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Feature Article

Electronically designed amorphous carbon and silicon

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We present a new approach to modeling materials. We show that Hellmann–Feynman forces associated with gap states may be used to drive the system to a preferred electronic structure that is also a total energy minimum. We use *a priori* information about the electronic gap to construct realistic models of tetrahedral amorphous carbon and silicon. We show that our method can be used to obtain continuously tunable concentration of tetrahedrally bonded carbon atoms in models of amorphous carbon. The method is carried out in the tight-binding approximation to produce computer-models of amorphous silicon that have fewer structural and optical defects than their conventional MD counterparts. We end by presenting a first test-case for the *ab initio* (plane-wave LDA) implementation of the method.

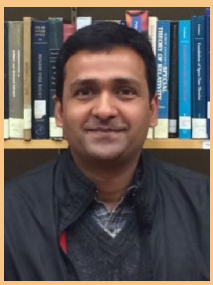
1 Introduction The tools of Monte Carlo and molecular dynamics (MD) simulation are at the heart of modern materials theory. The revolution of *ab initio* MD has changed the landscape in the field and enables direct links between theory and experiment that were formerly unthinkable. In many ways, these methods are maturing, as seen both in a number of outstanding codes available and the number and quality of publications in the area. Still, there is room for improvement. These methods are limited by size and time scale, and in their usual form allow no opportunity to include *a priori* information either to design materials with a specific property in mind or to compel the final model to agree with known information, e.g., from trusted experiments. It is for these reasons that we here further develop our "gap-sculpting" method [1] with an interesting new calculation on amorphous carbon and provide the first evidence that the method is likely to succeed for *ab initio* interactions as well. The method is useful as a new avenue to electronically engineer materials and also to efficiently build computer models with realistic structural properties by incorporating experimental information about band gaps.

Amorphous semiconductors are among the most important practically useful materials. These materials are usually readily fabricated, flexible, and inexpensive compared to their crystalline brethren. The semi-conducting and optical properties of these materials are of special interest in many applications, and these depend on fine details at atomic level such as short-range order, structural defects, internal voids, and surfaces, etc. Accordingly, major effort has been made to obtain realistic computer models of amorphous materials. Since such models provide the exact positions of atoms, it should provide scientists with as much information about amorphous phases as we know about crystals. However, the details of the nanometer-scale structure are not uniquely defined for these materials since an amorphous solid is not the global minimum of energy. In a celebrated work, Stillinger has shown that the number of energy minima scales exponentially with the system size [2]. Therefore, reducing the volume of configuration space explored is valuable. Information-based methods have attempted to invert experimental data. These include various types of reverse Monte Carlo (RMC) schemes that use diffraction data [3–5], diffraction data and constraints of spatial homogeneity [6], and diffraction data as well as information from electronic structure [7, 8] and nuclear magnetic resonance spectra [9]. Recently, an approach of including ionic forces "force-enhanced atomic refinement" (FEAR) has emerged [10].

In this paper, we significantly develop our "gap-sculpting" scheme [1], an effective method to produce a desired electronic gap, by including electronic information via biased molecular-dynamics simulations. We find that such biasing not only opens up the electronic gap but also has a

profound effect on the structural properties of the system, and is helpful to obtain more realistic network structures.

The optical gap is a crucial property of solids, and band-gap engineering is an important pursuit in its own right. Historically, gap tuning has been explored by introducing strain in the network, by altering the geometry or by doping. Our method [1] provides a novel tool for both gap engineering and structural refinement and modeling. We show that knowledge of the optical gap allows us to harness the power of electronic band structure of the material while paying a small cost in total energy (thanks, perhaps to Stillinger's explosive growth in configurations and the near degeneracy of bonding environments). This method can be built into regular MD as an extra knob to include the electronic structure information.



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Our method is efficient. We employ Hellmann–Feynman (HF) forces [11, 12], which are the byproduct of any electronic structure simulations, and demonstrate that HF forces can be used judiciously to push the system in the direction of most rapid change of the electronic gap. Further, we report in this paper electronically engineered models of amorphous carbon and silicon. The models are energetically stable and structurally and electronically superior to the corresponding models obtained using conventional methods. While the models themselves are better suited to describe phases of disordered carbon and silicon, the method presents a significant improvement on the conventional melt-quench method [13] and has the potential to become a mainstream tool in quantum-mechanical simulation of materials.

The paper is organized in the following way. In Section 2, we start by introducing Hellmann–Feynman forces and present a method to include these forces into tight-binding molecular-dynamics simulations. Section 3 addresses the results from biased MD simulations of amorphous carbon, which is followed by the results on pure amorphous silicon in Section 4. In Section 5, we provide a discussion of the results and the future development of the method. Section 6 concludes our work.

2 Method

The biased dynamics that we discuss here are carried out using forces that are formulated as a proxy for the conventional forces used in MD simulations. For any conventional electronic-structure-based MD scheme (tight-binding or density functional), the so-called band-structure force is a major component of the total interatomic force, and is given by the sum of Hellmann–Feynman forces [11, 12] from all occupied states.

$$\mathbf{F}_{\alpha}^{\mathrm{BS}} = -\sum_{i}^{\mathrm{occ}} \left\langle \Psi_i(r) \left| \frac{\partial H}{\partial R_\alpha} \right| \Psi_i(r) \right\rangle = -\sum_{i}^{\mathrm{occ}} \frac{\partial \lambda_i}{\partial R_\alpha}. \quad (1)$$

Here, Ψ_i represents the ith eigenstate of Hamiltonian H and λ_i is its eigenvalue, R_α are the $3N$ positional degrees of freedom. The sum in the right-hand side runs over all occupied states. In our recent work [1], we have shown that the eigenstates with conjugate eigenvalues in an *a priori* known energy range, $(E_{\mathrm{min}}, E_{\mathrm{max}})$, can be pushed out of this range using a biasing force, $\mathbf{F}_{\alpha}^{\mathrm{bias}}$, of the following form:

$$\mathbf{F}_{\alpha}^{\mathrm{bias}} = -\sum_{i:E_{\mathrm{min}}<\lambda_i<E_{\mathrm{max}}} \gamma g(\lambda_i) \left\langle \Psi_i(r) \left| \frac{\partial H}{\partial R_\alpha} \right| \Psi_i(r) \right\rangle. \quad (2)$$

Here, $g(\lambda_n) = +1$ or -1 for $\lambda_n > \lambda_{\mathrm{HOMO}}$ or $\lambda_n \leq \lambda_{\mathrm{HOMO}}$, respectively. These forces act on atoms along the direction of most rapid change of λ_i. The net effect of this force is that states below the Fermi level are driven toward the (desired) valence edge (chosen to be E_{min}) and states above shepherded toward the conduction edge (chosen to be E_{max}). We refer to these forces as gap forces hereafter. The parameter γ can be

used as a knob to control the magnitude of the gap forces or to reverse their direction (e.g., to maximize model metallicity).

In this work, we demonstrate biased dynamics using the tight-binding parametrization for carbon by Xu et al. [14] and that of Goodwin, Skinner, and Pettifor [15] for Si. In a conventional melt-quench method, a well-equilibrated liquid model is quenched below the glass-forming temperature by performing dissipative dynamics. We take the same point of view here, except that we bias the dissipative dynamics toward a configuration with fewer states in the gap region. The biasing is done by adding the gap forces given by Eq. (2) to the band-structure and ionic forces. The total force in this scheme is as follows:

$$\mathbf{F}_\alpha^{\text{total}} = \mathbf{F}_\alpha^{\text{BS}} + \mathbf{F}_\alpha^{\text{ion}} + \mathbf{F}_\alpha^{\text{bias}}, \tag{3}$$

where the first two terms on the right side of Eq. (3) are, respectively, the total band-structure force (Eq. (4)) and repulsive force (Eq. 5) of conventional tight-binding molecular dynamics (TBMD) simulations. The last term is the biasing force, which is given by Eq. (2). For completeness,

$$\mathbf{F}_\alpha^{\text{BS}} = -\sum_i f_i \left\langle \Psi_i(r) \left| \frac{\partial H}{\partial R_\alpha} \right| \Psi_i(r) \right\rangle, \tag{4}$$

$$\mathbf{F}_\alpha^{\text{ion}} = -\frac{\partial U_r}{\partial R_\alpha}, \tag{5}$$

as more fully discussed in Ref. [1].

3 Amorphous carbon Amorphous carbon is technologically important and has intriguing microscopic structure. Carbon forms strong bonds in both sp^2 and sp^3 environments and can be prepared in various forms. Sputtering and evaporation usually produce disordered phases that are rich in sp^2 bonds, whereas mass-selected ion beam deposition produces a disordered phase with more than 90% sp^3 character [16]. Structural, electronic, and optical properties of these materials are of great technological and scientific importance, which have led to considerable works in this field [14, 16–26].

There have been many attempts at modeling amorphous carbon [14, 20, 22, 23, 26]. Particularly, sp^2 -bonded carbon is modeled and characterized by using empirical potential [23], tight-binding approximation [14], and *ab initio* methods [20, 22, 26] with a varying degree of success. Tight-binding MD simulations were employed in Ref. [24, 27] to model diamond-like carbon but the authors used, as a critical requirement, much higher density than the experimental density of 2.9 g cm^{-3} [20]. Drabold et al. used first-principles methods to model *ta*-C at the experimental density and produced 64-atom models of *ta*-C with 91% fourfold coordination [20]. Djordjevic, Wooten, and Thorpe used the bond-switching algorithm of Wooten, Weaire, and Winer [28] to prepare perfectly tetrahedral models of *a*-C [29]. However, modeling alloy systems with a significant fraction of both sp^2 - and sp^3 -bonded carbon has not been accomplished to our knowledge.

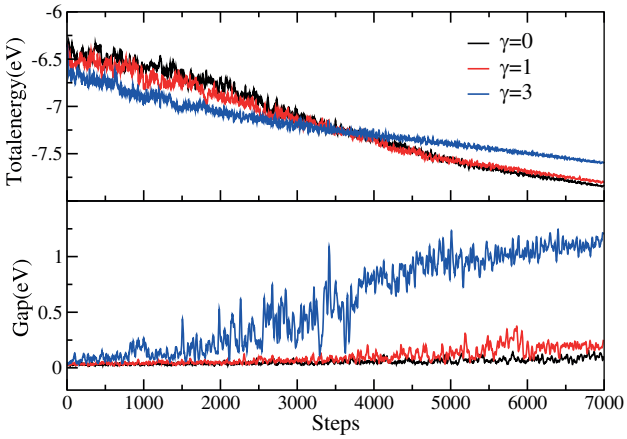


Figure 1 (Top) The total energy per atom of the system upon quenching for 7000 to 600 K at density 2.9 g cm^{-3} . For small γ, the energy penalty is very small. Note that these models are relaxed using unbiased TB forces (i.e., $\gamma = 0$) following the quench to ensure that we obtain a "true" minimum. The total energy of these systems after relaxation is −7.92, −7.88, and −7.70 eV atom^{-1} for $\gamma = 0$, 1, and 3, respectively. (Bottom) The evolution of the gap during the quench. For clarity and reduction of noises in the data, a running-window average of the gap values is presented here.

It has been observed that systems with a higher fraction of sp^3 -bonded C atoms have a wider electronic gap than its sp^2 counterpart. For example, evaporated *a*-C has a gap of 0.4–0.7 eV, whereas diamond-like *a*-C has gap of 0.5–1.5 eV (see Ref. [16] and Table 1 therein). This correlation between the gap size and concentration of sp^3 -bonded atoms is valuable and can be used as *a priori* information to bias the dynamics in order to tune the concentration of sp^3 -bonded atoms in a model. Here, we have implemented such a biased dynamics using the tight-binding approximation and reported models of disordered carbon, which consist of both sp^2 - and sp^3 -bonded carbon atoms at various concentrations.

Figure 1 (bottom) shows the evolution of the electronic gap for amorphous carbon during TBMD simulations using the tight-binding Hamiltonian of Xu et al. [14]

It is notable that imposing electronic information not only opens up the electronic gap, but also influences the structural properties by changing the character of carbon–carbon bonding from sp^2 to sp^3 . The fraction of sp^3 -bonded atoms increases with increasing γ, and thereby provides a previously unavailable knob to tune the sp^3 concentration in the network – *in this mode using an electronic constraint to obtain a desired structural result*. For this calculation, we relaxed Djordjevic's model [29] with TB Hamiltonian and used the size and location of the gap of the relaxed model as required electronic information for biased MD simulations.

We have chosen three densities to conduct biased dynamics: 2.9, 3.2, and 3.5 g cm^{-3} . The conventional melt-quench MD simulations at these densities produce amorphous carbon with more than 90% sp^2 concentration as observed in our present work and in work by others [25, 30]. Melt-quench procedure at higher pressure has been shown to produce a

strong sp^3 character of C–C bonding in the liquid state [30, 31]. On the other hand, quenching at higher densities have been employed to force the models into a diamond-like structure [24, 27].

The models reported here are constructed by quenching from equilibrated liquid C. For each density, a cubic supercell of 216 atoms in diamond lattice with periodic boundary condition was heated beyond its melting temperature.[1] We verified that the these well-equilibrated liquid models bear the standard signatures of liquid carbon (radial distribution, bond-angle distribution, coordination numbers, and electronic structure) reported in Refs. [30, 31]. We have observed that conventional TBMD has led to results, which are consistent with the earlier results obtained by others using this Hamiltonian.

To produce gap-engineered models, we bias the quenching from the liquid by modifying the TB forces according to Eq. (3) in Section 2. To impart diamond-like character in the network, we biased the dynamics toward the electronic structure of a perfectly tetrahedral amorphous carbon model.[2] Finally, the quenched models at 600 K were relaxed to their local minimum using true (unbiased) TB forces. Hence, the final structures are true inherent structures of the carbon system, and the models are stable.

We note that for small γ, the energy penalty of biasing the dynamics is small. Figure 1 (top) shows the total energy per atom during quenching. The energy penalty is reconciled to some extent by the relaxation with respect to true forces and the final models are less than 0.15 eV atom^{-1} apart for $\gamma = 1$. The dynamics steers the network to wider gap configurations as seen in Fig. 1 (bottom) and that has a strong effect on the nature of bonding in the network that results. We see that for increasing value of γ at a particular density, the concentration of sp^3 bonds increases. For density 2.9 g cm^{-3}, which is the experimental density of *ta*-C, we get 22.7, 48.1, and 55.5% sp^3 character in the models for $\gamma = 1$, 2, and 3, respectively, compared to 6.5% sp^3 -bonded atoms for $\gamma = 0$ (see Fig. 2). We find that the leverage on γ declines after $\gamma = 3$ because further increase in γ significantly alters the dynamics and does not increase the sp^3 concentration.

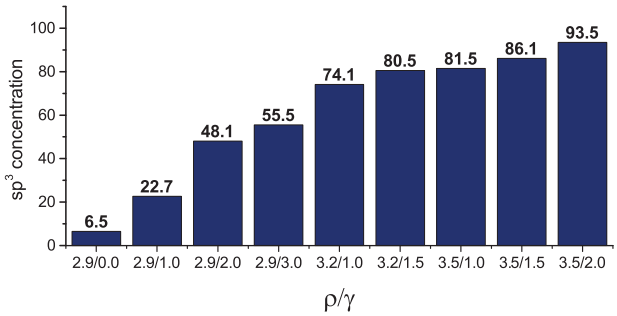


Figure 2 The concentration of tetrahedrally bonded carbon atoms in the relaxed models. The labels along the horizontal axis designate the density (ρ) and the strength of gap forces (γ) used to bias the forces. For clarity, (ρ, γ) is written as ρ/γ.

Similar behavior is observed at higher densities. At density 3.2 g cm^{-3}, the final models have sp^3 concentration of 74.1 and 80.5% for $\gamma = 1$ and 1.5, respectively. Similarly, biased dynamics at density 3.5 g cm^{-3} produced models with sp^3 concentration of 81.5, 86.1, and 93.5% for $\gamma = 1$, 1.5, and 2, respectively. It is important to note here that, while increased pressure at 3.2 and 3.5 g cm^{-3} has certainly helped to lead the dynamics to tetrahedral geometry, an application of biasing forces is absolutely necessary to obtain to these models. Our calculations have shown that unbiased dynamics at all three densities presented here produce a predominantly sp^2 network. The alloy systems with comparable concentrations of sp^2 and sp^3 have the character of both types of network. Figure 3 shows the RDF of the relaxed models with 48.1 and 80.5% sp^3 bonding respect to predominantly sp^2 and sp^3 networks. This demonstrates the magnitude of structural consequences of electronic constraints in atomistic simulations.

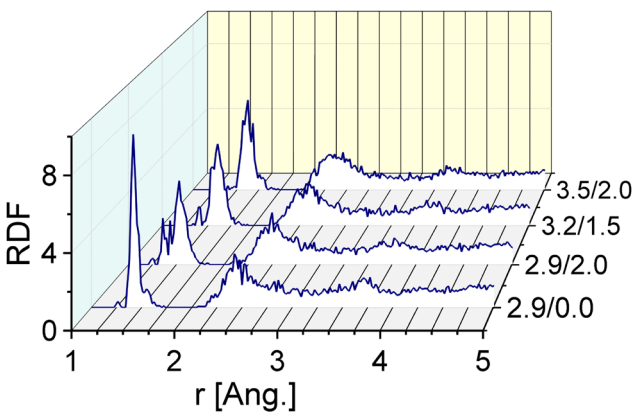
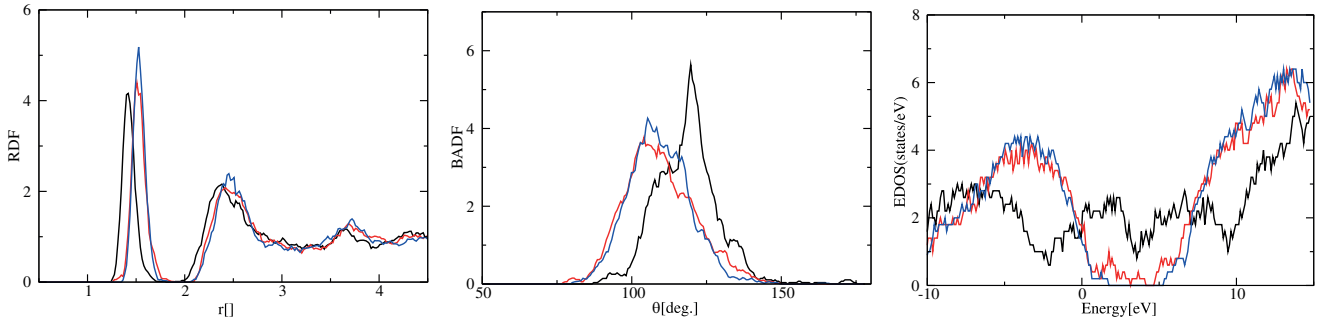


Figure 3 The radial distribution function of various relaxed models of amorphous carbon. The labels along the horizontal axis designate the density (ρ) and gamma (γ) used to bias the TB forces. These models correspond to increasing concentration of tetrahedral character in the network. This change in character is reflected in the gradual widening and shift of the first RDF peak from 1.41 Å(for lowest sp^3 density) to 1.53 Å(for highest sp^3 density).

[1] We note that, with increasing density, the cell needs to be heated to higher temperature and for longer duration in order to impart sufficient disorder to fully melt the cell. Accordingly, we heated the cell at density 2.9 g cm^{-3} to 7000 K and then equilibrated it at that temperature for 7.5 ps. The cell at density 3.2 g cm^{-3} was heated to 9000 K and equilibrated for long time following two successive equilibrations at 7000 and 8000 K, respectively. The cell at density 3.5 g cm^{-3} was heated to 10,000 K and then equilibrated after two successive equilibrations at 8000 and 9000 K, respectively.

[2] We rescaled Djordjevic's perfectly tetrahedral model [29] to densities 2.9, 3.2, and 3.5 g cm^{-3}, then relaxed the rescaled models using Xu's tight-binding Hamiltonian [14] until the forces on each atom vanishes. These relaxed models have gap of size 3.14, 3.80, and 4.10 eV, respectively. We used the size and location of these gaps at the respective densities to bias the dynamics (i.e., the values of E_{min} and E_{max} in Eq. (2) were set equal to the gap limits of these relaxed models). The strength of the biasing forces was tuned by appropriately choosing γ.



a) Radial distribution function b) Bond angle distribution function c) Electronic density of states

Figure 4 RDF, BDF, and EDOS for unbiased model ($\gamma = 0$, black), biased model ($\gamma = 2$, red), and relaxed Djordjevic model (blue) [29] at density 3.5 g cm^{-3} . The biased model plotted here has 93.5% four-coordinated C atoms and resembles closely with Djordjevic's model.

In Fig. 4, we compare some key features of the models obtained using biased and unbiased dynamics at density 3.5 g cm^{-3} . To be able to appreciate the sp^3 character in the network, we compare these two models with Djordjevic's model. We see that the biased model very closely resembles the radial distribution function of Djordjevic's model and has the bond length of 1.51 Å(original Djordjevic model has bond length of 1.54 Å[29].) Similarly, the unbiased model registers a peak in the bond-angle distribution (BAD) around ≈120°, characteristic of sp^2 networks. The bond-angle distribution of the biased model closely resembles that of Djordjevic's model. Finally, we show that the biased model has the diamond-like electronic structure.

4 Amorphous silicon A realistic model of disordered silicon is needed in order to understand the material for technological as well as scientific purposes. Amorphous silicon has electronic and optoelectronic applications and this material has long been used by the community as archetypal material to understand various structural, electronic, as well as vibrational properties of disordered materials. It has been difficult to make reliable models of a-Si using MD simulations even with the most advanced *ab initio* methods. Models of a-Si due to Wooten, Winer, and Weire [28, 29] are widely recognized as among the best models so far. Their agreement with structural and electronic properties of bulk a-Si is well established [32–34]. But, these models are created using a guided metropolis algorithm (the "bond-switching method") which is obviously less general and intuitive than the conventional melt-quench method. The later mimics the glass formation process by performing dissipative dynamics on well-equilibrated liquid models. But, the models of a-Si created using the melt-quench method usually show many remnants of the liquid silicon (*l*-Si): too many floating, strained, and dangling bonds leading to far too many defect states in the electronic gap region. Silicon, despite its ubiquity in nature and the literature is particularly difficult to model because of its over-constrained bonding topology.

In this section, we show again that *a priori* knowledge of the electronic gap can be coupled with the conventional TB forces to produce models of a-Si that are structurally and electronically superior to the models using conventional TB forces. Much of the method of conducting biased dynamics is similar to that used for *a*-C in Section 3.

Here, we carry out the melt-quench method using the tight-binding Hamiltonian of Goodwin, Skinner, and Pettifor [15]. The melt-quench process is similar to those used in earlier works [30, 35–37]. We started with a random collection of 216 atoms at a density of 2.33 g cm^{-3} and we equilibrated the system at 2500 K for 4 ps, followed by three successive equilibrations: at 2300 K for 2 ps, at 2100 K for 2 ps, at 1900 K for 2 ps. The system was then equilibrated at 1780 K (close to the melting point of Si) for 50 ps to arrive at *l*-Si model. We checked the *l*-Si model by computing its radial distribution function (RDF), bond-angle distribution function (BADF), and electronic density of states (EDOS). These calculations conform to earlier calculations on *l*-Si by Kim and Lee [35]. We then obtained 25 distinct configurations of *l*-Si by equilibrating the model at 1780 K for 25 ps and capturing the instantaneous configurations at the interval of 1 ps. These 25 configurations are then quenched to 300 K at a rate of ≈ 100 K ps^{-1} using biased dissipative dynamics. We used the electronic gap of WWW model as the target gap and used $\gamma = 1$. The models are then relaxed by damping the velocity of atoms by 1% at each step until the forces on the atoms become smaller than 0.05 eV Å^{-1}. We point out here that the biased dynamics is used only while quenching the system and, for the particular choice of $\gamma = 1$, the average magnitude of the biasing force remains smaller than 18% of the average TB force throughout the quench. For the sake of comparison, we also quenched all 25 models using only the conventional TB forces. The quenched models were then relaxed using the method described above.

We have examined structural and electronic features of an array of relaxed models following biased quenching runs (referred to as "biased TBMD models"), as well as the corresponding conventional TBMD models (referred to as "TBMD models"). The merits of these two ensembles of models can be determined by validating them against the WWW model. The quality of the latter has been well established in the literature of amorphous silicon.

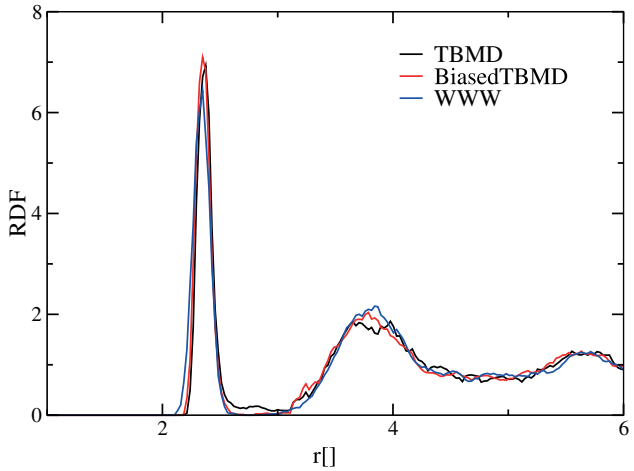


Figure 5 Radial distribution functions of an unbiased model ($\gamma = 0$), biased model ($\gamma = 1$), and relaxed WWW model [28]. The biased model has a clean first minimum and closely resembles with the WWW model.

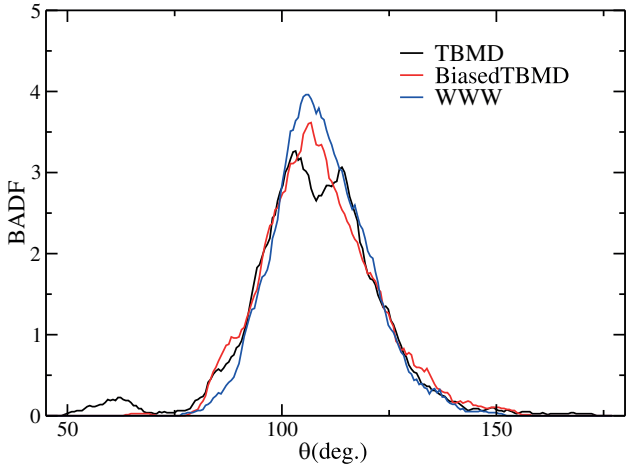


Figure 6 The bond-angle distribution function of unbiased model ($\gamma = 0$), biased model ($\gamma = 1$), and relaxed WWW model [28]. The biased model is nearly free of over-coordinated atoms corresponding to the small hump around 60°. Biases model closely resembles with the WWW model.

Biasing forces skew the dynamics toward a structure with a clean gap. In direct consequence of this, the network organizes with higher structural order while still in a topologically disordered state of tetrahedral character.[3] Durandurdu et al. [38] have pointed out that models with a cleaner gap (narrower band tails) are also the ones with narrower bond-length and bond-angle distributions [38]. The radial distribution function of the biased model presents significant structural order, indicated by a clear first minimum (see Fig. 5) compared to that of the unbiased model. The biased model clearly agrees more closely with the RDF of the WWW model. The structural order is also indicated by the bond-length and bond-angle distributions. The biased model presents a narrower bond-angle distribution as evident in Fig. 6. We note that the biased model is free of the presence of small (60°) bond angles that arise in conventional MD. We have computed the variance of bond length for both TBMD models, as well as for the biased TBMD models. We observe that out of 25 models sampled, 20 of the biased models show a smaller variance in bond length. Also, the number of four-coordinated atoms is higher for models following the biased dynamics in 19 out of 25 instances (see Fig. 7).

The electronic density of states of the relaxed models is plotted in Fig. 8. It is observed that the biased TBMD models have cleaner gap than the TBMD models. Note that for the particular instance plotted in Fig. 8, the gap of biased model is wider than that of the WWW model.

We characterized models described in this section in local density approximation (LDA) using density functional code VASP [39, 40]. Interestingly, the biased TBMD model has lower energy than the TBMD model. Similarly, biased model exerts cleaner gap in LDA. To study the dependence of the method on system size, we carried out the biased dynamics in 512 atom cell with the same quenching rate and biasing parameter. For five out of five samples that we tested, biased dynamics produced models with higher concentration of fourfolds and cleaner gap.

5 Discussion It is worth observing that in the event that the preferred gap is not known either for the material or the Hamiltonian applied, the gap may be opened incrementally starting with a very small gap, and slowly increasing it until the final quenched models are inconsistent with the gaps selected (which is guaranteed to happen when the gap gets unphysically large). This is admittedly slower than the case for which we have *a priori* knowledge of the gap, and suggests that the best approach in general is to systematically explore the topology of the system as a function of

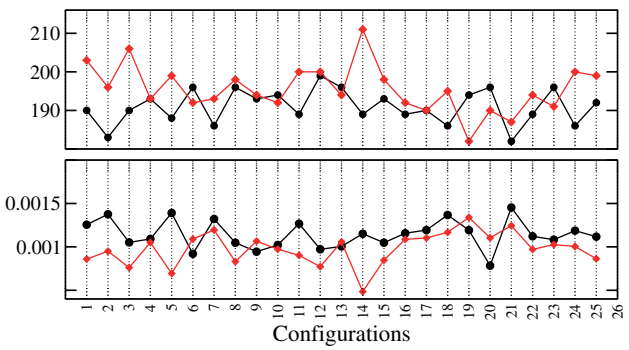


Figure 7 (Top) The number of four-coordinated Si-atoms in models that are quenched and relaxed from 25 different liquid models at 1780 K. For models plotted in red, biased TB forces with $\gamma = 1$ were used during quenching whereas for those in black, conventional (unbiased) TB forces were used. Both batches of quenched models were relaxed using unbiased TB forces. (Bottom) The variance of bond lengths (in $Å^2$) for the corresponding models.

[3] This leads us to suspect that simulations of crystallization might be significantly accelerated in this framework.

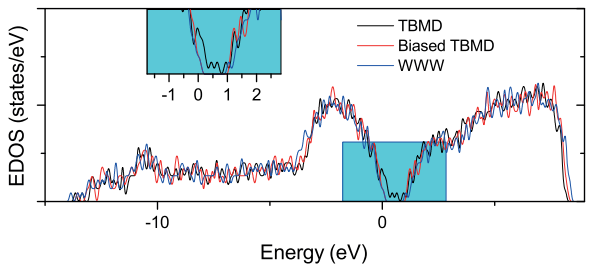


Figure 8 The electronic density of states of the unbiased model ($\gamma = 0$), biased model ($\gamma = 1$), and relaxed WWW model [28]. The unbiased model (labeled "TBMD") registers few states in the gap while the biased model is free of defect states. The gap of the biased model is wider than that of the WWW model by ≈0.1 eV.

gap, starting with small gaps. This will be especially helpful for density functional simulations for which the "theoretical gap" differs from the experimental gap.

In connection with the parameter γ, our only guidance for it's selection is that is should be near unity (indeed, in our first report [1] we employed only $\gamma = 1$), and of course the final conformations must be stable with $\gamma = 0$. We confess that this is somewhat empirical at present, and is a direction for future development.

So far in this paper, we have worked only with orthogonal empirical tight-binding Hamiltonians. This is hugely limiting, since such Hamiltonians have only been devised and tested for a handful of systems, mostly elemental, and suffer from significant limitations with respect to transferability [41]. To substantially extend the reach of the method, we are developing an *ab initio* implementation. As a test case, we carried out biased dynamics using density functional code VASP [39, 40]. We began with a 64-atom model that is made using Stillinger–Weber classical potential [42] and carried out biased annealing at 1000 K. We see that the biased forces are effective in steering the configuration to cleaner gap (see Fig. 9) and the resulting structures are stable under relaxation. The relaxed model following the biased dynamics retains the

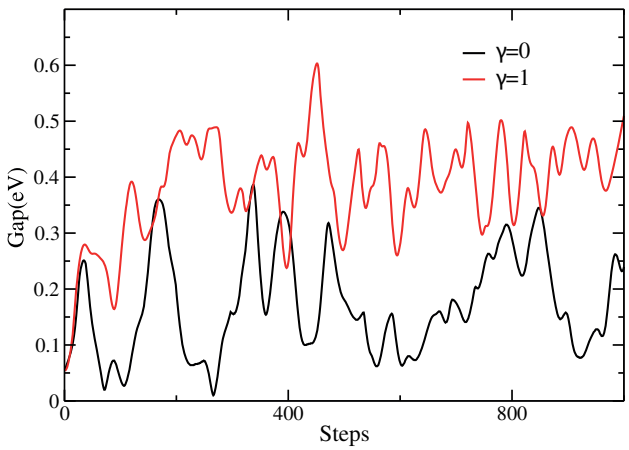


Figure 9 The evolution of electronic gap of the 64-atom silicon cell during annealing at 1000 K. $\gamma = 0$ is conventional MD using VASP and $\gamma = 1$ represents biased dynamics.

wider gap and has higher fraction of four-coordinated atoms compared to a parallel unbiased simulation. Further results of biased dynamics using *ab initio* calculations will be published later.

6 Conclusions We conclude that biasing MD simulations using Hellmann–Feynman forces is effective in imparting structural features of a reference model into the system. We have demonstrated that such tools can be effectively used to tune sp^2 / sp^3 ratio in amorphous carbon models. Similarly, biasing the TBMD to a cleaner gap improves the structural homogeneity in the model. The method has potential to be a mainstream tool in structural modeling of ordered and disordered materials.

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