

Approximate *ab initio* calculation of vibrational properties of hydrogenated amorphous silicon with inner voids

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We have performed an approximate *ab initio* calculation of vibrational properties of hydrogenated amorphous silicon (*a*-Si:H) using a molecular dynamics method. A 216-atom model for pure amorphous silicon (*a*-Si) has been employed as a starting point for our *a*-Si:H models with voids that were made by removing a cluster of silicon atoms out of the bulk and terminating the resulting dangling bonds with hydrogens. Our calculation shows that the presence of voids leads to localized low-energy ($30\text{--}50\text{ cm}^{-1}$) states in the vibrational spectrum of the system. The nature and localization properties of these states are analyzed by various visualization techniques. [S0163-1829(98)02647-2]

I. INTRODUCTION

It is well known now that typical *a*-Si:H, grown using conventional techniques, has certain characteristic features: it contains a significant amount of nanovoids,²⁻⁵ and it has an average hydrogen concentration of approximately 10 at.%.² Hydrogen, present in the bulk of the material, can generally be found in three different states: it can be bonded, passivating dangling silicon bonds in the network or on the surfaces of the voids, it can be nonbonded (most of it, because the concentration of dangling bonds in *a*-Si is much lower than the concentration of hydrogen atoms²), and it can also exist in a condensed phase inside the voids.

An important recent work with a hot wire form of *a*-Si:H has recently been reported,⁶ which might connect a low density of voids with unique vibrational properties. We have, therefore, performed studies of a dense continuous random network, and models with hydrogenated voids intentionally introduced to compare the vibrational modes in the two cases in detail. This study leads us to believe that hydrogenated voids lead to low-frequency modes, though not at energies small enough to be tunneling modes.⁷ We are also interested in experimentally discernible vibrational signatures linked to voids and/or hydrogen.

In Sec. II of this paper we present the detailed algorithm of construction of the models and calculation techniques used to study their vibrational behavior. Then in Sec. III we discuss our results received for different models of *a*-Si:H with voids and compare them with the results obtained for a pure *a*-Si model. Finally, in Sec. IV we draw some conclusions regarding the following question: do voids lead to low energy states in *a*-Si:H?

II. MODEL CONSTRUCTION AND CALCULATIONS

In this section we present our scheme for constructing a model of hydrogenated amorphous silicon with a void. We use a model generated from a Wooten, Winer, and Weaire⁸ scheme, involving 216 atoms for pure *a*-Si by Djordjevic, Thorpe, and Wooten¹ as a "base" for construction of models for *a*-Si:H with voids in the bulk. We label this the DTW model in what follows. For our molecular-dynamics (MD)

simulations we employ a code developed by Sankey and co-workers,⁹ based upon the density-functional theory within the local-density approximation.¹⁰ The main features of the method are a spin-averaged, non-self-consistent version of density-functional theory based on a linearization of the Kohn-Sham equations,¹¹ a minimal pseudoatomic orbital basis set with an interaction confinement radius, and nonlocal, norm-conserving pseudopotentials.¹² In the equilibrium geometry search, we consider our models fully relaxed when total forces on any atom in the supercell are less than 0.03 eV/\AA .

In the first step (which we need to perform only once) we relax the DTW model, obtaining its equilibrium geometry configuration by dynamical quenching. In our case relaxing the model resulted only in minor network rearrangements.¹³ The radial distribution function, obtained for the relaxed model, appeared to be in good agreement with experimental data, as was the case for the original model before relaxation.

In the second step we remove a cluster of Si atoms, thus creating a void in the silicon network. As the removal of some silicon atoms out of the network results in dangling bonds, we must terminate these bonds with hydrogen atoms. In our models, presented in this paper, we consider entirely passivated networks, where every dangling bond in the network is terminated by a hydrogen atom, initially placed directly on the bond 1.5 \AA away from the Si atom, that we keep.

After discarding the chosen cluster of Si atoms and saturating the dangling bonds on the surface of the void with hydrogens we perform the third step—another MD relaxation, which gives us the equilibrium configuration for the structure with void. At this point the actual number of relaxation steps required to make forces on every atom sufficiently small varies greatly, depending on the size and form of the void.

Once the equilibrium state is reached, we can proceed with the dynamical matrix calculation, displacing every atom in the supercell in three orthogonal directions (by 0.03 \AA , which is suitable for this purpose) and computing the resulting spring constants as second derivatives of the total energy of the system. Diagonalizing the dynamical matrix we finally receive its eigenvalues together with the corresponding

eigenvectors, which enables us to carry out the full investigation of vibrational behavior of a given model.

We plot a vibrational density of states (VDOS) for a set of dynamical matrix eigenvalues $E_i, i=1, \dots, N$, where N is the number of atoms in the system, which gives us information about vibrational states distribution along the energy axis. In the figures, we use a Gaussian broadened form for $\delta(E-E_i)$, with width 10 cm^{-1} . Then, in order to understand the localization properties of vibrational states, we construct inverse participation ratio¹⁴ (IPR) graphs.

Finally, for any energy mode we can estimate vibrational activity for every separate atom, examining the components of the eigenvector “belonging” to this particular atom and comparing, for example, the sum of their squares on the reference atom, with the sum over all atoms in the supercell. After forming this chart of individual atomic IPR’s we can employ this information for the dynamical animation of the vibrational mode (by creating a file, consisting of a set of frames, each containing coordinates and displacement vector components for every atom in the supercell, which can be used as an input for XMOL molecular display and animation program¹⁵) or for creating its static equivalent in a form of a gray scale (where atoms are assigned different shades according to their vibrational activity).

III. DISCUSSION OF RESULTS

In this section we will discuss our results received for two different *a*-Si:H models with voids. The first model has five Si atoms removed and 12 H added (we refer to it as a “small bubble” model), the second one has 23 Si atoms removed and 36 H added (“big bubble” model).

To be able to compare the results for our *a*-Si:H models and results, obtained for a pure *a*-Si DTW model, which serves as our “reference” model, we have performed the set of all calculations, described in the previous section, for DTW as well as for both models containing voids.

In Fig. 1 our results for a pure *a*-Si model are presented; note that the calculations show that there are no vibrational states present with energies up to approximately $55\text{--}60 \text{ cm}^{-1}$. Now, if we compare these results with the results obtained for the “small bubble” model, shown in Fig. 2, and restrict our attention only to low-energy states, we can see that for a model with void a vibrational mode emerges at 32 cm^{-1} (which is practically right in the middle of the low-energy gap in the *a*-Si vibrational spectrum) and this mode has high IPR and can be considered spatially localized. The gray scale map for the aforementioned mode is presented in Fig. 3. It enables us to estimate where this vibration is localized in the supercell and how it decays in space. We can see that the mode has a rather complicated structure, and although it is mostly localized around the surface of the void and decays very rapidly when we move away from the void, there are certain directions where it decays more slowly and a whole cluster of vibrationally active atoms to the side of the void. For comparison in Fig. 4 we present one of the low-energy (64.4 cm^{-1}) modes for the “small bubble” model that has relatively low IPR and, according to the picture, is rather uniformly distributed in space.

Now comparing the results for the first two models, discussed in the previous paragraph, with the results received

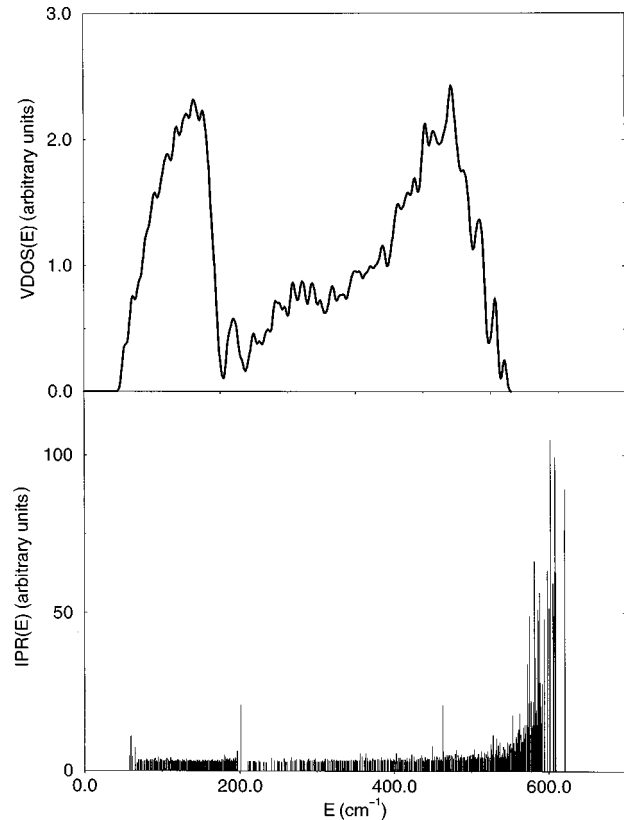


FIG. 1. Vibrational density of states (upper panel) and inverse participation ratio (lower panel) for 216-atom DTW model for pure *a*-Si.

for the “big bubble” model (Fig. 5) we can see that now we have three low-energy states, but only one of them, at 21.8 cm^{-1} has a high IPR (more than two times larger than for the similar mode in the “small bubble” model) or is localized. Examining the gray scale map for this mode, presented in Fig. 6, we also notice that spatial localization of the mode is quite similar to the “small bubble” model mode with the exception that the former decays much faster and its localization on a cluster of Si atoms to the side of the void is much sharper.

Our hydrogenated models also produce highly localized states at $600\text{--}630 \text{ cm}^{-1}$ (hydrogen bend) and $2000\text{--}2200 \text{ cm}^{-1}$ (hydrogen stretch). Other hydrogen related states, corresponding to mixing of the first two, fill out the region of $700\text{--}1000 \text{ cm}^{-1}$.

IV. CONCLUSIONS

Studying the models for *a*-Si:H we have found localized low-energy modes in the vibrational spectrum of the system. The nature of these modes is quite complicated but evidently connected with the existence of voids—for both, localized low-energy modes considered a number of silicon atoms located close to the surface of the void exhibits high-vibrational activity. We can call the low-energy modes “floppy” because the introduction of void-type defects into a silicon network significantly reduces the coordination numbers for atoms situated around the defect (thus making this particular region of the network “floppy”), but, due to their local origin, these modes are not exactly the same as the

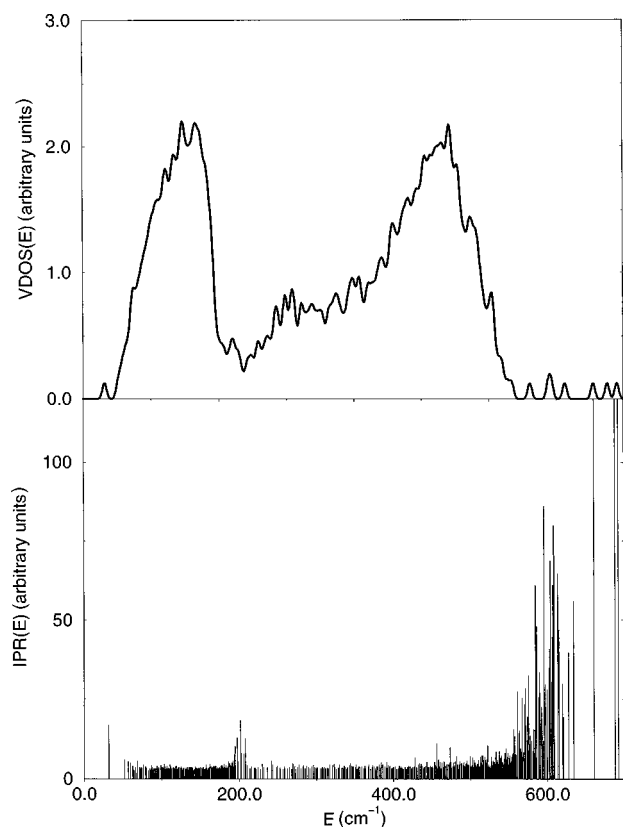


FIG. 2. Vibrational density of states and inverse participation ratio for “small bubble” model (211 Si atoms, 12 H atoms) for α -Si:H with void (high-energy modes are not shown).

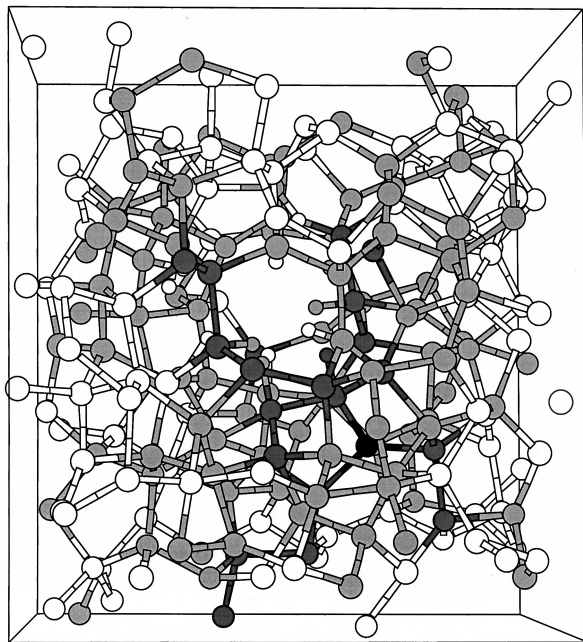


FIG. 3. Localized low-energy vibrational mode for “small bubble” model. Vibrational energy is 32.0 cm^{-1} . Here every atom pictured in black accounts for more than 10% of total supercell excitation. Atoms, represented by dark gray, light gray, and white, account for more than 1% and up to 10%, more than 0.1% and up to 1%, and less than or equal to 0.1% of total supercell excitation accordingly.

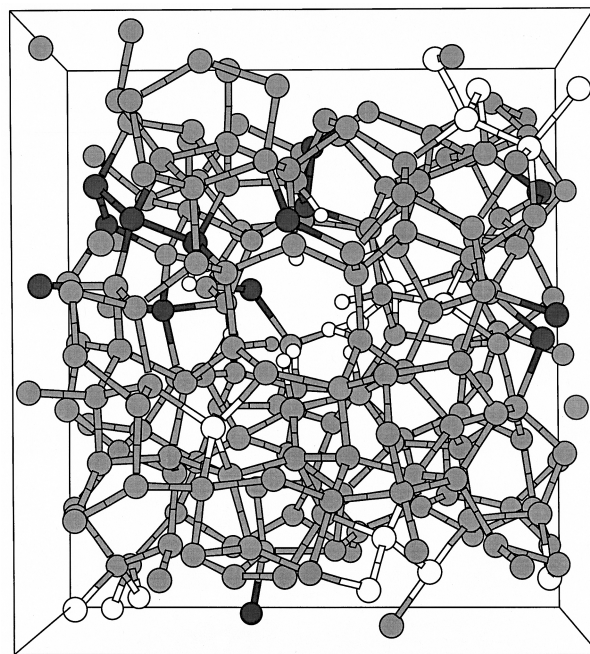


FIG. 4. Low-energy vibrational mode for “small bubble” model that is delocalized. Vibrational energy is 64.4 cm^{-1} . Gray scale conventions are the same as for Fig. 3.

celebrated Phillips-Thorpe “floppy” modes, associated with the average coordination in the system.

The principal shortcoming of this calculation is its finite size, which can be interpreted as an artificial void-void inter-

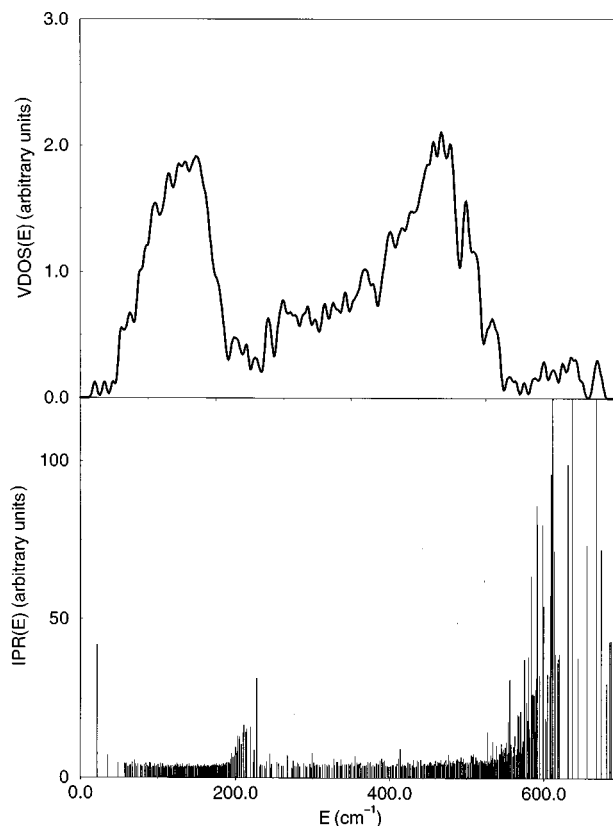


FIG. 5. Vibrational density of states and inverse participation ratio for “big bubble” model (193 Si atoms, 36 H atoms) for α -Si:H with void (high-energy modes are not shown).

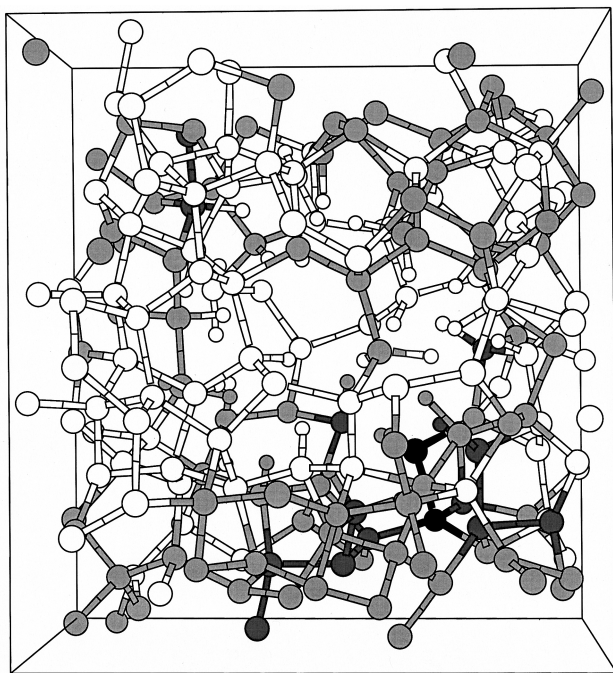


FIG. 6. Localized low-energy vibrational mode for “big bubble” model. Vibrational energy is 21.8 cm^{-1} . Gray-scale conventions are the same as for Fig. 3.

action, or a very high density of the voids. For the “small bubble” model, this is apparently not a serious problem, since the void-induced low energy state is well localized. The main point of this paper is that voids lead to low-

frequency modes, and contribute (along with extended low-frequency modes) to the vibrational spectrum. Such modes could contribute to thermal conductivity by resonant mixing with each other and acoustic modes.¹³

Also, in connection with the important discoveries of Ref. 6, this paper suggests that indeed the small density of voids in their material should lead to a reduction in low energy (but not tunneling mode energy) vibrational excitations. It is quite possible that the tunneling modes are not directly accessible through the usual harmonic approximation we have invoked here, and require other methods (such as direct dynamical simulation for long times) to be studied.

Note added in proof. We see that the origin of tunneling states from defects (not disorder) has been observed in experiments [X. Liu *et al.* Phys. Rev. Lett. **81**, 3171 (1998)]. Because we see an expected decrease in mode frequency with increasing void size and the “no-friction” material of Liu *et al.* has few voids, we *speculate* that tunneling modes are just very low-frequency void surface excitations of voids larger than we discuss here.

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