

Inverse approach to atomistic modeling: Applications to a-Si:H and g-GeSe₂

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Abstract

We discuss an inverse approach for atomistic modeling of glassy materials. The focus is on structural modeling and electronic properties of hydrogenated amorphous silicon and glassy GeSe₂ alloy. The work is based upon a new approach ‘experimentally constrained molecular relaxation (ECMR)’. Unlike conventional approaches (such as molecular dynamics (MD) and Monte Carlo simulations (MC), where a potential function is specified and the system evolves either deterministically (MD) or stochastically (MC), we develop a novel scheme to model structural configurations using experimental data in association with density functional calculations. We have applied this approach to model hydrogenated amorphous silicon and glassy GeSe₂. The electronic and structural properties of these models are compared with experimental data and models obtained from conventional molecular dynamics simulation.

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1. Introduction

In conventional electronic structure problem one starts with a formulation of a model that consists of a set of atomic or molecular coordinates and an interacting potential or Hamiltonian. The electronic density of states is obtained either by solving the Schrödinger equation within the first-principles density functional formalism or by constructing a semi-empirical Hamiltonian to compute the electronic eigenstates, total energy, and response functions to compare with experiments [1]. For a crystalline system, such an approach is fairly straightforward (at least in principle), although in many cases it can be computationally very expensive. Disordered materials, however, pose the problem that is highly non-trivial due to lack of structural information about the materials. Amorphous materials are

archetypal examples of this class, which are characterized by presence of short and medium range order ranging from few angstroms to several nanometers [2]. Since the position of an atom is not known in the amorphous state, one needs to proceed by simultaneously optimizing the geometry and calculating the electronic properties and structure for that geometry. While there exists a number of methods that can address this problem with a varying degree of accuracy (such as Car–Parrinello [3] and first-principles molecular dynamics [1]), almost all cases where the problem is characterized by long time and large length scale, these techniques are computationally overkill and largely inapplicable for problems that require realistic modeling of complex amorphous systems. The so-called order- N methods (that scale linearly with system size N) can deal with large number of atoms; however, their use is often severely limited in structural modeling of amorphous materials due to lack of knowledge in spectral properties (e.g. the nature of density matrix and the presence of spectral gap). First-principles molecular dynamics is, therefore, not practically

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viable for large scale modeling that are necessary to study some of the novel properties of materials associated with amorphous state (such as medium range order and diffusion in glasses). The use of empirical potentials make it possible to run molecular dynamics simulation for several thousands atoms with a time scale of the order of several nanoseconds, but for many complex systems empirical potentials are not reliable enough to describe the geometry and local chemistry correctly.

In this paper, we discuss applications of an alternative approach to model materials using a combination of experimental data and a suitable force-field (either first-principles, tight-binding or empirical). Instead of taking a direct approach, we take an inverse approach where experimental data are enforced to build atomic configurations that have the desired structural and electronic properties. Reverse Monte Carlo (RMC) is a classic example of such a method that has been discussed by several authors [4–7]. Here we briefly mention an extension of reverse Monte Carlo by merging experimental data using a suitable force-field known as experimental constrained molecular relaxation (ECMR), and discuss its application to hydrogenated amorphous silicon and glassy GeSe₂.

2. Experimentally constrained molecular relaxation (ECMR)

The reverse Monte Carlo (RMC) method developed by McGreevy and colleagues is a classic example of an inverse problem in materials modeling [4]. The method constructs a model configuration by making use of all available experimental information. The central idea is to set up a generalized cost function containing as much information as possible, and then to minimize the function for generating configurations toward exact agreement with one or more experiments. In order to reduce the solution space and to explore a limited part of physical subspace of configuration, a number of chemical, geometrical and topological constraints can be added. The mathematical structure of this problem is equivalent to the constraint optimization ‘traveling salesman’ problem

$$\xi = \sum_{j=1}^K \sum_{i=1}^{M_K} \eta_i^j \{F_E^j(Q_i) - F_c^j(Q_i)\}^2 + \sum_{l=1}^L \lambda_l P_l. \quad (1)$$

The coefficients η_j and λ_j are the appropriate weight factors for each data set (F) and the constraints (P). The quantity Q is the appropriate generalized variable associated with experimental data $F(Q)$. In order to prevent the atoms getting too close to each other, a certain cutoff distance is imposed, which is typically of the order of interatomic spacing. RMC has been applied successfully to variety of materials [4]. However, the principal difficulty is the lack of uniqueness of the method. In absence of information from high order correlation functions, the method produces a range of configurations that are consistent with input experimental data, but may not be physically

meaningful. The imposition of topological or chemical constraints can ameliorate the problem, but cannot eliminate completely.

The experimentally constrained molecular relaxation (ECMR) has been designed to overcome some of the problems above [8]. Instead of relying on experimental information and a set of constraints only, one additionally employs an approximate energy functional to describe the dynamics correctly by merging first-principles density functional (or semi-empirical) as well as experimental data. The purpose of the energy functional is to guide the system *approximately* in the augmented configurational space defined by experimental data and other constraints. This largely reduces the number of unphysical solutions that are mathematically correct but fail to satisfy the dynamical behavior correctly. Introduction of an approximate energy functional constrains the system to evolve on a restricted *but* more realistic energy surface, and thereby accelerates to converge toward reliable structural configurations during the course of simulation. The configuration obtained from the method is not only a minimum (metastable or global) of an appropriate energy functional but also consistent with the input experimental information. Symbolically, we can write the grand penalty function in the ECMR as

$$\Xi(\mathbf{Q}, \mathbf{r}) = \xi(\mathbf{Q}) \oplus \gamma E(\mathbf{r}). \quad (2)$$

In Eq. (2), the symbol \oplus stands for direct sum of the configuration space of penalty function $\xi(\mathbf{Q})$ and that of the energy functional $E(\mathbf{r})$ [9]. In the limit γ is infinitesimally small, the method reduces to a inverse method (RMC in the present case), whereas for a very large value of γ the method is equivalent to a direct method of minimizing the total energy.

3. Applications: glassy GeSe₂ and a-Si:H

Amorphous GeSe₂ is a classic glass former and has interesting physical properties that are difficult to model via conventional molecular dynamics simulation [10]. The material strongly shows the presence of intermediate range order in the form of a first sharp diffraction peak (FSDP) in neutron diffraction measurements. The origin of this intermediate range order is generally attributed to the presence of tetrahedral motifs having edge- and corner-sharing topology. Raman spectroscopy and neutron diffraction provide useful information about the topological structure of the material [11,12]. The GeSe₂ model simulated in our ECMR work consists of 647 atoms. The static structure factor (neutron-weighted) of the final model is plotted in Fig. 1 along with the experimental data and the data obtained by Cobb et al. in Ref. [10]. It is clear from the figure that experimental data fit with the theoretical values obtained from ECMR model reasonably good. The structure at large Q matches quite well, but at small Q there exists deviations from the experimental peak position.

Since the network topology of g-GeSe₂ is very much influenced by the presence of edge- and corner-sharing

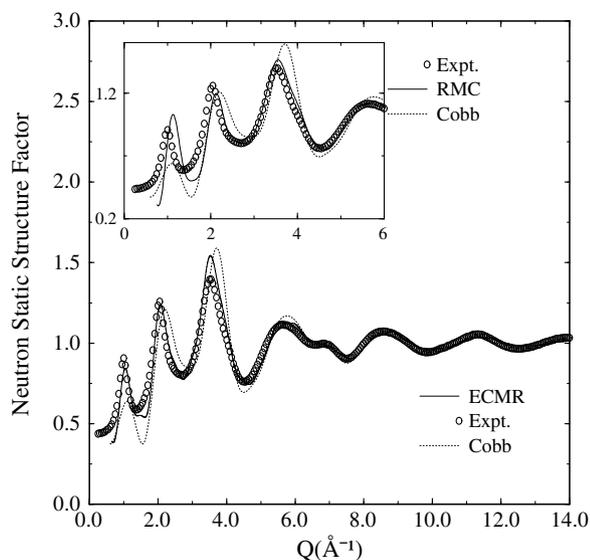


Fig. 1. Neutron-weighted static structure factors for the ECMR, reverse Monte Carlo (RMC) and decorate-and-relax (DR) model. The result for the DR model is taken from Ref. [10]. The low wave vector part is magnified in the inset for comparison to our model with experimental data and the DR model.

tetrahedra, we have studied the presence of such tetrahedra in our model. As mentioned before, Raman and neutron experiments [11,12] revealed that about 33–40% of Ge atoms are involved in forming edge-sharing tetrahedra. The corresponding percentage in our model is found to be 38%. This is particularly important in view of the fact that such information is not included in our starting ECMR model. It is remarkable to note that imposition of partial pair correlation functions and first-principles relaxation via ECMR does introduce the correct topological structure in the network. We have also observed that 81% of Ge atoms in our model are 4-fold coordinated of which approximately 75% form predominant Ge-center motifs $\text{Ge}(\text{Se}_{\frac{1}{2}})_4$ while 6% are ethane-like $\text{Ge}_2(\text{Se}_{\frac{1}{2}})_6$ units. The remaining Ge atoms are 3-fold coordinated and are mostly found to be bonded as Ge–Se₃ units. The experimental radial distributions (partial) provide the partial nearest neighbor coordination number. The values for Ge–Ge, Ge–Se and Se–Se are given by 0.25, 0.20 and 3.7, respectively, whereas the corresponding values from our ECMR model are 0.17, 0.30 and 3.68, respectively. In addition to studying the structural properties, we have also computed the electronic properties of the model. The electronic density of states provide an additional check and can be compared with X-ray photo emission data (XPS). In Fig. 2, we have plotted the electronic density of states along with the experimental data. The electronic density of states of the ECMR model (shown in the inset) are in good agreement with the XPS data, and establishes further credibility of our method.

We have also applied our ECMR approach to model hydrogenated amorphous silicon. For this purpose, we started with a pure amorphous silicon configuration

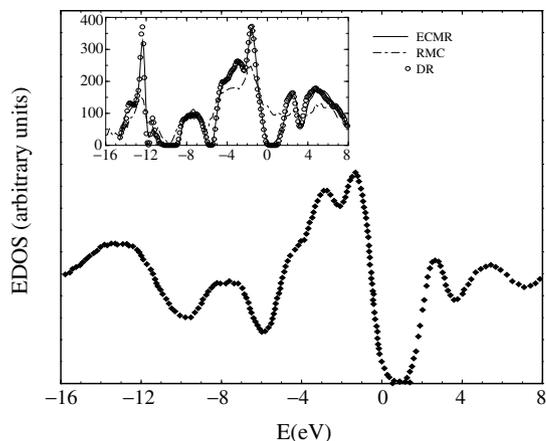


Fig. 2. The experimental and computed electronic density of states (inset) of g-GeSe₂. The results for models obtained from the ECMR, reverse Monte Carlo (RMC), and decorate-and-relax (DR) are shown in inset. The results for the DR model are taken from Ref. [10] for comparison.

obtained via Reverse Monte Carlo simulation. The particular RMC scheme to generate amorphous silicon is discussed in Ref. [13]. The initial size of the model is 500 atoms, which is then hydrogenated following a method similar to but not identical to Holender and Morgan [14]. In our scheme, the dangling bonds are passivated by introducing H atoms in the RMC-generated continuous random network. Once the dangling bonds are identified, passivation is done by placing a H atom at a distance of 1.45 Å to 1.65 Å. The atoms are placed along the direction vector opposite to the sum of the three vectors connecting the central atom and its three neighbors. Once the passivation is done, the density of the model is adjusted to experimental density and the system is subjected to ECMR iteration to make the resulting configuration consistent with both experimental data and the total energy. Any additional dangling bonds generated during ECMR iteration are also passivated, and the process is repeated until the dangling bonds cease to exist. The resulting model of hydrogenated amorphous silicon consists of 540 atoms with 7.4% H atom in the network. The model has defect concentration of about 2%, which consists of 5-fold coordinated floating bonds.

The partial radial distribution functions for the model are plotted in Fig. 3. For the Si–Si case, most of the information are already included in the starting model, and hence we do not expect much changes in the final model. For Si–H part, however, it is important to note that during hydrogenation and subsequent relaxation of the model via ECMR, the system does not change much of the pair correlations between Si and H atoms. The electronic density of states (EDOS) for this 540-atom model is plotted in Fig. 4. The EDOS is obtained using the first-principles density functional code SIESTA within the local density approximation. The model clearly shows the presence of a gap in the spectrum along with a few tail states near the band edges. This is due to presence of few 5-fold floating bonds in the

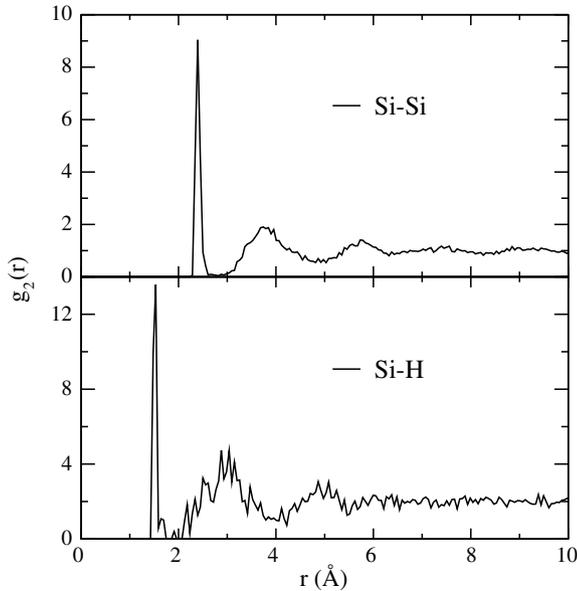


Fig. 3. The partial pair correlation functions for Si-Si (upper panel) and Si-H (lower panel) atoms for the 540-atom ECMR model described in the text.

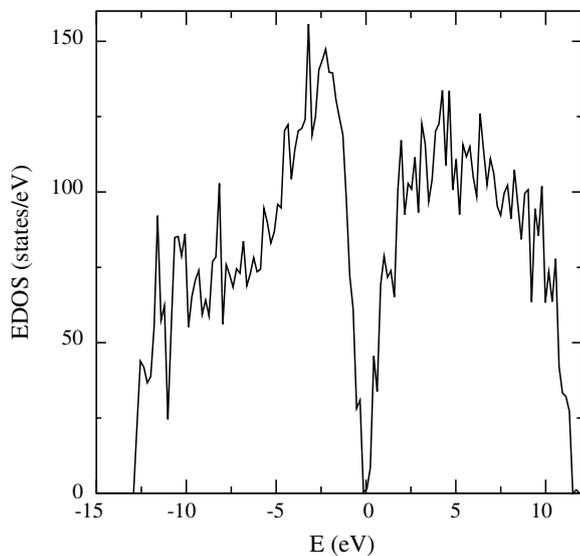


Fig. 4. The electronic density of states of the 540-atom model of a-Si:H obtained from ECMR method within the local density approximation. The band gap is clearly visible in the spectrum along with a few tail states originated from the floating bonds present in the network.

network. As a further test of our model, we have also computed the vibrational density of states (VDOS) within the harmonic approximation by constructing the dynamical matrix using the electronic forces. The eigenvalues of the dynamical matrix are related to the square of the angular frequency of vibrations. The VDOS in Fig. 5 distinctly show the presence of acoustic and optical peaks due to vibration of Si atoms. The high frequency vibrations in the density of states correspond to the H atom movement in the network (see Fig. 5).

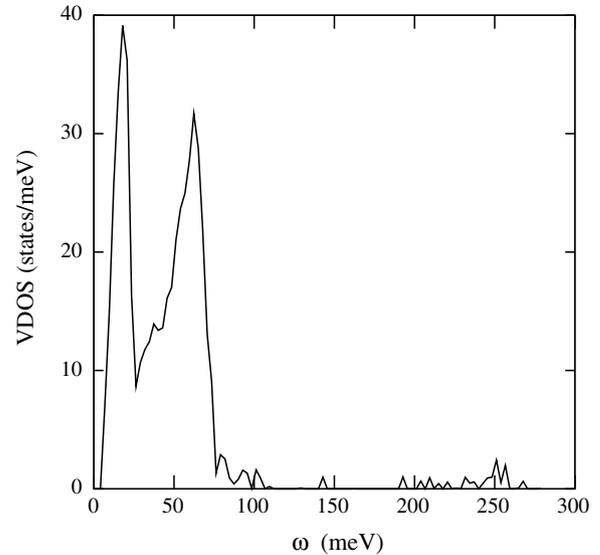


Fig. 5. The vibrational density of the 540-atom model a-Si:H obtained within the harmonic approximation. The high frequency vibrations correspond to H atom movement in the network. The acoustic and optical peaks are clearly visible in the vibrational spectrum.

4. Conclusion

We present an inverse approach to construct atomistic models of materials using a combination of experimental data and a suitable first-principles force-field. Using a generalized penalty function, we merge both the power of density functional theory with experimental data so that the configurations are not only a minimum (metastable or global) of an energy functional but also consistent with available experimental data. The method is applied to construct model configurations for two technologically important materials: glassy GeSe₂ and hydrogenated amorphous silicon. The structural, electronic and vibrational properties of the models are compared with experiments, and have been observed to be in very good agreement with experimental data.

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