# Finite-Temperature Properties of Amorphous Silicon

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*Ab initio* local-orbital quantum molecular dynamics is used to study the finite-temperature properties of amorphous silicon. Using two structural models of *a*-Si with 63 and 216 atoms, we examine the structure and temperature dependence of conduction and valence band tails. An explanation is suggested for the recent experimental observations of an asymmetry in the temperature dependence of the band-tail widths of the conduction and valence bands in *a*-Si. Finally, we connect these simulations to other theoretical descriptions of band tailing.

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Amorphous silicon continues to attract researchers both for the intrinsic interest of the microstructure of the network, and because of continuing interest in developing inexpensive *a*-Si:H films for electronic devices. An issue central to both classes of investigations is the *dynamical finite-temperature* behavior of the network. A natural approach to understanding the $T > 0$ properties is to perform *ab initio* molecular-dynamics simulations and study instantaneous and time-averaged properties. Here for the first time, we present a study of the time dependence of the *electronic* properties, and connect these to experiment and theoretical models. In recent years, photoemission and its variants [1] have become standard experimental techniques to study the electronic structure of materials. A by-product of "band-structure-based" molecular dynamics (QMD) (in which interatomic forces are computed directly from the electronic structure) is detailed information about the system's electronic structure at each time step. This provides a direct theoretical connection to experimental probes of the electronic density of states: Time averages of eigenvalues can be directly related to measured densities of states. All QMD simulations reported in this paper are obtained from the density-functional, local-orbital method of Sankey and Niklewski [2]. We perform QMD simulations with the 63-atom, two-defect cell of Drabold *et al.* [3], and the 216-atom cell of Wooten, Weaire, and Winer [4] (WWW) relaxed to equilibrium with our band-structure code. We describe the details of the simulations on the WWW cell separately [5]. The 63-atom and WWW cells are generally quite similar. They have almost identical total energies and similar radial distribution functions. Vibrational power spectra are also in close agreement, though the 63-atom cell seems to be in slightly better agreement

with experiment. For a complete discussion see Refs. [3–5].

A preliminary to discussing our results is to define two kinds of defects in *a*-Si. A *geometrical defect* involves an atom which does not have four neighbors in a sphere of some coordination radius $R_c$. A *spectral defect* involves a configuration of atoms leading to a localized [6] gap state. We show here that the existence of a geometrical defect is neither a necessary nor a sufficient condition for the existence of the more fundamentally important spectral defect. An important example is from the WWW cell, which, after rearrangements toward equilibrium
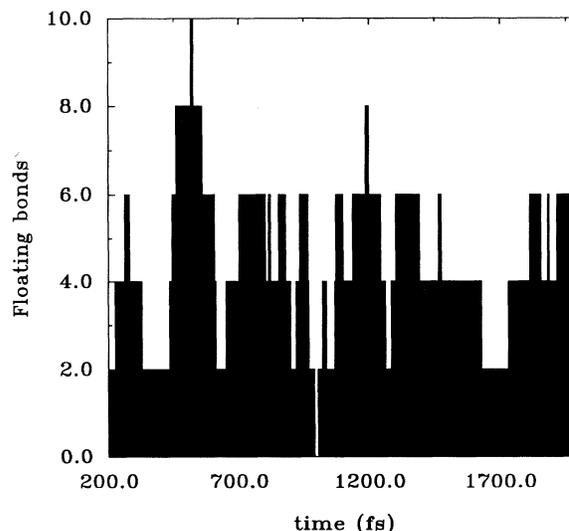


FIG. 1. Number of fivefold-coordinated atoms plotted against time step using $R_c = 2.74$ Å.
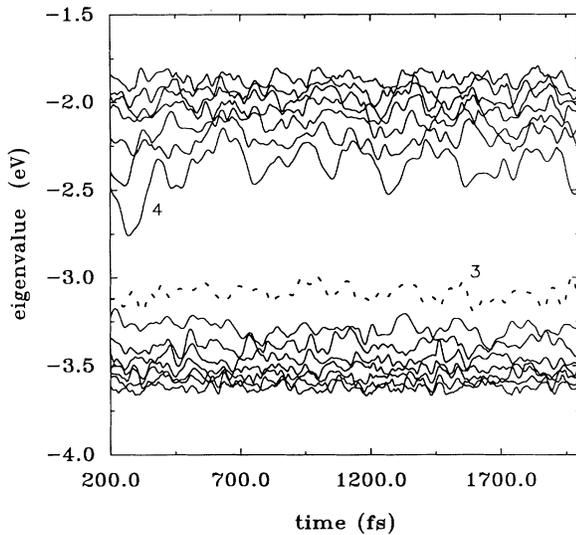
FIG. 2. The LDA-Harris functional eigenvalues near the gap plotted vs time. The highest-energy occupied state (dashed line) is eigenvalue 3. The valence-band maximum in $c$-Si is near $-3.5$ eV. Eigenvalue 0 is the highest occupied extended state.
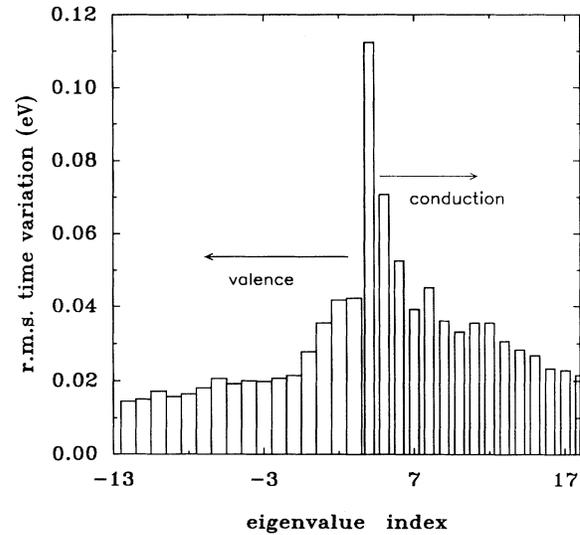


FIG. 3. Histogram of rms time variations of eigenvalues near the gap. Eigenvalue 3 is the highest occupied state. The rms variations are computed for 2 ps of time evolution. Wide bars are occupied (valence) levels; thin are not.

from a relaxation with our *ab initio* code, yields at least three spectral, but two geometrical, defects. Thus, the usual consideration of a coordination criterion as a means for characterizing the electronic structure of a network of Si atoms is not only *incomplete* but can be very misleading. This is particularly true at finite temperature. To illustrate this we have performed a 2-ps QMD simulation starting from the relaxed 216-atom WWW cell and examined the number of floating (fivefold) bonds and the near-band-gap eigenvalues as a function of time. The average kinetic temperature was approximately 350 K. Here a coordination radius of $R_c = 2.74$ Å is used to define a geometrical defect. The number of floating bonds shown in Fig. 1 varies in an apparently random fashion from 0 to 10 over the simulation. These "geometrical defect fluctuations" do *not* yield correlated variations in the LDA eigenvalues near the gap. In Fig. 2 we plot the time evolution of the eigenvalues at the $\Gamma$ point of the supercell Brillouin zone (BZ) for the 216-atom cell. This time variation yields the rms eigenvalue time variations of Fig. 3. Equivalence of geometrical and spectral defects would imply that eigenvalues drastically change as the number of defects fluctuates. This result is qualitatively insensitive to $R_c$.

Examination of the eigenvalue time evolution also leads to other important consequences: (1) Localized states fluctuate more than extended states. States near the gap are the most localized. The top three occupied and six lowest unoccupied states show appreciable localization. (2) Unoccupied (conduction) states fluctuate more than occupied (valence) states. Point (1) may be understood as a consequence of the sensitivity of localized eigenval-

ues to distortions in that part of the cell where the charge is localized. These distortions that yield localization may simply be overcoordinated or undercoordinated atoms such as the geometrical defect defined earlier. It is more likely that they are of a more general nature and involve badly distorted bond angles and very nontetrahedral topology which induces localization even though atoms may be nominally fourfold coordinated. Point (2) is discussed further in the context of photoemission experiments on $a$-Si.

Regarding the connection to experiment, Aljishi, Cohen, Jin, and Ley [1] reported novel experiments on $a$-Si in which total photoelectron-yield spectroscopy was used to obtain separately the conduction and valence electronic densities of states. A central result of their paper was the surprising observation that the width of the (exponential) band tailing of the valence-band edge was nearly temperature ($T$) independent, while the conduction-band tail (CBT) broadened substantially with temperature in a linear fashion. Previously, it was believed that the same mechanism (strained bonds) controlled both band tails. By performing QMD simulations of the 63-atom two-defect cell for several kinetic temperatures, we compare the rms (time) variation of the highest-energy, occupied, and extended electronic eigenvalue with the experimental valence-band tail (VBT) width, and compare the rms variation of the lowest-energy, unoccupied, and extended eigenvalue to the CBT width. Denote these theoretical rms variations as $\sigma_V(T)$ and $\sigma_C(T)$, and the experimental widths as $E_{0V}$ and $E_{0C}$. In Table I we illustrate the results of this calculation and compare them to experiment. We find excellent agreement be-

TABLE I. QMD simulations vs experiment [1]. $\sigma_{struc} = (E_{0V}^2 - \sigma_V^2)^{1/2}$. $\sigma_{V,C}$ are from QMD; $E_{0V,C}$ are from Ref. [1].

| $T$ (K) | $\sigma_V$ (K) | $E_{0V}$ (K) | $\sigma_C$ (K) | $E_{0C}$ (K) | $\sigma_{struc}$ (K) |
|---|---|---|---|---|---|
| 300 | 360 | 603 | 696 | 383 | 348 | 484 |
| 400 | 418 | 626 | 720 | 441 | 452 | 466 |
| 500 | 452 | 650 | 754 | 534 | 580 | 467 |

TABLE II. Simple phonon theory. $\epsilon_{0V} = [\sigma_{struc}^2 + (\sigma_V^{phon})_{rms}^2]^{1/2}$.

| $T$ (K) | $\epsilon_{0V}$ (K) | $\sigma_C^{phon}$ (K) |
|---|---|---|
| 300 | 603 | 348 |
| 400 | 622 | 393 |
| 500 | 644 | 435 |

tween the CBT width from our simulation and the $E_{0C}$ of experiment. Both the absolute rms width *and the slope* of $E_{0C}(T)$ are well reproduced (experiment and simulation both yielding $d\sigma_C/dT \approx 1$). However, for the VBT width, we find that $\sigma_V(T)$ is *smaller* than the experimental $E_{0V}$. This is consistent with the notion that only part of the valence-band tailing is due to dynamic effects, with another part due to structural disorder $\sigma_{struc}$. Two columns are given for $E_{0V}$, corresponding to two samples [1]. Table I implies the existence of a roughly $T$-independent contribution to $E_{0V}(T)$ from $\sigma_{struc}$. From these observations, we conclude that the broadening of the conduction-band tail is a *dynamical effect* due to vibration-induced fluctuations in the electronic energies, while the valence-band tails are affected roughly equally by structural and dynamical effects.

This study has led us to an explanation of the difference in $T$ dependence between the CBT and VBT. The $T$ dependence of the band tail implies that phonons play a role in these observations. In companion studies of $c$-Si, we observed that the eigenvalue at the top of the valence band was strongly modulated by only one phonon mode—the TO mode ($\hbar\Omega_{TO}/k_B \approx 700$ K), while the CBT was modulated by all the modes present (TA, LA, LO, TO). This is easily understood: In $c$-Si, the valence-band maximum occurs at the $\Gamma$ ($\mathbf{k}=0$) point of the BZ. Viewing the electron-phonon interaction ($H_{e-p}$) as a (time-dependent) perturbation on the eigenvalue, we expect a strong electron-phonon coupling only for $\mathbf{k}=0$ (optic) phonons. On the other hand, the conduction-band minimum occurs at a point of low symmetry in the BZ, and all phonon modes contribute to the modulation of the conduction-band edge eigenvalue. In $a$-Si the situation is less clear, but we empirically find that the dominant modulation of the VBT eigenvalue is still TO, and the CBT eigenvalue has lower phonon frequencies present. This leads us to suggest that the weak $T$ dependence of the VBT is to some extent a consequence of the small number of TO phonons excited at moderate temperatures, whereas the CBT is affected even by TA phonons ($\hbar\Omega_{TA}/k_B \approx 230$ K). To crudely quantify these notions, let $\lambda_{v(c)}$ denote the valence (conduction) eigenvalues, respectively. If $\Psi_{v(c)}$ is the corresponding electronic eigenstate, we expect $\lambda_{v(c)}$ to differ from the zero-temperature value at time $t$ by an amount

$$\delta\lambda_{v(c)}(t) \approx \langle \Psi_{v(c)} | H_{e-p}(t) | \Psi_{v(c)} \rangle.$$

The predicted rms variation is roughly given by

$$\langle \delta\lambda_{v(c)}^2 \rangle_\tau = \text{const}\langle \delta x^2 \rangle_\tau, \tag{1}$$

where $\langle \rangle_\tau$ denotes a time average, and $\delta x$ denotes a small phonon-induced distortion from the $T=0$ structure. It is easily seen [7] that, for a single phonon mode of frequency $\Omega$,

$$\langle \delta x^2 \rangle_\tau = (\hbar/2\Omega)\coth(\hbar\Omega/2k_BT). \tag{2}$$

Taking the dynamical part of the broadening to be

$$(\sigma_C^{phon})_{rms} = D_C \left[ \sum_{\mu=\text{TO,LO,TA,LA}} \frac{\coth(\hbar\Omega_\mu/2k_BT)}{\Omega_\mu} \right]^{1/2} \tag{3}$$

and

$$(\sigma_V^{phon})_{rms} = D_V \left[ \frac{\coth(\hbar\Omega_{TO}/2k_BT)}{\Omega_{TO}} \right]^{1/2}, \tag{4}$$

we obtain the results of Table II, where we have adjusted $D_V$ and $D_C$ to reproduce experiment at $T=300$ K, and we use $\sigma_{struc}=472$ K (the average of $\sigma_{struc}$ of Table I). Experiment ($E_{0V}$) and theory ($\epsilon_{0V}$) are now in close agreement. The very simple phonon model presented here is in some ways reminiscent of the detailed calculations of Grein and John [8], and others.

Another use of this work involves applications to theories of band tailing and temperature dependence of electronic properties. Bar-Yam, Adler, and Joannopoulos [9] (BAJ) have proposed an explanation for the Urbach form of band tailing in $a$-Si. An assumption of this model is a correlation between electronic energy levels near the band edges and the total energy of the system. Using an obvious notation this conjecture may be stated as

$$\delta\lambda = \text{const} \times \delta V. \tag{5}$$

Small thermally induced variations in the atomic coordinates are supposed to lead to shifts in total energy $V$ and eigenvalue $\lambda$ via Eq. (5). We take the highest occupied and extended state (indexed as 0 in Fig. 3) as the valence-band edge, and, plotting $\delta\lambda$ vs $\delta V$, we obtain the result of Fig. 4. Clearly there is little correlation of the form Eq. (5). We have studied a variety of eigenvalues near the band edges, different structures, and different temperatures, and always find results qualitatively similar to Fig. 4. The observed lack of correlation is not unex-
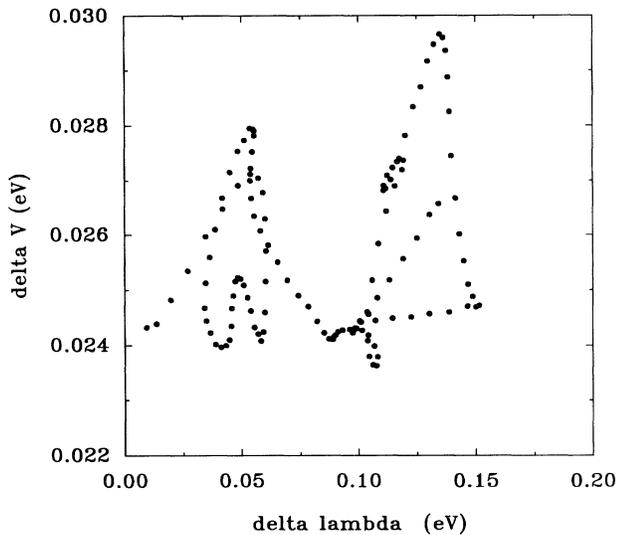
FIG. 4. Plot of eigenvalue variation vs configurational energy variation for a 216-atom WWW cell at about 200 K. Each solid circle gives $(\lambda, V)$ for different time steps. A correlation between $\delta\lambda$ and $\delta V$ of the form Eq. (5) would yield a straight line.

pected. For example, density-functional theory within LDA relates $V$ and $\lambda_i$ by [2]

$$V = 2\sum_{i,occ} \lambda_i - (\text{Hartree}) + (\text{exchange correlation})$$

$$+ (\text{nuclear Coulomb}), \qquad (6)$$

where all but the nuclear Coulomb term is an intricate function of average electron density. A simple relation between $V$ and a particular $\lambda_i$ would be remarkable from this point of view.

Though we have not seen the correlation suggested by Eq. (5), we have observed correlations between the different terms in Eq. (6). For example, variations in the

band-structure energy (first term) *is* correlated with variations in $V$. But this does not lead so easily to the Urbach form of the band tails obtained by BAJ. Consequences of this correlation will be published elsewhere.

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[6] The criterion for real-space localization of an eigenstate in this paper is that $Q_v^2 \geq 3/N$, where $N$ is the number of atoms and $Q_v^2 = \sum_i q_{i,v}^2$. $q_{i,v}$ is the part of the charge on atom $i$ derived from the eigenstate $v$. The charges for each eigenstate are assigned to atoms in a manner analogous to a Mulliken population analysis as described by Attila Szabo and Neil S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989), p. 151. Note that $Q_v^2 = 1/N$ for completely delocalized states and $Q_v^2 = 1$ for a state localized on one atom.

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