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Binary continuous random networks

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Abstract

Many properties of disordered materials can be understood by looking at idealized structural models, in which the strain is as small as is possible in the absence of long-range order. For covalent amorphous semiconductors and glasses, such an idealized structural model, the continuous random network, was introduced 70 years ago by Zachariassen. In this model, each atom is placed in a crystal-like local environment, with perfect coordination and chemical ordering, yet longer-range order is nonexistent. Defects, such as missing or added bonds, or chemical mismatches, however, are not accounted for. In this paper we explore under what conditions the idealized CRN model without defects captures the properties of the material, and under what conditions defects are an inherent part of the idealized model. We find that the density of defects in tetrahedral networks does not vary smoothly with variations in the interaction strengths, but jumps from close to zero to a finite density. Consequently, in certain materials, defects do not play a role except for being thermodynamical excitations, whereas in others they are a fundamental ingredient of the ideal structure.

1. Introduction

Since the work of Zachariassen [1], the continuous random network (CRN) model has been considered an idealized yet reasonable representation of oriented glasses and amorphous semiconductors such as silica and chalcogenide glasses, amorphous silicon and amorphous gallium arsenide. As such, these idealized networks were the subject of extensive studies during the 1970s and the 1980s [2–4], including studies by a number of researchers present in this workshop celebrating the 60th birthday of Mike Thorpe. It turns out that, even though it is easy to assemble a generic CRN, it is much more difficult to create a network that minimizes the strain and yet satisfies fully the basic constraints of coordination. Much effort, therefore,

has gone into simply generating high-quality—i.e., low-strain—CRNs and comparing their properties to well annealed a-Si or g-SiO₂.

Let us consider the simplest CRN model, a tetrahedral network consisting of elements connected in such a way that each element has exactly four bonds. This network represents the ideal state for elemental amorphous semiconductors such as silicon, germanium and binary alloys such as SiGe, GaAs and InP. Experimentally, this state is not uniquely defined and depends strongly on the method of preparation as well as on the annealing history. However, well annealed samples are thought to be represented by low-strain CRNs.

This relation is not universally accepted as the model suffers from some limitations. In particular, the CRN model does not allow defects, which could play an important role in decreasing strain in amorphous networks. High- Q measurements of the radial distribution function in a-Si generated by ion implantation [5] indicate, for example, an average coordination of 3.88, significantly below 4.0. The question of defects is possibly even more important when considering binary semiconductors, such as a-GaAs, where the strain energy is in competition with the chemical energy and for which two types of defects can then be generated: coordination and chemical defects.

This additional competition makes the generation of low-strain binary-alloy models even more difficult and relatively little work has been done on these systems. Connell and Temkin [6] produced a 64-atom CRN with periodic boundary conditions and no odd-membered rings, demonstrating that a chemically ordered CRN was possible. Recently, Mousseau and Lewis [7, 8] generated models with a low density of coordination and chemical defects, showing that the cost of a chemically unfavourable bond in GaAs was sufficient to strongly favour even-membered rings.

The models generated in the studies by Mousseau and Lewis had some coordination and chemical defects, however, leaving open the question as to whether it is possible to construct a CRN with only even-membered rings, and still the same strain level as a non-constrained CRN. In this paper, we revisit this question using a modified version of the celebrated bond-switching algorithm of Wooten *et al* [9, 10] to generate CRNs with a specific density of coordination and chemical defects.

To study the role of defects in disordered materials, we start with the ordinary tetrahedral CRN model, a high-quality and well defined reference state. Two types of defects are then introduced: *dangling bonds*, associated with undercoordinated atoms, and *wrong bonds*, defined in this case as a bond between two atoms of the same species in a binary alloy. Dangling bonds are found in any elemental and alloyed amorphous semiconductors; wrong bonds belong only to the later type, GaAs or InP, for example.

Using a simple quadratic potential [15], we find a linear relation between the density of defects and the strain in the lattice for the lowest-energy structures. This suggests that chemical defects are either very rare or exist with a density of at least 16% since the energy gain of adding or removing a defect is the same at all concentrations.

2. Computer generation of well relaxed CRN

Because of its link with a simple elemental material, the most studied CRN model has been the tetrahedral one.

The first method for producing efficiently, and in a reproducible fashion, numerical models of CRN was introduced in 1985. The 1970s had seen a number of hand-built models with a large surface-to-volume ratio and, in 1980, Guttman proposed a first numerical algorithm for preparing tetrahedral CRNs [4]. However, this algorithm only worked for small cells of less than 100 atoms and was not easily implemented. Assembling three ‘W’s a few years before

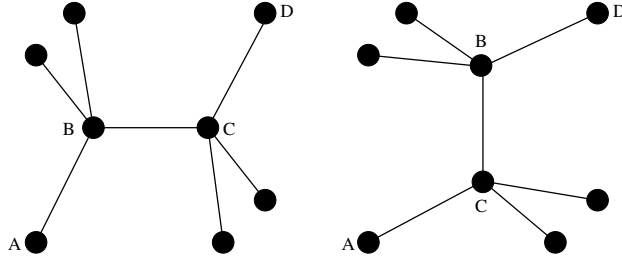


Figure 1. Diagram depicting the WWW bond transposition. Four atoms A, B, C, and D are selected following the geometry shown left; two bonds, AB and CD, are then broken and atoms A and D are reassigned to C and B, respectively, creating two new bonds, AC and BD, resulting in the geometry shown right.

their time, Wooten *et al* [9, 10] devised a clever algorithm, involving local bond switches, that could rapidly transform a crystalline diamond structure into a low-strain amorphous structure.

This method, and the original models, were used by many groups over the following decade to study flexibility and other structural and electronic properties of fully coordinated a-Si networks as well as related materials such as SiO₂ and a-Si:H.

Twenty years after its introduction, the WWW algorithm remains a useful tool. Improving computational aspects of the algorithm, we could gain about two orders of magnitude in efficiency [11, 12], allowing us to generate low-strain models of a-Si with up to 100 000 atoms and v-SiO₂ up to 300 000 atoms [13], as well as studying paracrystalline Si [17], a controversial new phase identified recently.

2.1. The WWW bond-switching algorithm

In the WWW approach, a configuration consists of the coordinates of N atoms and a list of the $2N$ bonds between them. The structural evolution consists of a sequence of bond transpositions as illustrated in figure 1: in 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. The generation of a CRN starts with a cubic diamond structure which is randomized by a large number of such bond transpositions. After randomization, the network is relaxed through a sequence of bond transpositions, accepted with the Metropolis acceptance probability [14]:

$$P = \min \left[1, \exp \left(\frac{E_b - E_f}{k_B T} \right) \right], \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, and E_b and E_f are the total quenched energies of the system before and after the proposed bond transposition.

With an explicit list of neighbours, it is possible to use a simple harmonic interaction such as the Keating potential [15] to calculate energy and forces:

$$E = \frac{3}{16} \frac{\alpha}{d^2} \sum_{\langle ij \rangle} (\vec{r}_{ij} \cdot \vec{r}_{ij} - d^2)^2 + \frac{3}{8} \frac{\beta}{d^2} \sum_{\langle jik \rangle} \left(\vec{r}_{ij} \cdot \vec{r}_{ik} + \frac{1}{3} d^2 \right)^2, \quad (2)$$

where α and β are the bond-stretching and bond-bending force constants, and $d = 2.35 \text{ \AA}$ is the Si-Si strain-free equilibrium bond length in the diamond structure. For Si, the standard values for the force constants are $\alpha = 2.965 \text{ eV \AA}^{-2}$ and $\beta = 0.285\alpha$. Since the list of interacting atoms is explicit and not based on the interatomic distance, it is possible for two atoms to be virtually on top of each other but still not interact if they are not explicitly bonded.

This unwanted situation becomes however increasingly rare with improved quality of the CRN structure.

Wooten and Weaire followed this approach to generate a 216-atom model with an angular distribution of 10.9° [10]. A decade later, Djordjević *et al* exploited the advance in computing hardware and produced two large 4096-atom networks with a bond-angle distribution of 11.02° for configurations without four-membered rings and 10.51° when these rings are allowed [16].

The WWW algorithm in its original form is not well suited to generate CRNs much larger than a few thousand atoms. This is mostly due to the fact that for each proposed bond transposition about 100 energy and force calculations are required, each scaling as $\mathcal{O}(N)$ with system size N . These $\mathcal{O}(N)$ operations are the bottleneck of the algorithm. A few years ago, we presented a number of modifications to the original WWW algorithm, partially aimed at resolving these poor scaling properties [11].

Using the improved WWW algorithm, we generated two 1000-atom models with bond angle deviations as low as 9.20° [11]. Furthermore, using the same algorithm we generated a 4096-atom model with an angular deviation as low as experimentally accessible—around 9° . With some more improvements in the implementation of the algorithm, we succeeded in generating well relaxed configurations of up to 100 000 atoms [12, 13].

2.2. Extension to binary networks with defects

The original WWW algorithm was designed to generate generic tetrahedral CRNs. Here, we introduce a series of modifications to this algorithm that allow us to control the degree of chemical ordering and the proportion of coordination defects.

The crystalline structure of binary networks does not provide a good starting point, since the temperatures at which it starts to melt in a reasonable time are so high that, before the crystalline structure has been left behind everywhere, some parts of the network develop lots of unwanted anomalies which require a lot of effort to anneal. We therefore construct initial CRNs with a different procedure, guaranteed to have no remainders of the crystalline state. Atoms are initially placed in the box at random, and labelled A and B, in equal proportions. Bonds are then assigned to pairs of differently labelled atoms, with a strong preference for near atoms, until the desired total coordination of four is reached. The elastic strain, defined by the Keating potential (equation (2)) plus a repulsive constant in the case of wrong bonds, is then minimized under fixed topology. This whole procedure results in initial CRN configurations with a bond-angular spread of around 35° , without long-range order, or chemical or coordination defects.

The topology of these initial configurations is then relaxed through a series of local and non-local Monte Carlo moves, as described in figure 2. Some of these moves can introduce chemical defects, if the move results in a sufficient reduction in the elastic strain; although the initial configuration is chemically ordered, the chemical state of the final configuration depends on the cost assigned to wrong bonds. A thorough relaxation for 1000-atom models requires several million attempts per atom, which can be done in a few days on a fast workstation.

On a tetrahedral CRN without any penalty for odd-membered rings, a smart assignment of the atomic labels results in a defect density around 15%; a lower density of defects can only be obtained by chemical ordering leading to a lower proportion of odd-membered rings in the network.

3. Results

We generated well relaxed configurations with a varying degree of chemical ordering by tuning the energetic penalty for chemical defects. All the configurations used in this work are 1000-

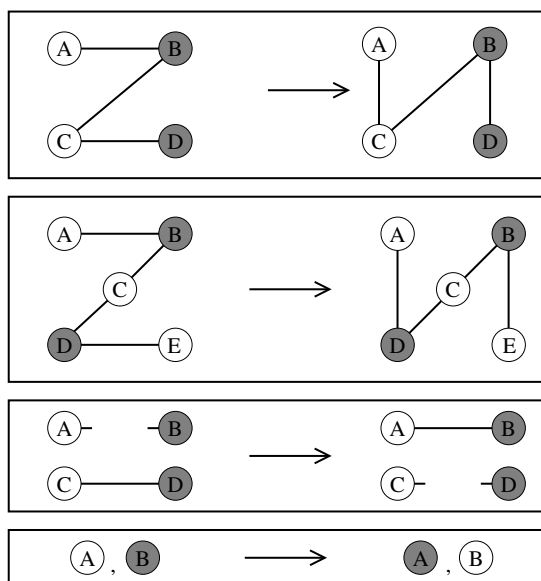


Figure 2. Diagrammatic representation of the moves used in our simulations on binary CRNs. (a) We employ the usual bond transposition as proposed by Wooten *et al.* This move introduces (and sometimes removes) chemical defects, as can be seen by the appearance of the bonds between two white atoms and between two grey atoms. (b) If instead of two nearest-neighbour atoms two next-nearest-neighbour atoms exchange their neighbours, a sample without chemical defects stays chemically perfectly ordered. (c) Simultaneously a pair of dangling bonds is bonded, while a bond is removed elsewhere. (d) Two chemically different atoms exchange their chemical nature.

atom cells at the density of the diamond crystal structure, i.e., near zero pressure. Depending on the ratio of the potential parameters tuning the bond length and angles, there is a limited trade-off between these two quantities. To be physically relevant, the bond-length fluctuation in these models should not exceed a few per cent. In this case, the width of the bond-angle distribution becomes a good indicator for structural properties of the networks, scaling linearly with the total energy, irrespective of the details of the interaction potential.

Without any defect, the best model we can construct still shows a bond-angle distribution of 15° , much higher than the 9° – 10° that can be reached in a model without chemical order.

As mentioned above, with about 15% chemical defects and suitable labelling, the network topology is equivalent to that of a-Si. Similarly, 15% of under-coordination is sufficient to ensure no chemical defect with ring statistics identical to that of a-Si with the same density of defects. The similarity between these two defects can be seen in figure 3, which shows the radial distribution function (RDF) for a perfectly ordered and coordinated lattice as well as for lattices with 5, 10 and 15% chemical defects. The bottom panel compares the RDFs of two models with 10% of chemical and coordination defects. Even though the RDF changes as a function of defects, as was demonstrated previously [7], this is not a very sensitive quantity and it is not precise enough to provide a well defined experimentally measured defect density.

This is confirmed by plotting the bond-angle distribution as shown in figure 4. We could have expected that coordination defects would be better at removing the strain in the model, as each defect also removes a constraint on the bond-length, yet the effect is surprisingly small. The two systems relax with a bond-angle distribution width of 8.12° and 9.16° .

The main result is presented in figure 5, where the minimal angular spread is plotted as a function of the density of coordination and chemical defects. The resulting surface defines the

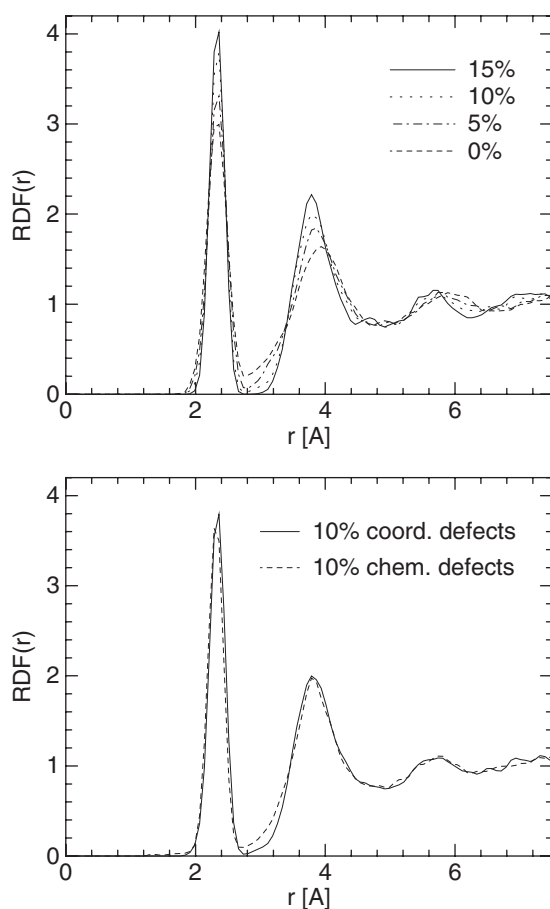


Figure 3. Top: radial distribution functions obtained from the samples without coordination defects, but with 0%, 5%, 10% and 15% chemical defects (wrong bonds). Bottom: comparison of radial distribution functions obtained with samples with either 10% chemical defects, or 10% coordination defects.

‘optimal’ surface, i.e. a characterization of networks with the lowest elastic strain. Networks above this optimal surface will eventually evolve to this surface by reducing the number of coordination or chemical defects, or by reducing the elastic strain. It should not be possible to find experimental samples falling well below this surface.

Excepting densities below one per cent, where our relaxation algorithm is less efficient, there is a linear relation between these two quantities, and thus between this defect density and the total energy; the surface is well fitted by a plane, described by

$$\Delta\theta = a - b\rho_c - c\rho_t, \quad (3)$$

where ρ_c is the density of chemical defects, and ρ_t is the density of topological defects. A least-squares fit to the parameters a , b and c gives $a = 15.59 \pm 0.05$, $b = 49.8 \pm 0.5$ and $c = 45.1 \pm 0.7$.

Apparently, the release in elastic strain per defect added is constant, i.e., it is equally hard to remove the first defect and the last one. If the nature of the interaction strengths in the material is such that it can remove a single defect, it will be strong enough to remove *all* defects!

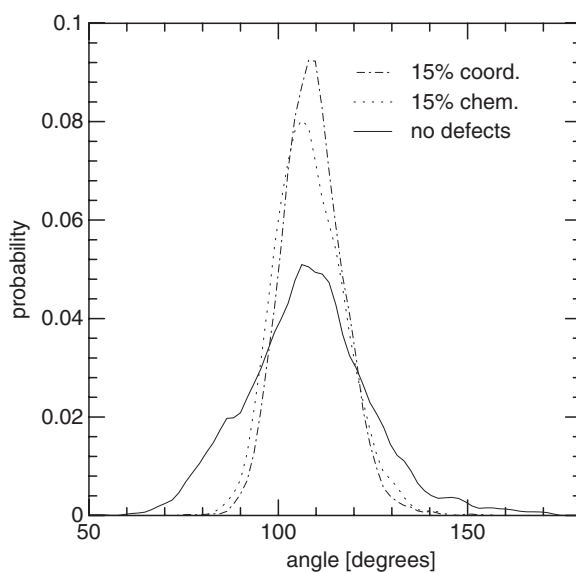


Figure 4. Bond angle distribution for the perfectly coordinated and chemically ordered model with a width of $\Delta\theta = 16.42^\circ$, with 15% chemical defects ($\Delta\theta = 9.16^\circ$), and with 15% coordination defects ($\Delta\theta = 8.12^\circ$).

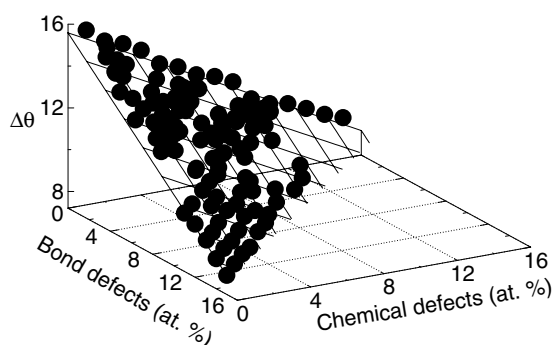


Figure 5. Minimal angular spread obtained in our binary tetrahedral networks, as a function of the density of coordination and chemical defects.

4. Conclusion

Generating a set of well relaxed configurations with various densities of chemical and coordination defects, we studied the impact of chemical ordering and bonding on the structural properties of continuous random networks. For this, we use an enhanced WWW algorithm with millions of attempted moves per atom. In view of this extensive sampling, the configurations we obtain should be close to the optimal ones in terms of strain, allowing the following conclusions.

First, a perfectly coordinated and chemically ordered binary CRN cannot be relaxed to a structure with a bond-angle distribution below about 15° . Comparing with other amorphous networks, this is a high degree of strain. It is unlikely, therefore, that a material such as a-GaAs can be found without a sizable density of defects.

Interestingly, if the sample cannot tolerate this kind of strain, then it should display about 15% of defects—either coordination or chemical—as the relation between strain and defects is linear. Should a single defect be preferable to none, then the sample cannot be stable at any defect density below 15%. At this defect density, the strain becomes equal to or slightly below that of an elemental CRN.

These results hinge of course crucially on the issue of whether the CRN model is a reasonable description of amorphous binary semiconductors. For elemental amorphous semiconductors, it is possible to generate perfect CRN models with a strain density equal to annealed samples. No such information is available for binary semiconductors. Experimental measurements to establish whether the CRN model can be used for studying the structure of these materials would be of great interest, as direct structural values offer little precision on defect densities in these systems [18].

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