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Studies of the phonon density of states in ab initio generated amorphous structures of pure silicon

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Abstract

Using a 216-atom amorphous periodic cubic supercell generated with the ab initio 'undermelt-quench' procedure previously reported, we have undertaken the study of vibrational properties of pure amorphous silicon, a-Si, with a density of 2.33 g/cm^3. The radial distribution function obtained for the 216-atom random structure agrees with previous results for a 64-atom structure. For the density functional calculation the Harris-relaxed structure was used to obtain the vibrational modes. For the classical calculation the structure, obtained with the Harris functional, was relaxed using the Tersoff potential and the vibrational modes calculated. Both results agree very well with experiment indicating that our amorphous cell closely resembles the real material.
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1. Introduction

The study of vibrational properties of amorphous solids has been somewhat overlooked in contrast to the study of their electronic and optical properties. Experimental studies go back to 1984 when Kamitakahara et al. reported 'the first detailed' inelastic neutron scattering results on the vibrational spectra of a pure a-Si sample [1]. They claimed their results showed that the vibrational features of crystalline silicon, c-Si, were present in the amorphous sample, a-Si, albeit smoothed out due to the lack of periodicity. It was argued that the four major peaks in the phonon density of states, PDOS, for c-Si, conventionally referred to as the TA, LA, LO, and TO peaks, also appeared in the PDOS for a-Si and that there was, overall, a substantial similarity between the two distributions.

Simulationally, the PDOS was one of the first properties of amorphous semiconductors evaluated [2–4] using diverse techniques, such as classical potentials acting on the atoms of hand-generated random networks [5]. Such calculations [2] provided a PDOS in reasonable agreement with the experimental phonon spectra reported for a-Si [1] and for a-Ge [6]. This pioneering work, as relevant as it was, left some questions unanswered. For instance, the amorphous structures on which the calculations were based had been generated ex profeso to fit the experimental radial distribution functions, RDFs, and had no defects like dangling bonds, just distorted bonds and angles. Even recent work [7] on related subjects relies on 216-atom 'perfect' structures generated by hand according to the well known Wooten, Winer and Weaire method [8]. Furthermore, of the two prominent peaks of the PDOS, the simulated results indicated that the more energetic peak was more pronounced whereas experiment indicated the opposite. Finally, the simulated peaks were displaced to higher energies with respect to the experimental ones [1].

Within the supercell approximation the study of the vibrational properties of amorphous materials involves two main aspects. First, one has to generate an amorphous structure that closely represents the bulk material, and second, you have to find an efficient manner to calculate – and diagonalize – the vibrational matrix; the larger the number of atoms the more representative the supercell becomes. We shall concentrate on the first aspect, although there are recent developments, within the tight binding (TB) approximation, that use force algorithms of $O(N)$ allowing the study of supercells with thousands of atoms [9]. The methods to generate random structures are varied: some use static models generated ad hoc to fit the experimental RDFs, as mentioned above, some use empirical potentials and some use ab initio techniques that are parameter free but computationally costly.

The first quantum–mechanical, parameter-free, molecular-dynamic calculation of the PDOS is that due to Car and Parrinello [10] who computationally generated amorphous structures by melting (2200 K) an otherwise crystalline fcc supercell with 54 atoms, and after the liquid evolved they quenched it to 300 K (an example of a melt-and-quench process), and thermally treated it. Then they proceeded to calculate the PDOS and found that it was reasonably similar to the experimental results of Ref. [1], but systematically displaced towards higher energies. The ab initio generation of structures followed this pattern with variants like the one due to Drabold et al. [11] where they start with a $(64 - 1)$-atom diamond supercell with a vacancy 'to assure that the system does not quench into the diamond structure'. They melt the sample to temperatures of 8000 K and, after allowing the cell to freely evolve until it is very disordered, they dynamically quench it to find local minima in the cells' electronic total energy for each of several preparation times. This method is of the melt-and-quench type, with varying degrees of disorder. The agreement of their PDOS and experiment is difficult to appreciate since the experimental results are not included in their paper. Another attempt at the ab initio study of the structure and vibrations of amorphous silicon is the TB approach of Feldman et al. [12] where a 216-atom diamond cell is amorphized by two methods: in one method they relax the sample, and in the second method, they carry out a melt-and-quench process. The agreement of their vibrational results with Ref. [1] is only good for the low frequency TA peak.

Instead of melting and quenching crystalline samples we decided, several years ago, to use a different procedure that avoids the presence of liquid features in the amorphous supercells and this has led to good results. We have generated amorphous structures of covalently bonded materials like silicon and hydrogenated silicon [13], germanium, carbon, silicon–nitrogen and carbon–nitrogen alloys, as well as for porous silicon and carbon, whose RDFs and coordination numbers agree quite well with experiment. We have also explored the predictive power of our method by calculating RDFs for alloys that at present have not been studied experimentally. In the process we devised a semiempirical method to determine the optical gaps of the ab initio Si–N structures and the results are in agreement with experiment (see Refs. [14]).

In the present work we report the ab initio generation of the 216-atom amorphous sample and the calculations, both classical and quantum, of its vibrational properties. The agreement of our present results with experiment and with previous work is very good.

2. The amorphizing procedure; the undermelt-quench method

The *undermelt-quench* process that we devised randomizes the crystalline supercell by heating it to just below the melting point of the corresponding crystalline material, then quenching it to 0 K, and removing the stresses afterwards by applying annealing and quenching cycles to the amorphized sample. Finally we relax its geometry. This is based on the fact that for semiconductors the glass transition temperature is at least tens of degrees below the melt and amorphous structures can be found at these temperatures.

As in our previous work [13,14] we employ a quantum molecular dynamics approach developed originally by Harris to rapidly obtain the structures of atomic aggregates. These aggregates are initially disrupted randomly, then heated using molecular dynamics to foster the rearrangement of their atomic constituents, and finally cooled down to what would be the structure of minimum energy, at least locally. The code uses the Harris functional [15] and therefore the process is not self consistent. The linear combination of atomic orbitals utilized makes the minimum-energy atomic structures very close to those found experimentally. As a benchmark, the interatomic distances fall within 1% of the experimental ones for a large variety of small molecules [16,17]. This is the essence of FASTSTRUCTURE SIMANN [16] (FAST for short) the code developed by Harris. Rather than using this code to find the minimum-energy atomic structure of a periodic cell, we use it to generate random structures from an originally crystalline supercell with periodic boundary conditions.

Our crystalline, diamond-like supercell, with 216 atoms and an experimental density of 2.33 g/cm³, is amorphized by linearly heating it using FAST, from 300 K to 1680 K (a value below the melting temperature) in 100 steps of 10 fs and immediately cooling it down to 0 K in 122 steps. In this manner we avoid melting the system and then quenching it from the molten state. The atoms were allowed to move within each cell with periodic boundary conditions, whose volume was determined by the experimental density. We next subjected it to annealing cycles at 300 K, with intermediate quenching steps down to 0 K. At the end of these processes a geometry optimization was carried out to find the amorphous structures with a local energy minimum.

Once the geometry-optimized structure is found two procedures are followed. For the classical calculations we opti-

mized the amorphous structure again using the Tersoff potential option in the OXON package [18] to assure consistency. The Tersoff potential is an empirical interatomic classical potential designed for covalent systems [19] that uses a set of adjustable parameters and is specially tuned for silicon. The OXON package is a TB program developed at the Department of Materials at Oxford University that includes the Tersoff potential both for geometry optimization and for frequency calculations. For the quantum calculations we used the Harris option within the density functional approach in the DMol3 code of the Materials Studio suite of programs [20]. Once the relaxed structures are obtained, we proceed to calculate the dynamical matrix by displacing every atom in the amorphous supercell in three orthogonal directions (0.03 Å both ways for a given direction) and the second derivatives of the total (classical or quantum) energy are evaluated. From these derivatives the spring constants are calculated, and the frequencies can be deduced after diagonalizing the dynamical matrix [21].

3. Results and discussion

Fig. 1 shows the results due to Kamitakahara et al. compared to the simulated crystalline and amorphous PDOS

(see Ref. [1]), where as mentioned before the following observations are pertinent:

- The amorphous structures on which the calculations were based were generated *ex profeso* to fit the experimental RDFs, and had no defects like dangling bonds, only distorted bonds and angles.
- Of the two prominent peaks of the PDOS, the simulated results indicate that the more energetic peak was more pronounced, whereas experiment indicates the opposite.
- Finally, the simulated peaks are displaced to higher energies with respect to the experimental ones.

It is clear then that the early simulations and the experiment do not agree.

Our aim now is to show that our a-Si structure has an RDF that agrees with the 64-atom RDF previously reported by us [13], and that its vibrational spectrum is very similar to experiment, whether we calculate it classically or quantum mechanically.

In Fig. 2 we present the RDFs both for the 64-atom amorphous supercell of Ref. [13], and for the 216-atom supercell of this work. The agreement is evident. Ref. [13] has also a calculation of the electronic density of states for the 64-atom a-Si sample. Fig. 3 presents the comparison of the calculated classical PDOS for our amorphous supercell using the Tersoff potential and the experiment. The simulational results for the quantum Harris approach and its comparison with experiment is given in Fig. 4.
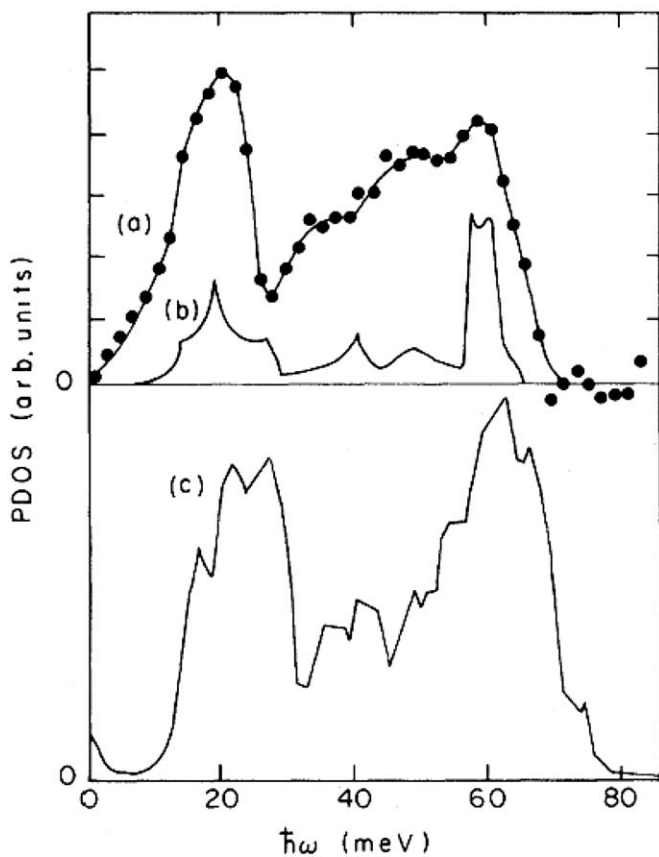

Fig. 1. Curve (a) is the experimental PDOS for a-Si as determined by Kamitakahara et al. [1], compared to (b) a c-Si calculation of the PDOS and (c) an a-Si 61-atom simulation [2]. The vertical units are arbitrary. Figure taken from Ref. [1].
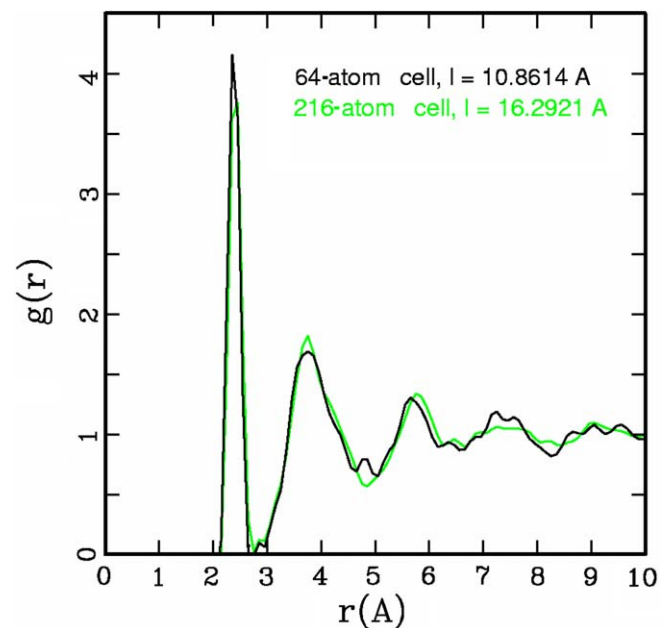

Fig. 2. RDFs for two amorphous silicon samples, the dark curve is for the 64-atom sample [13] and the light one (light gray – green in the Web version) is for the 216-atom sample. Both were prepared using the undermelt-quench method. The edges of the cubic supercells are shown. The agreement is clear.
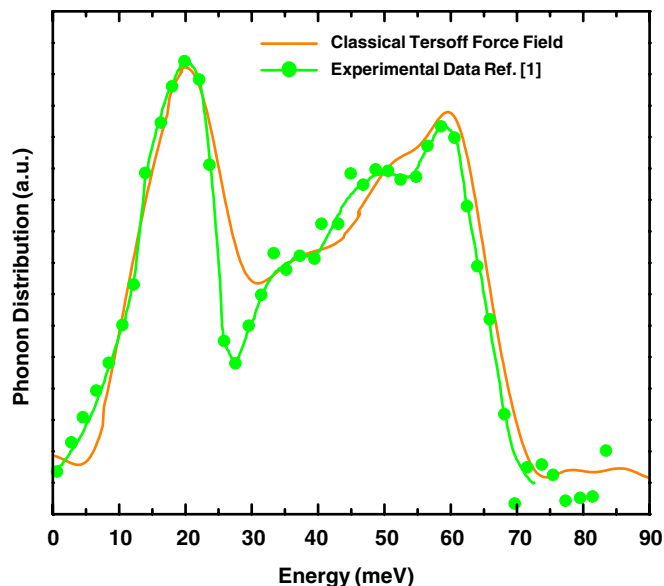
Fig. 3. Classical PDOS for the 216-atom amorphous network (dark gray curve – orange in the Web verison), compared to experiment (light gray dotted curve – green in the Web version) [1]. The position, relative heights of the peaks and overall shape agree.

Fig. 5. Comparison between the quantum (Harris) (dark curve) and the classical (Tersoff) (light gray curve – orange in the Web version) PDOS for the 216-atom ab initio generated amorphous network.

4. Conclusions

Summarizing:

- Our frequency calculations are based on random structures generated ab initio using the undermelt-quench approach.
- The heights of the two prominent peaks of the PDOS from both experiment and simulation essentially coincide.
- The positions of the two prominent peaks are essentially the same for simulation and experiment. The first peak of the Harris calculations is somewhat displaced towards *lower* energies.
- In the region 30–50 meV the Harris simulation agrees better with experiment.

Clearly, the agreement of our classical and quantum results with experiment is better than those shown in Fig. 1, and better than previous ab initio results. This agreement indicates that our 216-atom amorphous structure adequately describes the material used in Ref. [1]. Since all calculations referred to here are always compared to the results of Kamitakahara et al. it seems evident that more experimental work is needed. Work is in progress to discern the influence of bonding and structure on the calculated spectra.
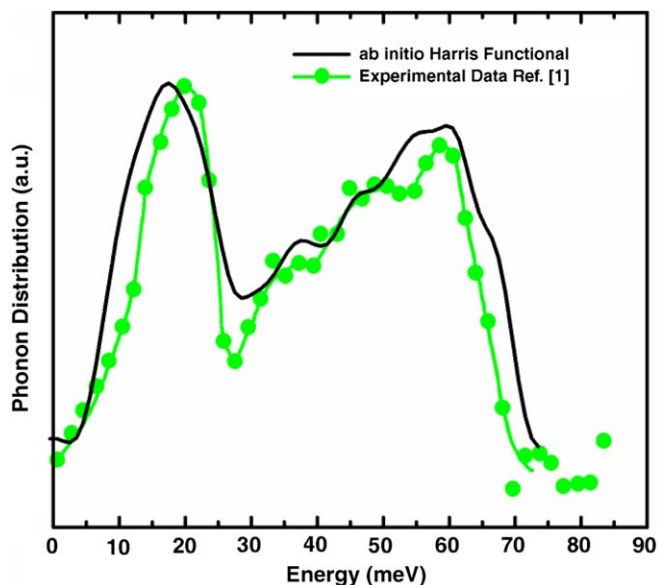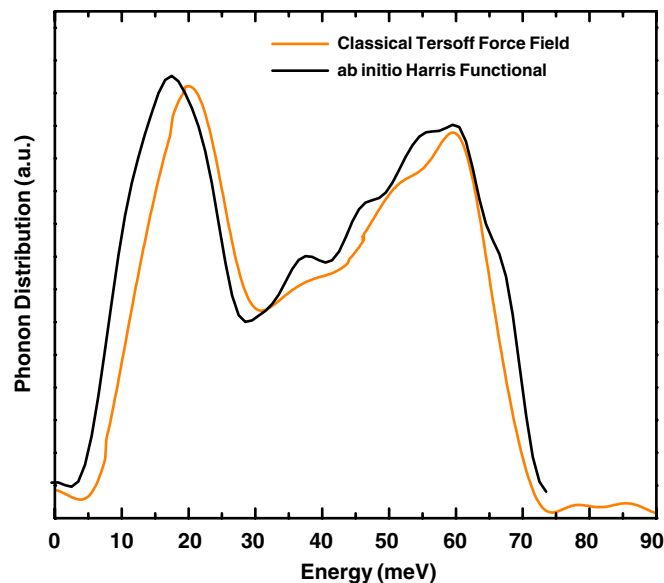

Fig. 4. Quantum PDOS for the 216-atom amorphous network (dark curve), compared to experiment (light gray dotted curve – green in the Web version) [1]. The position, relative heights of the peaks and overall shape agree.

Finally, Fig. 5 shows the agreement of the Tersoff classical simulational result and the Harris quantum–mechanical simulational result. A three point FFT smoothing has been used throughout.

It is clear then that our results, both classical and quantum, agree quite well with experiment. A point worth mentioning is that both classical and quantum results present low energy frequencies modes; the experimental results also have low lying states.

Acknowledgements

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