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Computer simulation of low-energy excitations in amorphous silicon with voids

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Abstract

We use empirical molecular dynamics technique to investigate the low-energy vibrations in a large 4096 atom model for pure amorphous silicon and a set of models with voids of different size based on it. Numerical vibrational eigenvalues and eigenvectors for our models are obtained by exact diagonalization of their dynamical matrices. Our calculations show that localized low-energy vibrational excitations of rather complex structure are present in amorphous silicon models with voids. According to their spatial localization patterns we make an attempt to classify these excitations as modes associated with the void and 'mixed' modes associated with the interaction of the void with strained regions of silicon network. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Using ab initio molecular dynamics (MD) in a small 216 atom model for amorphous silicon we have recently demonstrated [1] that a spherical void type defect in a-Si network results in localized low energy excitations. To gain a better understanding of the properties of these vibrational modes and verify our previous results we perform computer MD simulations for a large 4096 atom model for a-Si and models with voids constructed from it. Thanks to the large size of the supercell for this model (approximately 4.3 nm) we are able to track the 'void size dependent properties' of the system by building a set of models with bigger and bigger voids, but of course at the expense of losing all the merits of ab initio approach, which makes the calculations too slow for models containing thousands of atoms.

In our current investigation we employ an environment-dependent interatomic potential (EDIP) for amorphous silicon developed by Bazant and Kaxiras [2–4] which enables us to improve the speed of calculations in comparison to ab initio technique. Due to the fact that this potential is relatively new it is interesting to test its accuracy for calculations of vibrational properties of models for a-Si and a-Si with voids, especially on small ones – to verify that EDIP can reproduce (at least, qualitatively) the features we calculate with ab initio method.

In Section 2 of this paper we describe the construction routine for the models we study and the calculation scheme for analyzing their vibrational properties. In Section 3 we discuss the properties of vibrational excitations obtained for 216 atom (for verification purposes) and 4096 atom models and their derivatives with voids, including their spatial localization and dependence on the size of the void. We conclude in Section 4 by giving a summary of our results on computer simulation of low-energy excitations in amorphous silicon.

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2. Models, their construction and calculation scheme

The model construction routine we make use of resembles the one that is described in our previous paper [1] with a single major difference: in its current state EDIP can work only with one atom type – silicon, which makes it impossible to simulate hydrogenated a-Si.

In everything else our model constructing routine works as follows: we employ 4096 atom model for pure a-Si made by Djordjevic et al. [5] (referred to as DTW in what follows) with the help of Wooten et al., bond switching algorithm [6] as a 'base' for building a family of models with voids. The model is relaxed with our MD code with EDIP until the forces on every atom in the system are smaller than 0.01 eV/Å. Then an arbitrary atom [7] is chosen and all the atoms (including the chosen one) within certain radius from it are removed to make a void. After this procedure the model with a void is relaxed once again to obtain its equilibrium configuration, so that the harmonic approximation for the total energy of the system is appropriate. Finally we compute the dynamical matrix of the system by displacing every atom in the cell by 0.03 Å in three orthogonal directions and calculating the originating EDIP forces on all the atoms in the system. Due to the fact that dynamical matrix for a system containing thousands of atoms is huge we have to extensively exploit its sparse nature discarding terms smaller than 10^{-4} eV Å^{-2} aum^{-1}, which in our opinion is a good compromise between the accuracy of the calculation and compactness of the output. Once the sparse dynamical matrix for the system is obtained we use a separate computer program to calculate its eigenvalues and eigenvectors together with their inverse participation ratios (IPR). Again, for the sake of compactness, only low-energy (less than 200 cm^{-1}) eigenvectors with significantly large IPRs – and this is the point of our main interest – are written out.

We make use of gaussian broadened representation for $\sum_i \delta(E - E_i)$, where $E_i, i = 1, \ldots, N$ are the eigenvalues of the dynamical matrix to plot the graphs for vibrational density of states (VDOS) for our system. The width of broadening is 20 cm^{-1} for the 'full scale' graphs and 0.1 cm^{-1} for the close-ups of the low-energy region.

We finish our investigation by creating color or gray scale vibrational activity maps for the 'low-energy, large IPR' modes in exactly the same way that has been already described in Section 2 of Ref. [1].

3. Discussion of results

We begin this section with presenting some testing results for small 216 atom DTW model and 211 atom model with a void constructed from it by removing a single atom from the network together with its four nearest neighbors. The results of our VDOS and IPR calculations are shown in Fig. 1. We note that the model with void has a localized state in the low-energy gap which complies with our previous findings [1] (we neglect all of the hydrogen motion in our a-Si:H model in Ref. [1] while making this comparison because hydrogen atoms do not 'participate' in vibrational excitations of such low energy). It also means that despite the fact that EDIP, comparing to the ab initio calculation, gives us a different low-energy gap edge, it is capable of reproducing the localized low-energy excitations. A 'vibrational activity' colormap for the excitation we see in 211 atom model with void (not shown here) also appears to be in agreement with our previous results.

The graph with a comparison of VDOS calculated for 216 DTW model with ab initio and EDIP is presented in Fig. 2. The experimental results are taken from Kamitakahara et al. [8] In our opinion this figure demonstrates that, at least for simulations of *vibrational* properties of a-Si, EDIP has the same affects as the well known Stillinger–Weber potential [9].

Now we are going to discuss the large 4096 atom DTW model and the family of models with voids based on it. Three models with voids of different size have been built: 4091 atom model with a 'small bubble' (analogous to 211 atom model derived from 216) – a void of approximately 5 Å in diameter, 4069 atom 'medium bubble' model with 10 Å void and 4008 atom 'big bubble' model with 15 Å void. The low-energy region VDOS and IPR close-ups for all the four models are shown in Fig. 3. We do not present 'full scale'

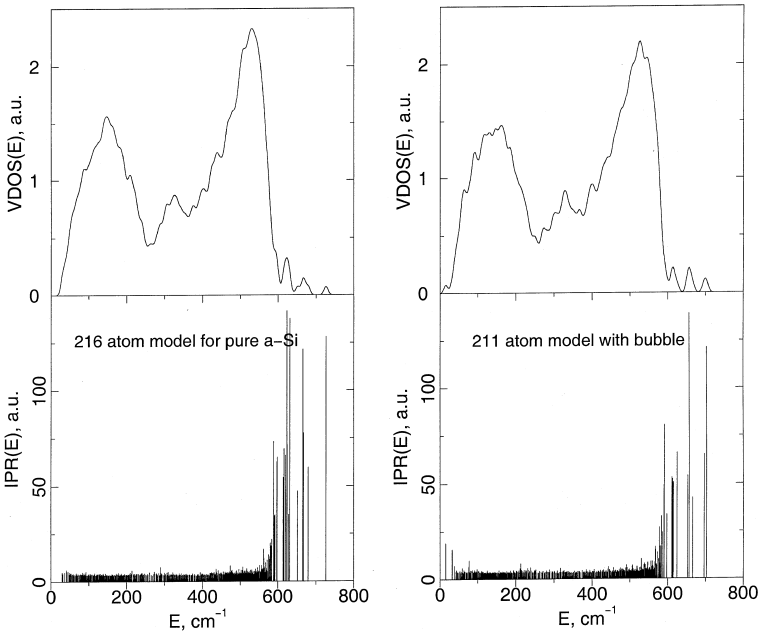

Fig. 1. VDOS and IPR for 'pure' 216 atom DTW model for a-Si (left set of panels) and 211 atom model with void (right set of panels).

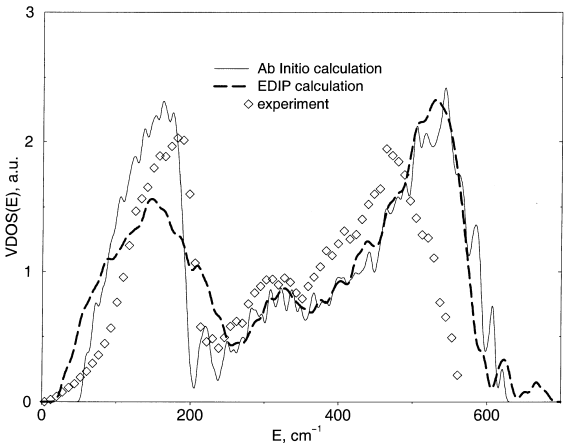

Fig. 2. comparison of VDOS for 216 atom DTW model calculated with ab initio (see Ref. [1]) and EDIP.

VDOS graphs here because (i) in that scale they all look indistinguishable from each other and (ii) generally, VDOS constructed for 4096 atom model doesn't provide much more information than the one of 216 atom model, shown in Fig. 1.

From Fig. 3 we see that the situation with the large models is more complicated than in the case of the family of 216 atom models. First of all, it turns out that 'pure' 4096 atom model has two localized low-energy modes [10] that are most probably associated with strained regions of silicon network. Consequently, we find modes of two major types in our void models: those associated directly with voids and modes produced by mixing of the former ones with localized excitations of the 'pure' model. The modes, associated with voids, have the same kind of localization properties that we have reported earlier [1], localizing to the side of the void, while the modes, produced by mixing, either localize on approximately the same strained regions of the cell as in 'pure' model (although they are not exact copies of the modes observed in 'pure' model, which we attribute to the fact that quenching of the model with void results in different system geometry even in the regions away from the void) or form strings between the strained regions and the void.

Curiously enough to us our data shows that for different models void modes of different types dominate in the low-energy region! In the 'small bubble' model a mode with the largest IPR at 10.58 cm^{-1} is of 'void' type, but the succeeding

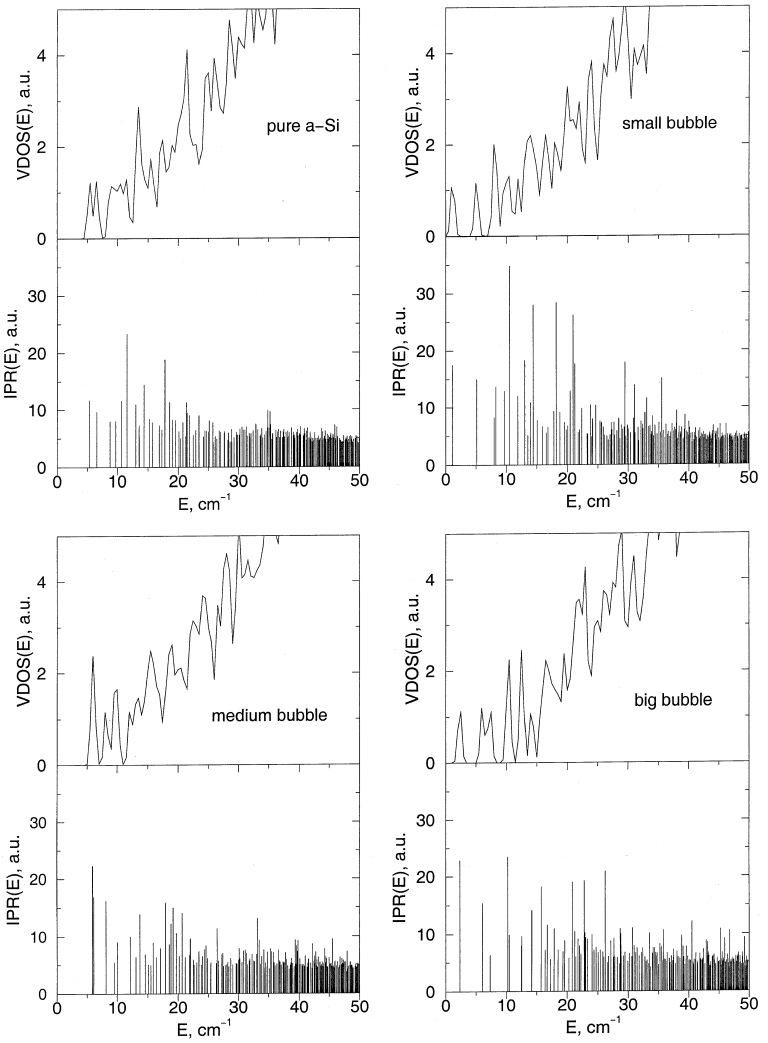

Fig. 3. VDOS and IPR low-energy region snapshots for 'pure' 4096 atom DTW model (upper left set of panels), 4091 atom 'small bubble' model (upper right), 4069 atom 'medium bubble' model (lower left) and 4008 atom 'big bubble' model (lower right).

three modes with large IPR at 14.43, 18.25 and 20.97 cm^{-1} are largely 'mixed' type. In the 'medium bubble' model, to the contrary, all three low-energy localized modes at 5.89, 6.12 and 8.13 cm^{-1} are of 'mixed' type. The mode with 'void' type property is also present but it is shifted to 17.97 cm^{-1}. Finally in the 'big bubble' model modes at 2.34 and 6.10 cm^{-1} are of 'void' type and all the others, including a strongly localized mode at 10.28 cm^{-1}, exhibit 'mixed' type of effects.

For the sake of compactness we have not included any of the colormaps for the 4096 atom family of models in this paper. However a colormap set for particularly interesting vibrational excitations in these models is available for Internet download [11].

4. Conclusions

We have studied low-energy vibrational excitations in 216 and 4096 atom DTW models for amorphous silicon and the families of models with voids based on them, employing the new

Bazant-Kaxiras environment-dependent interatomic potential. Based on the qualitative agreement between the data obtained for 216 DTW model and its derivative with a void and the results of our previous ab initio calculations for the same model we assume that EDIP can be used for probing localized low-energy modes in a-Si models. Our investigation of vibrational properties of 4096 atom model and its void derivatives shows that the latter posses a complex spectrum of localized low-energy excitations that we can divide into two groups – 'void' and 'mixed' type modes – according to their localization patterns. We have also found out that there is no simple dependence between the size of the void and the energy of its 'void' type mode. It seems that not only the size of the void but also the positions of the void and strained regions of the network with respect to each other and the particular network geometry are necessary for an understanding the dominance of modes of a certain localization nature (i.e. 'void' type or 'mixed' type) in some energy intervals.

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