

# Force-enhanced atomic refinement: Structural modeling with interatomic forces in a reverse Monte Carlo approach applied to amorphous Si and SiO<sub>2</sub>

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We introduce a structural modeling technique, called force-enhanced atomic refinement (FEAR). The technique incorporates interatomic forces in reverse Monte Carlo (RMC) simulations for structural refinement by fitting experimental diffraction data using the conventional RMC algorithm, and minimizes the total energy and forces from an interatomic potential. We illustrate the usefulness of the approach by studying *a*-SiO<sub>2</sub> and *a*-Si. The structural and electronic properties of the FEAR models agree well with experimental neutron and x-ray diffraction data and the results obtained from previous molecular dynamics simulations of *a*-SiO<sub>2</sub> and *a*-Si. We have shown that the method is more efficient than the conventional molecular dynamics simulations via “melt quench.” The computational time in FEAR has been observed to scale quadratically with the number of atoms.

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## I. INTRODUCTION

An ideal approach to computational modeling of complex amorphous materials should incorporate state-of-the-art total-energy and force methods and a judicious application of *a priori* information—experimental data pertaining to the material. When these schemes are suitably merged, the resulting structural models should reflect our full state of knowledge about the material. Conventional molecular dynamics (MD) simulations of amorphous materials suffer from several difficulties. Most serious of all is the high computational cost associated with simulating large models using quantum-mechanical methods, such as *ab initio* molecular dynamics (AIMD) based on the density-functional theory. Further, for amorphous solids with *weak* or no *glassy* behavior (e.g., *a*-Si and *a*-Ge), AIMD performs poorly, which requires the development of other approaches to address these materials. Similarly, computational approaches that attempt to construct structural models of amorphous solids by inverting experimental data, along with the local chemical and geometrical ordering of the networks, often fail. Such *inverse* approaches crucially rely not only on the quality and availability of experimental information, but also on the ability of the approaches to effectively include *a priori* information in simulations. An archetypal example is the reverse Monte Carlo (RMC) method [1,2], which constructs a three-dimensional model of a material by inverting the experimental diffraction data. While RMC is very simple to implement and has been used to model a variety of disordered solids [3–5] (e.g., glasses, liquids, polymers, etc.) in the past, the very scalar nature of diffraction data dictates that the method cannot be used to uniquely determine the structure of amorphous solids using diffraction data only. This has led to the development of a number of hybrid approaches that successfully couple a total-energy functional (quantum mechanical or otherwise) with *a priori* information. To this end, the purpose of this paper is to present a hybrid approach that effectively imposes *a priori* information on a simulation process.

Logically, one should include as much *a priori* information as possible from experimental data, as well as from chemical and geometrical knowledge of the material, to produce

structures consistent with experiments [6]. Compelling “uniformity” as a constraint, for the refinement of the atomistic-scale structures, was adopted by Goodwin and co-workers in their invariant environment refinement technique [7]. A liquid-quench procedure, combined with a hybrid reverse Monte Carlo (HRMC) approach, which incorporates both experimental and energy-based constraints, has been employed by Opletal and co-workers in their study of amorphous carbon [8]. A similar approach via HRMC with bonded and nonbonded forces was used by Gereben and Pusztai to study liquid dimethyl trisulfide [9]. Likewise, by refining the initial interatomic empirical potential-energy function and fitting the input experimental structure-factor data, empirical potential structure refinement (EPSR) has been quite successful in predicting liquid structures [10]. An alternative approach, experimentally constrained molecular relaxation (ECMR), which incorporates experimental information in first-principles modeling of materials in a “self-consistent” manner, was discussed in Ref. [11]. The approach presented in this paper provides an alternative scheme to develop a self-consistent implementation of the ECMR with a minimal computational overhead. Recently, a means for including *electronic a priori* information has also appeared [12].

In this paper, we report a structural modeling technique, called force-enhanced atomic refinement (FEAR). To test the effectiveness of this approach, we have conducted structural modeling of *a*-SiO<sub>2</sub> and *a*-Si. Our method uses RMC to fit the input experimental data and parsimoniously employs interatomic forces obtained from (classical) total-energy functionals to restrict the search in the energetically favorable region of the configuration space in a self-consistent manner. Unlike other hybrid approaches [8,9], where the total energy of the system is coupled to RMC for accepting and rejecting atomic moves, the movement of the atoms in FEAR, due to interatomic forces, is independent of the RMC moves. This enhances the efficiency of the method by reducing the total computational cost associated with force calls. The computational efficiency of the technique has been studied by comparing the number of force calls with other MD approaches.

The rest of this paper is organized as follows. In Sec. II, we describe the basics of the FEAR method and its implementation. Section III discusses the results for  $a$ -SiO<sub>2</sub> and  $a$ -Si. In Sec. IV, we present the conclusions of our work.

## II. METHODOLOGY: BASICS OF FEAR AND ITS IMPLEMENTATION

A review of reverse Monte Carlo (RMC) [1,3,4,8,11] and related methods suggests that diffraction data alone are insufficient to determine the structure of complex amorphous solids. This is particularly so for amorphous semiconductors, where the presence of directional bonding cannot be inferred directly from one-dimensional diffraction data only. While the inclusion of structural constraints proves to be particularly useful in RMC simulations [13], they do introduce additional complexities in the search space. For multicomponent systems, this can be a serious impediment and, in some cases, may render the problem intractable, even with gradient information. The choice of appropriate constraints itself can be highly nontrivial. Owing to the hierarchical nature of the geometrical/structural constraints in complex disordered systems, it is generally beneficial to include lower-order constraints first, which are followed by higher-order constraints of increasing complexity and information content. However, the presence of too many constraints can be detrimental to a problem due to the competition between the constraints. Such competing constraints can adversely affect the efficiency of a search procedure by introducing a complex rugged structure in the multidimensional configuration space, which makes it difficult for the optimizer to evolve and thus to determine the optimal solution space for a structural determination. Further, the correct structural solutions often crucially depend on the strength of the constraints (i.e., weight factors), which are generally obtained heuristically after several trial runs in optimizations based on stochastic search algorithms. Thus, the determination of the structure of complex disordered solids from a set of experimental data and structural/geometrical constraints continues to pose a challenging problem in condensed-matter sciences.

In the present approach, we intend to avoid some of these difficulties by introducing the following steps: (i) optimization of total-energy and penalty functionals in a separate subspace; (ii) inclusion of gradient information to optimize the total-energy functional; and (iii) incorporation of special atomic displacements to enhance the convergence of total energy during subspace optimization by moving a set of atoms associated with strained local configurations. Step I essentially eliminates the need for weight factors that are necessary for the optimization of an augmented “effective energy” functional. Instead, subspace optimizations proceed in tandem with each other and thereby establish a “coupling” between steps I and II. Unfavorable configurations, which are generated in step I, are either corrected or rejected in step II and vice versa. We emphasize that the approach is highly flexible; the exact implementation of the method can vary and may depend on the degree of accuracy and the efficiency one needs to achieve in optimizing models with several hundreds of atoms. While a number of sophisticated algorithms can be employed for subspace optimizations (such as deterministic conjugate-gradient [14] type

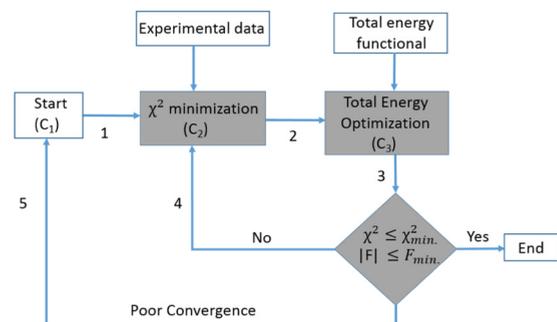


FIG. 1. (Color online) A schematic diagram of the FEAR method. The principal computing loop is highlighted in gray.

approaches to stochastic exchange-replica Monte Carlo [15] and evolutionary search procedures [16]), for the sake of simplicity and exploring the efficacy of this approach at its basic level, we confine ourselves to the steepest-descent method and reverse Monte Carlo approach for optimizing the total-energy and experimental structure-factor data, respectively. We show that even at this elementary level of implementation, the method is profitable and holds promise for further development using the state-of-the-art multiobjective optimization (MOO) techniques developed in recent years. Thus, in the FEAR approach, the statement of the problem can be written as

$$\min_{\{q\}} P(\{q\}), \quad P \equiv \chi^2 \otimes \Phi, \quad (1)$$

where  $\Phi$ ,  $\chi^2$ , and  $\{q\}$  stand for a total-energy functional, a penalty function involving experimental structure factor, and  $3N$ -dimensional configurational coordinates, respectively. Following McGreevy and others [1,5], we can write

$$\chi^2 = \sum_i \left[ \frac{F_E(k_i) - F_C(k_i)}{\sigma(k_i)} \right]^2, \quad (2)$$

where  $F_{E/C}(k_i)$  is the experimental/computational structure factor, and  $\sigma(k_i)$  is the error associated with the experimental data for wave vector  $k_i$ .

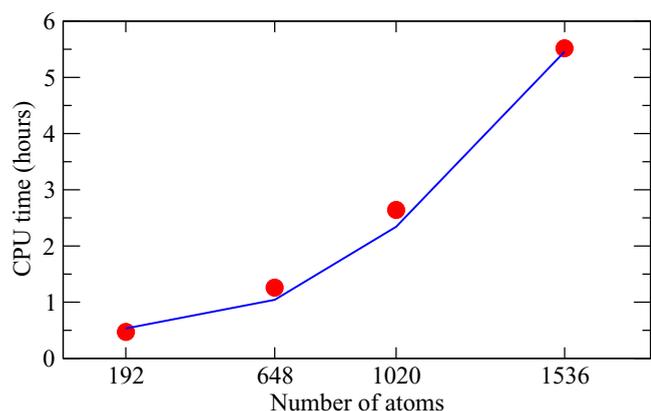


FIG. 2. (Color online) Scaling of total CPU time (red circles) vs system size in FEAR simulations. A least-squares fit of the data with a quadratic polynomial is shown as a blue curve.

TABLE I. Number of force calls and average CPU time in FEAR compared with classical and quantum melt-quench methods [25,26].

	192-atom	648-atom	1020-atom	1536-atom	CPMD [25]	Classical MD [26]
Number of force calls	$3 \times 10^4$	$3 \times 10^4$	$3 \times 10^4$	$3 \times 10^4$	$27 \times 10^4$	$6 \times 10^4$
CPU time (h)	0.47	1.26	2.64	5.52		

To illustrate our method, we have chosen two canonical examples of amorphous systems: amorphous silica ( $a\text{-SiO}_2$ ) and amorphous silicon ( $a\text{-Si}$ ). The former is a classic glass former, and can be readily obtained by quenching molten models at high temperature. The latter is preferably modeled via event-based approaches, such as Winer-Wooten-Weaire (WWW) [17] and activation-relaxation techniques [18]. Both systems have been studied extensively in the literature, which provides a wealth of information for comparing experimental data with computational results for various physical quantities. Here, we choose to employ the environment-dependent interatomic potential (EDIP) by Justo *et al.* [19] for modeling  $a\text{-Si}$ . For  $a\text{-SiO}_2$ , we choose the potential proposed by Beest *et al.* (BKS) and their parameters [20]. The functional form of the BKS potential is given by

$$\phi_{i\alpha,j\beta} = \frac{Q_\alpha Q_\beta}{r_{i\alpha,j\beta}} + A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{i\alpha,j\beta}) - \frac{C_{\alpha\beta}}{r_{i\alpha,j\beta}^6}, \quad (3)$$

where  $\phi_{i\alpha,j\beta}$  is the interaction energy between two atoms of species  $\alpha$  and  $\beta$  at sites  $i$  and  $j$ , respectively. The parameters  $Q$ ,  $A$ ,  $B$ , and  $C$  depend on atomic species and can be found in Ref. [21].

The presence of the electrostatic interaction in Eq. (3) stipulates that the Ewald summation [22] should be used in the calculation of the total energy and forces. However, as shown by Wolf *et al.* [23] in a recent communication, a pairwise sum can be constructed in real space by ensuring charge neutrality of the system such that the sum produces results very similar to that obtained from the Ewald summation. We have adopted this real-space approach to calculate the total energy and forces via Wolf's summation. Following these authors, the expression for the electrostatic force between two species  $\alpha$  and  $\beta$  at sites  $i$  and  $j$  can be written as

$$F^{i\alpha,j\beta} = Q_\alpha Q_\beta \left\{ \frac{\text{erfc}(\kappa r_{i\alpha,j\beta})}{r_{i\alpha,j\beta}^2} + \frac{2\kappa}{\pi^{1/2}} \frac{\exp(-\kappa^2 r_{i\alpha,j\beta}^2)}{r_{i\alpha,j\beta}} - \frac{\text{erfc}(\kappa R_c)}{R_c^2} - \frac{2\kappa}{\pi^{1/2}} \frac{\exp(-\kappa^2 R_c^2)}{R_c} \right\}, \quad (4)$$

for  $r_{i\alpha,j\beta} \leq R_c$ .

TABLE II. Peak positions of FEAR model compared with other MD models and experiments (Expt.).

Atom-atom	Peak position ( $\text{\AA}$ )		
	FEAR	MD [25]	Expt. [28]
Si-Si	3.15	3.10	
Si-O	1.62	1.62	$1.610 \pm 0.050$
O-O	2.64	2.64	$2.632 \pm 0.089$

The damping coefficient ( $\kappa$ ) and the cutoff radius ( $R_c$ ) play an important role in the calculation by including contributions from the reciprocal and real spaces. Since these parameters are not independent of each other, care must be taken to choose an appropriate set of values for accurate calculations of total energy and forces. Following Fennell and Gezelter [24], we have used a value of 0.2 and 9  $\text{\AA}$  for  $\kappa$  and  $R_c$ , respectively.

Figure 1 presents a schematic diagram of the FEAR method showing the principal steps of our calculations. Starting with an initial random configuration  $\mathbb{C}_1$ , the method proceeds via  $\chi^2$  minimization to generate a new configuration  $\mathbb{C}_2$  by enforcing an experimental structure factor using conventional reverse Monte Carlo (RMC) simulations. The output from this step is then fed to the next step for optimization of the total energy via a gradient-descent approach. The structure of the resulting configuration  $\mathbb{C}_3$  is then examined for continuation or termination. This self-consistent iterative scheme continues until the convergence criteria for each subspace optimization are met or a maximum number of iterations is reached. The total-energy optimization and the  $\chi^2$  fitting of the structure factor constitute the principal components of the method, and are indicated in Fig. 1 by the loop  $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$ . In the next section, we apply this method to  $a\text{-SiO}_2$  and  $a\text{-Si}$ , and discuss the results in detail.

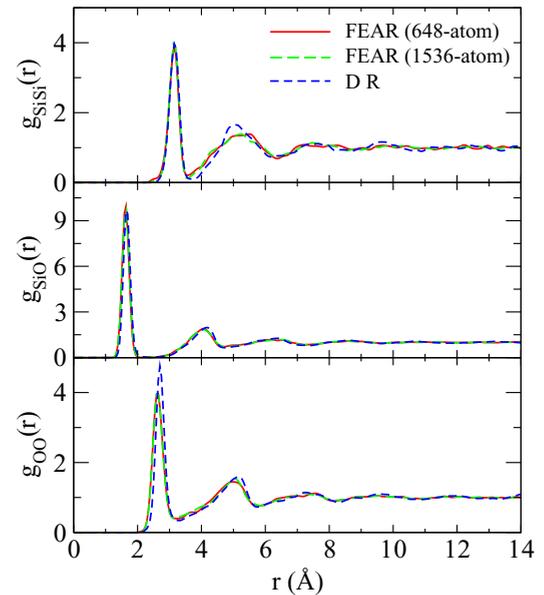


FIG. 3. (Color online) Partial pair-correlation data for  $a\text{-SiO}_2$  models from FEAR simulations. The corresponding data (dashed blue curve) for a decorate-and-relax (DR) model from Ref. [30] are included for comparison.

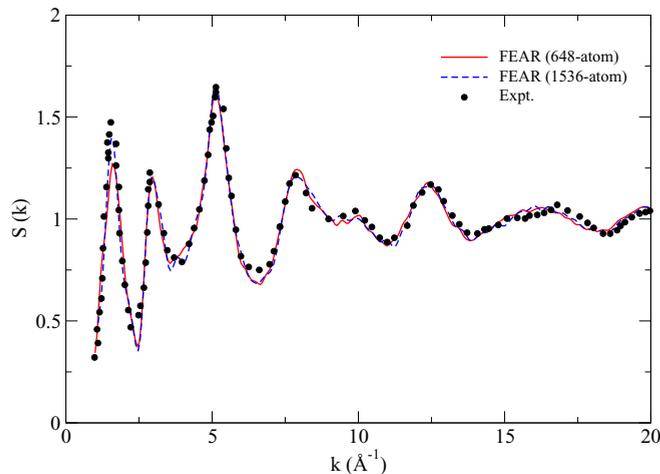


FIG. 4. (Color online) Calculated total neutron static structure factor for 648- and 1536-atom  $a$ -SiO<sub>2</sub> models from FEAR simulations. Experimental data from Ref. [6] are shown as solid circles.

### III. RESULTS AND DISCUSSION

#### A. Amorphous silica ( $a$ -SiO<sub>2</sub>)

In this section, we present results for  $a$ -SiO<sub>2</sub> from FEAR simulations. To this end, we use a total neutron static structure factor from Ref. [6] which is then coupled with the total-energy BKS functional to generate  $a$ -SiO<sub>2</sub> models consisting of 192, 648, 1020, and 1536 atoms. Starting with a random configuration with an experimental density of 2.20 g cm<sup>-3</sup> for  $a$ -SiO<sub>2</sub>, the structure factor of the model is fitted with the corresponding experimental data via RMC simulations. After 100 successful RMC moves, the total energy and forces on the atoms are calculated (using a single force call) and the atoms are displaced along the direction of the forces. This two-step process is then repeated until the convergence criteria for  $\chi^2$  and the total energy are satisfied. Analysis of  $\chi^2$  and total energy suggest that approximately  $3 \times 10^4$  force calls are sufficient for FEAR to converge to a reasonable accuracy of  $\delta\chi^2 \approx 10^{-4}$  and  $\delta F \approx 0.02$  eV/Å for system sizes we have studied so far.

To estimate the overall computational cost of the method, we have calculated the total CPU time for several system sizes, and compared the results with those obtained from classical and *ab initio* MD simulations reported in Refs. [25,26]. In Fig. 2, we have plotted the CPU time for  $N = 192, 648, 1020,$

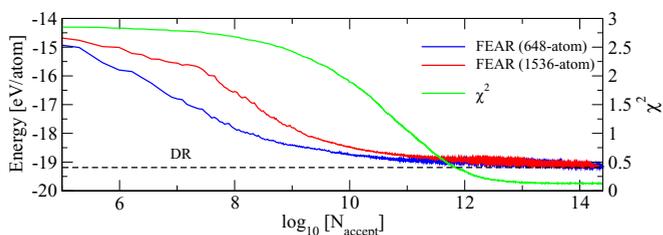


FIG. 5. (Color online) Total energy (of  $a$ -SiO<sub>2</sub>) and the cost function  $\chi^2$  vs RMC steps during FEAR simulations. The horizontal line corresponds to the energy of a DR model using the BKS potential for comparison.

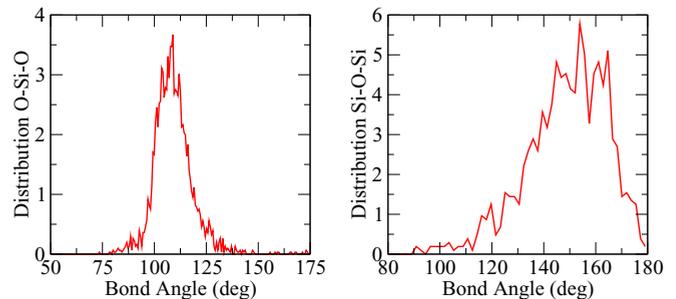


FIG. 6. (Color online) Bond-angle distributions of a 1536-atom model of  $a$ -SiO<sub>2</sub> from FEAR calculations. The average and width of the distributions are listed in Table III.

and 1536 atoms. While both RMC and force calculations can be implemented in an order- $N$  manner (see Ref. [27]), we made no attempts to obtain such improved scaling at this time in an effort to examine the usefulness of this approach in this exploratory study. Thus, the CPU time for a run has been observed to scale quadratically with the system size. This is indicated in Fig. 2 by a least-squares fit of the data using a quadratic polynomial. Despite this quadratic scaling of CPU time, a notable feature of the method is the parsimonious use of gradient information for structural optimization. FEAR makes significantly fewer force calls than conventional classical/*ab initio* MD or other gradient-based methods. A comparison of the number of force call relaxations between FEAR and melt-quench MD (classical and *ab initio*) [25,26] can be found in Table I.

The partial pair-correlation data for the FEAR models are shown in Table II and Fig. 3. The peak positions and bond lengths are comparable with the results from other MD models and experiments. The average coordination numbers of Si and O for the model with 1536 atoms are found to be 3.98 and 1.99, respectively. The presence of a few threefold (3.2%) and fivefold (0.45%) silicon and isolated (2.7%) oxygen atoms can be attributed to the BKS potential that lacks the three-body term [20]. None of the FEAR models shows any chemical disorder or heteropolar bonding.

The total structure factor  $S(k)$  is compared to the neutron diffraction experiments from Ref. [6], and is shown in Fig. 4. The origin of the peaks in  $S(k)$  can be inferred from partial structure factors. The second peak in Fig. 4 arises from Si-Si and O-O correlations with a partial cancellation from the Si-O anticorrelations. The third and fourth peaks receive contributions from Si-Si, Si-O, and O-O correlations. The first peak for both models is small compared to the experiment,

TABLE III. Bond-angle distributions from FEAR, MD, and DR models.

	Bond angle (deg)			
	FEAR	MD [25]	Expt. [31]	DR [6]
O-Si-O	109.5 (15.6)	109.6 (10)	109.5	109.5 (9)
Si-O-Si	154.3 (27.8)	142.0 (25)	144 (38)	140 (25)

TABLE IV. Ring statistics of  $\alpha$ -SiO<sub>2</sub> from FEAR models.

Ring size ( $n$ )	4	6	8	10	12	14	16	18
192 atom	0	7	9	26	17	28	16	12
648 atom	5	12	36	57	80	109	53	42
1536 atom	6	24	108	167	195	215	148	96

which can be attributed to finite-size effects in the intermediate range order [29].

In Fig. 5, we have shown the variation of the cost function ( $\chi^2$ ) and BKS energy per atom during FEAR simulations. The horizontal line in the plot corresponds to the BKS energy for a 648-atom model obtained from the decorate-and-relax approach described elsewhere [30]. The BKS energy, for both 1536- and 648-atom models, is close to  $-19.15$  eV/atom, which is comparable to  $-19.18$  eV/atom from the corresponding DR model. The use of atomic forces or gradient information improves the quality of structure.

The bond-angle distributions for the model with 1536 atoms are plotted in Fig. 6. The distribution of  $\angle$ O-Si-O shows that the silicon-centered O-Si-O angles are tetrahedral in character with an average value of  $109.5^\circ$  and a full width (at half maximum) of  $15.6^\circ$ . These values are consistent with the experimental data reported by Mozzi and Warren [31]. The corresponding values for  $\angle$ Si-O-Si are found to be  $154.3^\circ$  and  $27.8^\circ$ , respectively. The average value of  $\angle$ Si-O-S is about 6.4% higher than the experimental value of  $144^\circ$ , and the value obtained from other theoretical models [25,29]. This deviation, however, is not surprising, and is generally attributed to the lack of a three-body interaction in the BKS potential [32]. Since Si-O-S angles involve two neighboring tetrahedra connected via a bridging oxygen atom at a common vertex, it is difficult for the BKS potential to produce this delicate geometrical arrangement accurately via two-body interactions only. A full

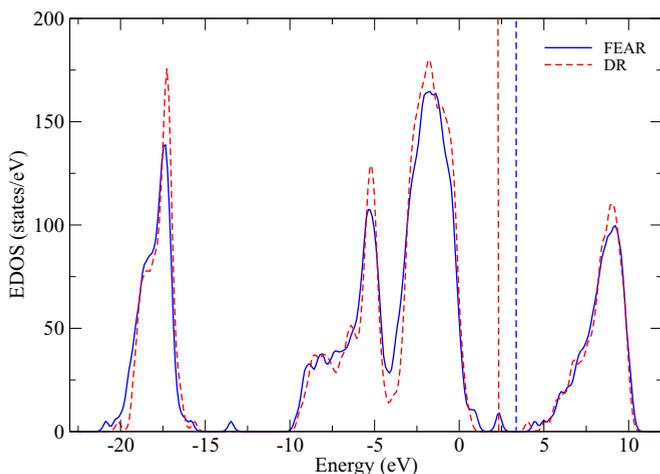


FIG. 7. (Color online) Electronic density of states (EDOS) for a 192-atom model of  $\alpha$ -SiO<sub>2</sub> obtained from FEAR simulations. The corresponding result from a DR model is included for a comparison. Fermi levels are indicated as vertical lines at 2.4 eV (DR) and 3.4 eV (FEAR).

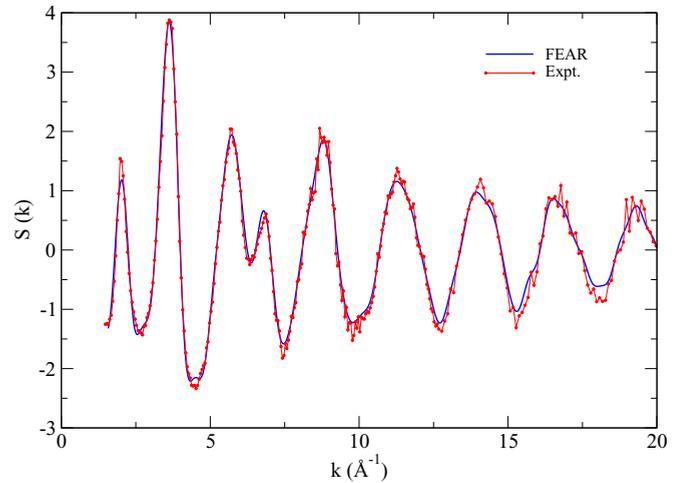


FIG. 8. (Color online) A comparison of the FEAR structure factor for a 216-atom model of  $\alpha$ -Si with the experimental data from Ref. [36].

comparison of FEAR results with experimental data and other theoretical models are provided in Table III.

Table IV presents the number of irreducible ring statistics for the models with 192, 648, and 1536 atoms using the ISAACS program [33]. The presence of only even-member rings implies the absence of chemical disorder in the network.

The structures obtained from FEAR have been relaxed using the density-functional code (VASP) using a local-density approximation (LDA), and the LDA energies have been found to be comparable with those obtained from the DR model [30]. The electronic density of states (EDOS) for a 192-atom  $\alpha$ -SiO<sub>2</sub> is shown in Fig. 7. The EDOS is comparable with the results obtained by Sarnthein and co-workers [26] and hence with the x-ray photoemission spectra (XPS) [34] in the sense that the states are well reproduced. There are three distinct regions of occupied states. The states about  $-18$  eV are oxygen  $2s$  states, while the ones between  $-10$  and  $-4$  eV are the bonding states between Si  $sp^3$  hybrids and O  $2p$  orbitals. The highest occupied states in the valence band about  $-4$  eV are the O  $2p$  states and the lowest unoccupied states of conduction band comprising antibonding states. However, the band gap of 3.96 eV is underestimated compared to 4.8 eV of that obtained from MD calculations [26] and the experimental value of 9.0 eV [35]. This is to be expected from LDA DFT calculations.

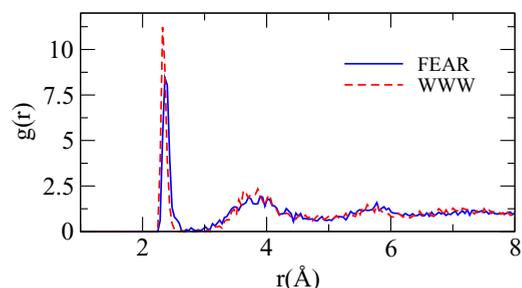


FIG. 9. (Color online) Pair-correlation data (blue) for a 216-atom model of  $\alpha$ -Si obtained from FEAR. The corresponding data (red) for a WWW model are also presented here for a comparison.

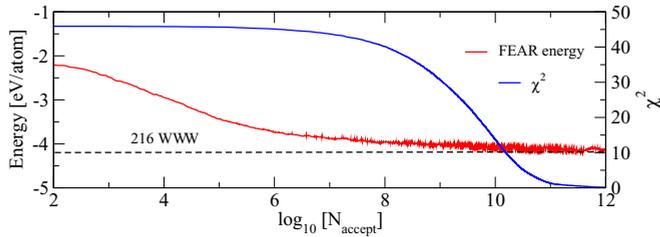


FIG. 10. (Color online) The variation of  $\chi^2$  and EDIP energy during FEAR simulations. The dashed line is the EDIP energy for a WWW model with an identical size and the number density.

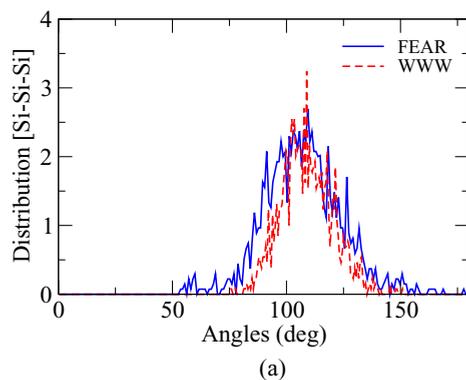
Finally, to verify the reproducibility of the method, we have generated 20 configurations of 192- and 648-atom models, and ten configurations of 1020- and 1536-atom models from different random starting configurations. Approximately 90% of the final configurations have been observed to have almost identical structural and electronic properties. The configuration fluctuations of various physical observables are found to be within the statistical limits, which ensure the reproducibility and consistency of the FEAR method.

### B. Modeling amorphous silicon (*a*-Si)

We have also employed FEAR to model the structure of *a*-Si starting from a random configuration with 216 atoms. The results of our calculations are plotted in Figs. 8–12. Figure 8 shows the structure factor obtained from a 216-atom FEAR model of *a*-Si along with the experimental x-ray diffraction data from Ref. [36]. It is evident from Fig. 8 that the structure factor agrees very well with the experimental data, except for a few points near the first peak. This is also reflected in the correlation data in real space in Fig. 9, where the pair-correlation function of the FEAR model is compared with the same from a WWW model.

The cost function  $\chi^2$  and the total EDIP energy is shown in Fig. 10. The energy is compared to the 216-atom *a*-Si WWW model which is 4.199 eV (shown by the dashed line). This shows that in FEAR, the energy is minimized, together with the structural refinement.

The bond-angle distribution is shown in Fig. 11(a) where the tetrahedral geometry is retained compared to the WWW model



(a)

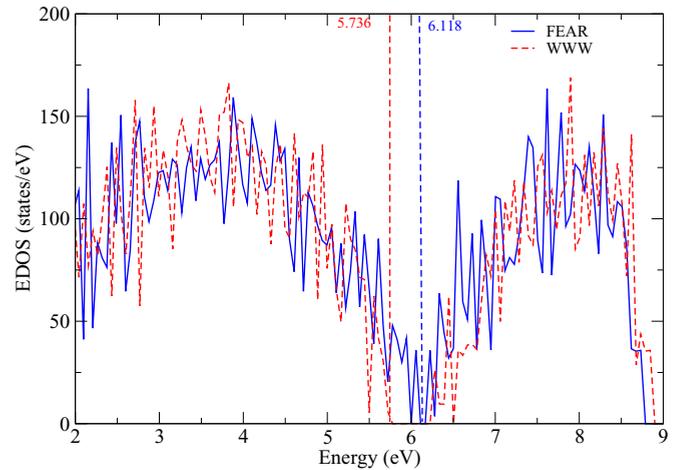
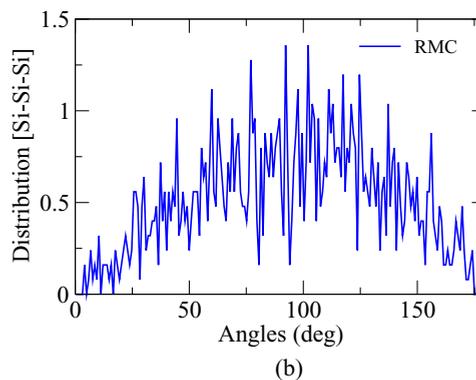


FIG. 12. (Color online) Density of electronic states of *a*-Si using VASP from FEAR (blue) and WWW (red) models. The corresponding Fermi levels are indicated as vertical lines at 6.1 eV (FEAR) and 5.7 eV (WWW).

of identical number of atoms. The corresponding bond-angle distribution using RMC is shown in Fig. 11(b) where the peaks are highly underestimated and the distribution is broad without a tetrahedral peak. We relaxed the structure obtained from FEAR using VASP and found the energy minimum to be  $-5.18$  eV/atom compared to  $-5.23$  eV/atom of the VASP-relaxed WWW model. This shows that the LDA energies are comparable. In Fig. 12, the electronic density of states for the FEAR model is compared with the same from a VASP-relaxed WWW model. The Fermi energies are shown by the vertical dashed lines. As compared to RMC and constrained RMC [2], the EDOS is in better agreement with the optical measurements. The FEAR model exhibits the presence of several defect states within the gap, which mostly arise from coordination defects. This is expected in view of the fact that approximately 10% of the total Si atoms have a coordination number, which is different from 4. This coordination number is better compared to the constrained RMC (88%) [2] and MD quench from melt using EDIP and Tersoff potentials [37,38]. The EDIP for Si overestimates the fivefold bond in Si which is evident in our FEAR calculation with almost 8% fivefold Si



(b)

FIG. 11. (Color online) (a) The bond-angle distribution for a 216-atom model of *a*-Si using FEAR (solid line) and a WWW model (dashed line). (b) The bond-angle distribution for a 216-atom “*a*-Si model” from RMC simulations using the experimental structure factor only. The approximate semicircular distribution is a characteristic feature of *unconstrained* RMC.

present in the network [37]. These floating bonds clutter the gap and form defect states that close the gap. The presence of these defect states, and the use of the LDA that is known to underestimate the optical gap, explains the small gap in the electronic density of states.

#### IV. CONCLUSIONS

In this paper, we have studied an approach, called force-enhanced atomic refinement (FEAR), to model complex amorphous solids by combining experimental structure factors with periodic usages of gradient information from a total-energy functional. The approach consists of employing experimental scattering data to generate an ensemble of possible structural solutions via reverse Monte Carlo simulations, which is followed by further refinement of the RMC solutions using gradient information from a total-energy functional. Since conventional RMC cannot describe a three-dimensional structure uniquely, and its constrained counterpart with additional structural information often transforms the original unconstrained problem to a difficult multiobjective optimization program, the emphasis on the present approach has been to develop a method that retains the simplicity of RMC and yet overcomes the problem of nonuniqueness in the structural determination via the economical use of a total-energy functional and forces. The approach can be viewed as a “predictor-corrector” method for structural refinement. Atomistic configurations predicted by RMC are corrected at regular intervals via the optimal usage of gradient information or forces from a total-energy functional. This enables FEAR to track solutions in the manifold of the solution space that jointly satisfies experimental structure-factor data and the total energy of the system. In this exploratory study, we have demonstrated by using two archetypal examples of amorphous solids (*a*-Si and *a*-SiO<sub>2</sub>) that the method performs on a par with the traditional MD simulations or other gradient-based relaxation approaches even at an elementary level of its implementation.

We have successfully implemented FEAR to model *a*-SiO<sub>2</sub> and *a*-Si. Structural and electronic properties of the FEAR models are produced as accurately as possible within the limit of the potentials and experimental input data. The

structural properties of FEAR models have been examined by analyzing the pair-correlation data, bond-angle distributions, ring statistics, and the distribution of the tetrahedral building blocks of the underlying network structure of *a*-SiO<sub>2</sub> and *a*-Si. Electronic properties of the models are also studied primarily by calculating the electronic density of states within the density-functional framework using the plane-wave based VASP code using a local-density approximation. A comparison of FEAR results with those obtained from *ab initio* and classical simulations [25,26] is also discussed.

We conclude this section with the following observations. First, the method can be improved further by using efficient algorithms for both RMC and total-energy calculations. The former can be readily implemented using an  $O(n)$  algorithm. Similarly, by using more sophisticated algorithms for the minimization of total energy, it is possible to accelerate the convergence of total energy and forces during FEAR simulations. Second, the very economical nature of the use of gradient information (or forces) suggests that the method would be particularly useful when employed with *ab initio* total-energy functionals. Since *ab initio* calculations of total energy and forces for complex disordered solids (with system size) are almost always proportional to  $O(n^3)$ , an implementation of FEAR within *ab initio* packages will provide an effective tool for total-energy relaxations. Last but not least, we anticipate it would be possible to develop a more effective coupling scheme between the solution space (defined by a set of experimental data) and the configuration space (of a total-energy functional) such that a mechanism can be built into FEAR to avoid solutions associated with unphysical or poor structures. In the future, we will address some of these issues.

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