Recent developments in the study of continuous random networks.

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We report on recent progress in the development of new techniques to generate high-quality models of continuous random networks, which are used as models for elemental and binary tetrahedral semiconductors such as \(\alpha\)-Si and \(\alpha\)-GaAs. The availability of such models has allowed us to look at a number of outstanding issues regarding their electronic properties, the fundamental role of defects and dynamics. We describe briefly our modifications made to the Wooten-Winer-Weaire bond-switching algorithm, allowing us to produce low-strain amorphous and paracrystalline networks of up to 10,000 atoms. Then some of the structural and electronic properties of these models are presented. We also discuss briefly some recent results on the recrystallization of amorphous networks.

I. INTRODUCTION

Continuous random network (CRN) models can be considered as an ideal representation of covalent glasses and amorphous materials. Formally, a CRN is only limited by a few constraints: (1) each atom is perfectly coordinated, (2) atoms form a disordered network without long-range order, i.e., do not show crystallinity, and (3) a CRN is uniform, i.e., it contains no coordination defects or voids. With these few rules, it is possible to construct a wide range of structures with different relevance to physical systems. This relevance can be assessed from purely structural properties, such as the bond-length and bond-angle distributions, or from energetic considerations; the latter requires, of course, a potential that grasps the essence of the energetics of the material.

The first CRNs were built in the 1960s by hand \[1\]. Rapidly, however, it became clear that the boundaries of these models in combination with their limited size makes them unsuited for studying bulk properties. In a tour de force, Henderson managed to construct by hand a network of 61 atoms with periodic boundary conditions \[2\], but further progress could be made only through computers. The first generic algorithm to construct CRN models was proposed by Guttman \[3\]. This algorithm did not scale very well, however, and the models remained limited to about 60 atoms. In 1985, Wooten, Winer and Weaire introduced a clear and straightforward algorithm for building amorphous networks of any size \[4\]. This algorithm, known as the WWW algorithm, remains the reference to this day.

In the mid-eighties another approach for building models of amorphous materials and studying their properties was developed: quench-from-the-melt molecular dynamics (MD). With the availability of the first empirical interatomic potentials describing multiple phases of given materials, it was possible to start from a melted crystal and then simulate the quenching to a disordered phase.\(^\ast\) In 1985, Stillinger and Weber generated the first such model for \(\alpha\)-Si \[5\], followed by a flurry of other models created using either the same potential (referred to as SW) or similar ones such as that of Biswas and Hamann \[6\] and Tersoff \[7\]. Four years after the first empirical MD simulation, Car and Parrinello \[8\] demonstrated that \textit{ab initio} MD could also be used to generate models of \(\alpha\)-Si, albeit small and highly strained.

The last ten years saw some noticeable refinements in the quality of models. Larger and better models were generated by Djordjević, Thorpe and Wooten \[9\] and Morgan and Holender \[10\] using the standard WWW approach. New potentials were also proposed by Tsuneyuki and co-workers for \(\text{SiO}_2\) \[11\] (refined later by van Beest et al. \[12\]), and for many other binary and ternary materials by the group of Kalia and Vashishtha \[13-16\]. Recently, Bazant and co-workers introduced a new environment-dependent interaction potential (EDIP) for all phases of \(\text{Si}\) \[17\], renewing some activity in the field.

Over the last few years, we have also been contributing to the model building. Using a modified SW potential, fitted directly to the amorphous phase \[18\], along with the activation-relaxation technique \[19\], we were able to

\(^\ast\) Actually, many amorphous semiconductors, such as \(\alpha\)-Si, cannot be obtained experimentally by cooling down the liquid; they are grown by deposition or created by ion-bombardment techniques.
generate the best models constructed with this type of potential. We found, however, that the bond-switching WWW algorithm still produces the best overall models, with the lowest strain and lowest angular distortion. We have since been considering a number of issues regarding these models, including effects of introducing crystallites in the networks and studying their stability.

In this paper, we review the recent advances in CRN model construction and present some of our new results.

II. AMORPHOUS STRUCTURES WITH THE ACTIVATION-RELAXATION TECHNIQUE

With the activation-relaxation technique (ART) [19] it is possible to study the low-temperature dynamics of a variety of disordered materials, and produce well-relaxed atomic configurations. Since ART does not forbid coordination defects, the resulting configurations are not ideal CRN models. Their low defect density, however, still allows for a direct comparison with ideal CRN models obtained, for instance, by the WWW approach.

For example, ART could be used to confirm that the low-temperature low-strain disordered configuration associated with the Stillinger-Weber potential is not the CRN but a much more liquid-like network, with a coordination significantly above 4 [19]. Many papers in the late eighties and early nineties had come to similar conclusions but without being able to separate the role of potential from that of molecular dynamics [20–22].

To establish clearly the role of the potential, we started from the completely randomly packed configuration with the SW potential as the model for atomic force interactions and applied ART, until the configurational energy converged to a stable value. We then repeated the ART-relaxation procedure (again with the SW interaction) but this time starting from a high-quality CRN. The final configurations obtained by structural relaxation from these two starting points were found to have similar liquid-like structural properties, in agreement with MD simulation but in disagreement with experimental data, confirming the limitations of the SW potential.

Recently, we used a similar procedure to fit a potential directly to the amorphous phase [18]. Most empirical potentials are fitted to a number of crystalline and liquid phases, and in addition to structural and surface defects. Since the structural properties of these phases are known, such fits are possible, and ab-initio energetic calculations can act as reference points. Fitting a potential to structural properties in an amorphous phase is much harder since it requires the availability of representative atomic structures. Using ART we could generate such structures, fitting parameters for the interaction potential directly to the amorphous phase. This new set of parameters, applied to the functional proposed by Stillinger and Weber, produced enhanced three-body interactions and a rescaled overall energy prefactor. Structures obtained with this modified SW potential have a low concentration of defects and correspond better to experiments and the CRN models.

ART was also used to simulate a number of other disordered materials such as GaAs [23] and SiO2 [24]. Using an approach similar to that for a-Si, the chemical interactions were adjusted in an ad-hoc manner for GaAs in order to obtain structures with a low density of chemical defects (Ga-Ga or As-As bonds). In the second case, we used available potentials without any modifications and found that the van Beest potential [12] led to a slightly lower density of defects in SiO2 than the screened-Coulomb potential developed by Nakano et al. [13], in much better agreement with experiment.

III. IMPROVED WWW ALGORITHM TO BUILD A CRN

An alternative approach to the generation of models for specific amorphous covalent materials is to start from a continuous random network model. A number of issues can be addressed this way. For example, we still do not know how the elastic strain scales with size in a CRN: does the choice of boundary conditions play a role for relatively small models, say, below 10 000 atoms? If so, the thermodynamic limit of CRN models could include a finite density of defects even at zero temperature. The overall question of the nature of basic defects in amorphous covalent materials remains open; more work in the construction of high-quality CRNs can help us to address this question, and to understand the degree of applicability of the CRN concept to real materials.

Along this line, we have recently revisited the WWW bond-switching algorithm and managed to improve its efficiency by more than two orders of magnitude [25]. The detailed description of these modifications can be found elsewhere [25] and we just discuss here the most important improvements, after reviewing the basics of the WWW algorithm.

The definition of the CRN, in the WWW-method, is purely topological. A list of neighbors is maintained for each atom, irrespective of the actual positions of the surrounding atoms. Although unlikely to occur, two atoms might be virtually on top of each other and still not interact if they are not explicitly bonded. The basic bond-switching move starts with the selection of a chain of four bonded atoms, ABCD. The two bonds AB and CD are replaced by two other bonds AC and BD, leading to a chain ACBD after the bond transposition. Figure 1 shows such an event.

The atomic interactions are described by a simple Keating potential:
\[ E = \frac{3}{16} \alpha \sum_{<ij>} \left( \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} - d^2 \right)^2 + \frac{3}{8} \beta \sum_{<ijk>} \left( \mathbf{r}_{ij} \cdot \mathbf{r}_{ik} + \frac{1}{3} d^2 \right)^2 \]  

(1)

The original WWW algorithm starts from a crystalline cell, which is then disordered by running at an elevated temperature; this bears the risk that the resulting configuration could still show signs of crystallinity. To avoid this problem, we start from a randomly packed configuration, with the list of neighbors constructed through a random process which ensures that all atoms have exactly four neighbors. Before starting the simulation the initial configuration is relaxed into a local minimum, keeping the list of neighbors intact.

FIG. 1. A basic WWW bond-exchange move: (a) initial chain ABCD before the bond exchange, (b) chain ACBD after the bond exchange, (c) chain ACBD after the bond exchange (unfolded).

The two major improvements over the original algorithm are the following:

- If at any stage during the relaxation of the atomic coordinates it becomes clear that the final configuration will be rejected, the relaxation is halted immediately without doing a full relaxation.

- A mixture of local/nonlocal relaxation steps is used to limit the number of global force evaluations. After a bond transposition, we first relax the configuration locally and perform a global relaxation only if the move has a chance of being accepted. This step makes the time per move almost independent of the system size.

Besides these modifications, we also perform regular quenches to zero temperature, change the volume and otherwise stress the model in order to allow the system to evolve as rapidly as possible and to reduce its strain (defined here by the bond-length and bond-angle distributions).

FIG. 2. Top: Electronic density of states for the 1000-atom model 2 as obtained using ab-initio tight-binding. Bottom: Close-up of the gap region. The dashed curve is an exponential fit, \( \rho(E) \propto \exp(-E/E_0) \), with \( E_0 = 0.2eV \). These modifications to the original WWW algorithm have allowed us to generate significantly better CRN models than what had been generated until then. Table I shows structural properties of these models compared with the best models previously available. The most important feature of these models is probably the absence of states in the electronic gap. These models are the first ones to provide a totally clean gap between the valence and conduction bands which makes it possible to employ them in detailed studies of the band-edges and other optical properties [26]. For comparison, we present in Table II some structural properties of models for \( \alpha \)-Si created with quench-from-the-melt MD utilizing local-density approximation (LDA) within the density functional theory, empirical tight-binding (ETB) or empirical potentials (here SW or EDIP) as models for atomic force interactions. It is clear that all these models have...
unphysically high concentrations of coordination defects and more strain (according to the width of the bond-angle distribution \(\Delta \theta\)) than the models created with both original and modified WWW algorithms.

**TABLE I.** Energetic and structural properties of models relaxed with the Keating potential. The first two models, DTW\(^{(1)}\) and DTW\(^{(2)}\) are the models prepared in [9] and refer, respectively, to a model with and without four-membered rings. Configurations 2 and 3 are 1000-atom models prepared according to the procedure described here and ‘4096’ is a 4096-atom model prepared the same way. All three models are without four-membered rings. The ring statistics are for irreducible rings and \(\rho_0\) is based on \(r_0 = 2.35\,\text{Å}\).

<table>
<thead>
<tr>
<th></th>
<th>DTW(^{(1)})</th>
<th>DTW(^{(2)})</th>
<th>Conf. 2</th>
<th>Conf. 3</th>
<th>4096</th>
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<tr>
<td>(E(\text{eV})/\text{atom})</td>
<td>0.336</td>
<td>0.367</td>
<td>0.267</td>
<td>0.264</td>
<td>0.304</td>
</tr>
<tr>
<td>(\rho/\rho_0)</td>
<td>1.000</td>
<td>1.000</td>
<td>1.043</td>
<td>1.040</td>
<td>1.051</td>
</tr>
<tr>
<td>(\langle r \rangle/\rho_0)</td>
<td>0.996</td>
<td>0.997</td>
<td>0.982</td>
<td>0.982</td>
<td>0.980</td>
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<tr>
<td>(\Delta r/\rho_0) (%))</td>
<td>2.52</td>
<td>2.65</td>
<td>3.94</td>
<td>0.371</td>
<td>4.17</td>
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<tr>
<td>(\langle \theta \rangle)</td>
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<td>109.25</td>
<td>109.30</td>
<td>109.27</td>
<td>109.28</td>
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<tr>
<td>(\Delta \theta)</td>
<td>10.51</td>
<td>11.02</td>
<td>9.21</td>
<td>9.20</td>
<td>9.89</td>
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**Rings/atom**

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<th>8</th>
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<td>0.000</td>
<td>0.000</td>
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<td>0.000</td>
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<tr>
<td>5</td>
<td>0.491</td>
<td>0.523</td>
<td>0.472</td>
<td>0.480</td>
<td>0.490</td>
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<tr>
<td>6</td>
<td>0.698</td>
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<td>0.761</td>
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<td>0.484</td>
<td>0.462</td>
<td>0.507</td>
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<tr>
<td>8</td>
<td>0.156</td>
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<td>0.034</td>
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**TABLE II.** Structural properties of quench-from-the-melt models for \(a\)-Si created by Stich, Car and Parrinello (CP), Cooper, Göring and McKenzie (CGM), Kim and Lee (KL), Urbassek and Klein (UK), Kluge, Ray and Rahman (KRR), Luedtke and Landman (LL) and Justo et al. (JJK). \(C_n\) is the percentage of atoms with coordination \(n\); \(n_C\) is the average coordination.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>SCP</th>
<th>CGM</th>
<th>KL</th>
<th>UK</th>
<th>KRR</th>
<th>LL</th>
<th>JJK</th>
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<td>Type</td>
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<td>ETB</td>
<td>ETB</td>
<td>SW</td>
<td>SW</td>
<td>EDIP</td>
</tr>
<tr>
<td>(N)</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>128</td>
<td>216</td>
<td>588</td>
</tr>
<tr>
<td>(T) (K)</td>
<td>300</td>
<td>300</td>
<td>0</td>
<td>300</td>
<td>472</td>
<td>360</td>
<td>1728</td>
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<tr>
<td>(C_3) (%)</td>
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<td>4.7</td>
<td>3.2</td>
<td>1.5</td>
<td>0</td>
<td>0.5</td>
<td>0.23</td>
</tr>
<tr>
<td>(C_4) (%)</td>
<td>96.6</td>
<td>92.6</td>
<td>82.8</td>
<td>96.9</td>
<td>88</td>
<td>87.8</td>
<td>94.43</td>
</tr>
<tr>
<td>(C_5) (%)</td>
<td>3.2</td>
<td>1.6</td>
<td>12.5</td>
<td>1.6</td>
<td>12</td>
<td>11.5</td>
<td>5.34</td>
</tr>
<tr>
<td>(n_C)</td>
<td>4.03</td>
<td>3.96</td>
<td>4.28</td>
<td>4.001</td>
<td>4.12</td>
<td>4.12</td>
<td>4.054</td>
</tr>
<tr>
<td>(\langle \theta \rangle)</td>
<td>108.32</td>
<td>107.38</td>
<td>106.7</td>
<td>108.4</td>
<td>108.3</td>
<td>108.6</td>
<td></td>
</tr>
<tr>
<td>(\Delta \theta)</td>
<td>15.5</td>
<td>15.2</td>
<td>16.3</td>
<td>13.6</td>
<td>14.7</td>
<td>14.0</td>
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</table>

**IV. PARACRYSTALLINE**

With a flexible and efficient algorithm such as the one presented in the previous section, it is possible to address a number of questions that were not yet considered with success. In the last few years, for example, indications of paracrystallinity in samples of amorphous silicon prepared by sputtering were found with fluctuation-electron microscopy [33], which directly samples structure on the 10–20 Å-lengthscale, corresponding to the so-called medium-range order. Previously, some paracrystalline models were constructed using quench-from-the-melt MD and the Stillinger-Weber potential [34], by allocating certain regions in the initial crystalline structure (the ones that would eventually become crystalline grains) and keeping these regions at zero temperature during melting thus not allowing them to dissolve. These paracrystalline models, however, contain unrealistically large concentrations of structural defects (miscoordinated atoms), leading to an unphysically high density of electronic states in the band-gap region [35].

We address this issue using a variation of the algorithm presented above [36], where we introduce crystalline grains in the random initial configuration, fully bonding all atoms and performing a series of bond transformations while not allowing the bonds inside the crystallites to be exchanged. The resulting models show clean electronic gaps and a very low level of strain even at the grain interfaces. Figure 3 presents a comparison of the radial distribution function for the 4000-atom paracrystalline model, the 4096-atom \(a\)-Si model presented in the previous section and an experimental measurement by Laaziri et al. [37] on fully annealed \(a\)-Si prepared by ion-bombardment. Even with 10% of atoms belonging to crystalline grains, the RDF of the paracrystalline model is essentially indistinguishable from the fully amorphous model (except, perhaps, for the shoulder at 4.5 Å, which corresponds to the third-neighbor peak in the crystal). We find similar results for other global properties of the model such as the bond-angle distribution and the vibrational and electronic density of states. The only standard structural quantity that does provide an indication of the crystalline order in the model’s structure is the dihedral angle distribution which cannot, however, be measured experimentally (Fig. 4).

Standard experiments, therefore, cannot distinguish between presence or absence of medium-range order in amorphous silicon. A calculation of the fluctuation microscopy signal \(V(k)\) for the models, however, shows that paracrystalline modes, in particular the 4000-atom model, show structure in the \(V(k)\) that is similar to that measured on samples prepared by sputtering (Fig. 5). Because it is currently still impossible to compare the absolute magnitudes of the simulated \(V(k)\) peaks for the models to experiment — only the overall shape — the
agreement between the experimental and simulated data does not imply a concentration of crystalline grains of 10% but simply the existence, at some density, of similar structures.

FIG. 3. Radial distribution function $g(r)$ for a 4000-atom paracrystalline model with four crystalline grains (px4000_4) and the 4096-atom $a$-Si discussed in the previous section. The experimental curve was measured by Laaziri et al. on a fully annealed sample of $a$-Si prepared by ion-bombardment. The small shoulder at the right of the second-neighbor peak in the paracrystalline model corresponds to a crystalline peak. Similar results were obtained for paracrystalline models with 400 and 1000 atoms.

FIG. 4. Dihedral-angle distribution for the 4000-atom paracrystalline and the 4096-atom CRN models.

FIG. 5. Simulated fluctuation microscopy signal $V(k)$ for 1000 and 4000-atom paracrystalline models, 1000-atom CRN model and the experimental measurement for thin film of $a$-Si prepared by sputtering. The scale on the simulation signal was adjusted by a multiplicative factor. (All the data for this figure has been provided by P. M. Voyles.)

V. CRystallization

One of the major differences between simulation and experiment regarding amorphous materials is the procedure for preparing the samples. The dynamics of WWW and similar bond-switching approaches is clearly unphysical and only the final product is realistic. Many MD simulations, for their part, attempt to produce $a$-Si by rapid cooling from the liquid phase. Although more realistic in appearance, this quench-from-the-melt approach is also unrealistic: even the longer simulations, using empirical potentials, can only reach 10 to 100 ns, for a cooling rate of at least $10^{10}$ K/s, which is far in excess of experimental cooling rates. The resulting structures, which are amorphous, are also formally in disagreement with experiment, where such a procedure leads to polycrystalline samples and not to $a$-Si; $a$-Si crystallizes under annealing at temperatures as low as 800 K.

Until now, all simulations have failed to reproduce crystallization either from the melt or during annealing at a lower temperature. The origin of this failure can be many-fold. It might for instance be due to the short time scales accessible by molecular dynamical simulations, in combination with shortcomings of the potential. Most empirical interactions form liquid-like structures in quench-from-the-melt simulations (see Table II), which indicates that the configurations freeze too early before
they reach a four-fold structure typical of the amorphous and crystalline phases. Similarly, crystallization is hard to achieve via the local WWW-type moves; the crystallization is likely to require a higher degree of collectivity to generate grains big enough to overcome the cost of creating an interface.

Preliminary results [38] of annealing of the amorphous models created with the modified WWW algorithm show that, at least with a well-relaxed configuration, and at a relatively high temperature, it is possible to replicate experimental results. In Figure 6, we present the number of crystallite units (three-ring structures forming the smallest 3D-unit found in the zincblende structure and four-ring structures associated with a hexagonal crystal) as a function of temperature for the 1000-atom paracrystalline model discussed in the previous section. The MD simulation is performed at the same volume for all temperatures, each for a length of 1 ns. Similar crystallization in paracrystalline Ge was found with the Tersoff potential, but at a much larger threshold (2 nm) for the diameter of the crystallite compared to 0.8 nm in our case [30].

Contrary to previous quench-from-the-melt work, we find also that it is possible to crystallize a fully amorphous structure through annealing at a temperature close to melting. Figure 7 shows the re-crystallized configuration of the 1000-atom CRN constructed using the modified WWW algorithm presented above. As expected, this is not a single crystal but a polycrystalline model. To our knowledge, this is the first time a simulation re-crystallizes a covalent material.

![Final configuration of the re-crystallized cell starting from a perfect 1000-atom CRN. Although the network contains many different crystallites, the system is no longer amorphous.](image)

**VI. CONCLUSIONS**

Advances in the preparation of continuous-random-network models have made it possible to generate structures that are in agreement with experiment with respect to structural, vibrational and electronic properties. These advanced algorithms and their variations can be used to address a range of questions, such as the role of defects, voids, and other structures in pure a-Si as well as some other covalent amorphous materials such as ν-SiO₂, a-GaAs and chalcogenide glasses.

The study of these materials is still hampered by a number of hurdles. The first one is obtaining realistic structural models. In spite of the advances described here, we still lack satisfactory (in terms of size and, sometimes, in terms of quality) models for many of these materials. Potentials also remain a significant barrier. Much interest remains in the field, however, and we are confident that the coming years will see much development in this area.

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