fig. 1). These values also produce good results for the crystalline $g(\omega)$. The low-frequency peak is

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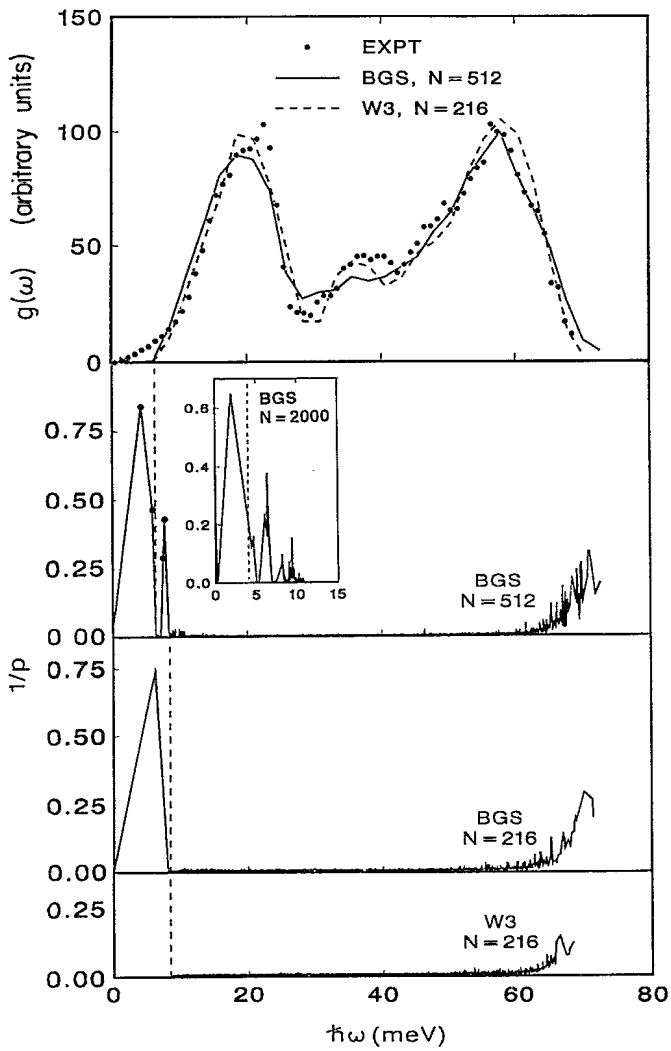

FIG. 1. Vibrational densities of states (upper panel) for N-atom a-Si models obtained by molecular-dynamics methods (BGS) and Monte Carlo methods (W3), compared with neutron-scattering data. Inverse participation ratios for all the vibrational modes of the BGS and W3 a-Si networks. For clarity low-frequency resonant modes for the $N=512$ BGS glass are displayed by points. Dashed lines indicate the energies below which extended modes cannot be found, because of finite cell size.

broader for both BGS and W3 models compared with the experimental $g(\omega)$. Details of the structural relaxation and optimization of the Keating-model parameters, together with $g(\omega)$ calculations for Si-Ge alloys, will be discussed in a forthcoming paper.[12]

The degree to which each vibrational mode is either localized or extended in nature can be characterized by its inverse participation ratio,[13] defined for each eigenmode as

$$p^{-1}=\sum_{j=1}^{N}(\mathbf{u}_j\cdot\mathbf{u}_j)^2\left(\sum_{j=1}^{N}\mathbf{u}_j\cdot\mathbf{u}_j\right)^{-2}, \qquad (1)$$

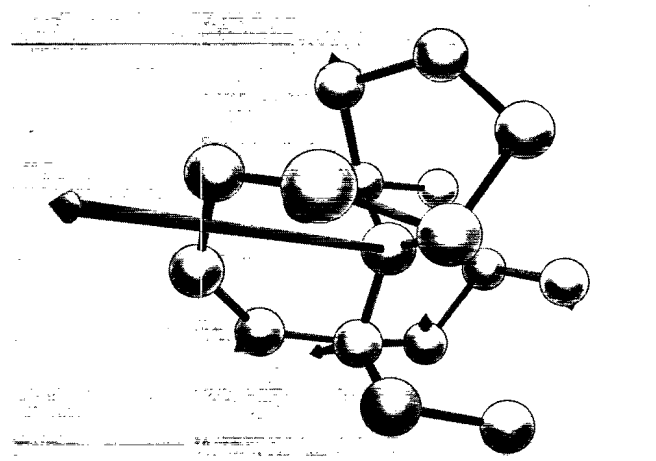

FIG. 2. Displacement pattern for a strongly resonant low-frequency mode of the $N=512$ BGS model ($\hbar\omega=6$ meV, $1/p=0.76$). For ease of visualization only the atom with the largest displacement and its immediate environment are shown. For clarity not all bonds are drawn.

where $\mathbf{u}_j$ is the displacement of atom j from its equilibrium position. The definition (1) implies that spatially extended modes have a small value of p^{-1}, on the order of $1/N$, N being the number of atoms in the system, whereas localized modes have large ratios that can reach a maximum value of 1 for a mode completely localized on a single atom.

Figure 1 shows that the BGS networks have strongly localized modes at the high-frequency edge of the vibrational spectrum, as does the W3 network. The high-frequency localization is considerably enhanced in the BGS glasses, a feature which can be traced to the presence of five-coordinated sites. In the BGS models, which contain coordination defects, a new and remarkable feature appears, a strong localization of some modes at low frequencies. This strong low-frequency localization is associated with the two- and three-coordinated atoms in the BGS model. No low-frequency localized modes occur for the W3 model, which has only four-coordinated atoms. For the different-size a-Si networks (Fig. 1), the average p^{-1} scales as $1/N$ for the extended modes, but is approximately independent of system size for the low-frequency localized region. The nature of the low-frequency localized states is illustrated (Fig. 2) by the mode displacement pattern for one of the strongly localized modes of the $N=512$ BGS model (having $\hbar\omega=6$ meV and $1/p=0.76$). The atom with the largest amplitude is three-bonded, whereas considerably smaller amplitudes are found on some of the neighboring three-, four-, and five-bonded sites.

The finite size of the supercell implies a cutoff for the smallest wave vector $k_{\min}$ possible for the calculated extended modes. Assuming that the transverse sound velocity c in the glass is close to the softest transverse velocity in the crystal, we estimate energy cutoffs $\omega_{\min}=ck_{\min}$ of 4.0, 6.3, and 8.4 meV, respectively, for the

$N=2000$-, 512-, and 216-atom systems, shown as dashed lines in Fig. 1. The only extended modes which can exist below these cutoffs in the calculations are the three translationally invariant modes at $\omega=0$, which we obtain.

Generally, extended and localized states do not coexist at the same energy because of hybridization effects. Because of the finite size of the *a*-Si networks, we exclude extended states below the energy cutoffs and inhibit the hybridization between localized and extended states at low frequencies. In the limit of an infinite-size system, the hybridization may lead to two possibilities at low frequencies: (i) formation of a band of localized states or (ii) formation of sharply resonant states with exponentially decaying wave functions away from the defect sites. The second possibility is more likely in which case the resonant states would have strong scattering properties that are usually attributed to localized states. Henceforth, we will refer to these modes with large p^{-1} as resonant instead of localized. Hybridization does not qualitatively diminish the essentials of the localization phenomena as illustrated by the presence of low-frequency resonant modes even *above* the energy cutoffs ($\omega_{\min}$) with p^{-1} of the order of 0.25–0.5 (for $N=2000$ and 512, Fig. 1).

The occurrence of two-level states (TLS), a feature of most glassy materials, is phenomenologically related to the presence of low-coordinated atoms, and it is plausible that the extra vibrational modes and TLS are closely related. Phillips and Thorpe[14,15] have recently shown that in networks with low average coordination number, a finite fraction of the modes are so-called "floppy" modes, having zero frequency in the absence of van der Waals interactions and forces opposing dihedral-angle changes. Although the floppy modes were predicted to disappear for average coordination number more than 2.4, it is reasonable to picture some of the low-frequency resonant modes in our BGS networks as finite-frequency remnants of the Thorpe modes, confined to regions of the *a*-Si networks which are locally floppy. The mode shown in Fig. 2 is more easily interpreted, though, as a defect mode, rather than associated with the Thorpe modes.

We have investigated whether the high-frequency localized or low-frequency resonant modes can be identified by neutron-scattering measurements on *a*-Si, i.e., whether the dynamic structure factors of such modes differ significantly from those of extended modes of nearby energy. For both types of modes, we have calculated the reduced structure factor[16]

$$f(k,\omega)=\left\langle\left|\sum_j \hat{\mathbf{k}}\cdot\mathbf{e}_{ij}\exp(i\mathbf{k}\cdot\mathbf{R}_j)\right|^2\right\rangle. \qquad (2)$$

The eigenvector components $\mathbf{e}_{ij}$ are vector displacement amplitudes for atom j in mode i. The angle brackets indicate an average over all $\mathbf{k}$ of the same magnitude. In the one-phonon approximation, the structure factor $S(k,\omega)$ that is observed in neutron scattering is directly proportional to k^2e^{-2W} times $f(k,\omega)$, where e^{-2W} is the Debye-Waller factor.

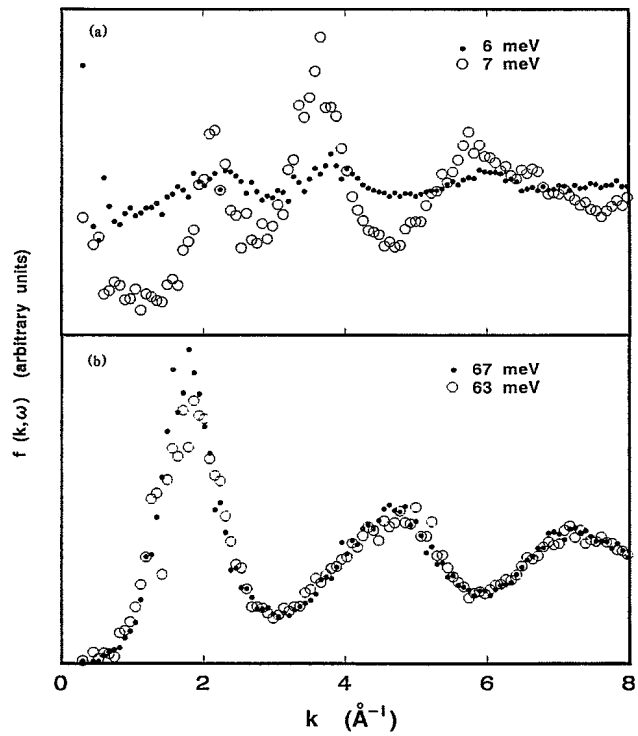

FIG. 3. Constant-ω cuts of the reduced structure factor $f(k,\omega)$ for resonant (dots) and extended modes (circles) of (a) low and (b) high energies in the $N=512$ BGS glass.

In Fig. 3(a), we see that $f(k,\omega)$ vs k for the 6-meV mode (drawn in Fig. 2), with a large value of p^{-1}, has far less pronounced structure than $f(k,\omega)$ for the first extended mode at 7 meV, in the 512-atom network. This is entirely reasonable, since Eq. (2) implies that for the limiting case of a mode completely localized on a single atomic site, $f(k,\omega)$ should be independent of k. The scattering from an 8-meV resonant mode (not shown) is very similar to the 6-meV mode. However, it is very difficult to distinguish between localized and extended modes at high frequencies on the basis of their $f(k,\omega)$ functions, as illustrated by the very similar scattering functions for a 67-meV localized and a 63-meV extended mode in Fig. 3(b). We found this to be true for a number of localized and extended modes that we examined in the high-frequency region above 59 meV. The dominant feature of both localized and extended high-frequency vibrations is the out-of-phase motion of neighboring atoms. At low frequencies, the in-phase motions that apply for extended modes are somewhat unlike those for resonant modes, which, by their nature, must have some out-of-phase character.

The scattering from the strongly resonant 6-meV mode is reminiscent of the extra structureless scattering seen in neutron experiments,[1] although the comparison is

not in quantitative agreement. In previous work[1] the experimental dynamic structure factor $S(k,\omega)$ from neutron measurements for $\omega = 12$ meV had a higher scattering intensity and less pronounced k-dependent structure than that calculated from the W3 a-Si model (Fig. 2 of Ref. 1). This difference is similar to that found between resonant and extended modes in Fig. 3(a). At lower frequencies (<4 meV), it was observed that the sound modes alone could not account for the large structureless scattering seen in neutron experiments.[1] The excess scattering is qualitatively similar to that from the coordination defects in the BGS model.

In summary, localization phenomena have been identified and investigated in detail in computer simulations of the vibrational spectra of amorphous silicon. Some of the a-Si networks we considered contain coordination defects which apparently produce locally soft or locally hard regions in their vicinity, giving rise to low-frequency resonant modes of novel character. Some of these modes are associated with, but are not primarily vibrations of, the low-coordinated atoms. The enhanced localization produced at high frequencies by overcoordinated (five-bonded) atoms is also noteworthy, presenting an interesting analogy to the localization of electronic states which has recently been proposed to explain some of the electronic properties of a-Si.

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