A genetic algorithm for the atomistic design and global optimisation of substitutionally disordered materials

Chris E. Mohn
Department of Chemistry and Centre for Materials Science and Nanotechnology, University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway

Walter Kob
Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR 5587, Université Montpellier II-CNRS, 34095 Montpellier, France
(Dated: September 9, 2008)

We present a genetic algorithm for the atomistic design and global optimisation of substitutionally disordered bulk materials and surfaces. Premature convergence which hamper conventional genetic algorithms due to problems with synchronisation is avoided using a symmetry adapted crossover. The algorithm outperforms previously reported Monte Carlo and genetic algorithm simulations for finding low energy minima of two simple alloy models without the need for any redesign.

INTRODUCTION

Crystal structure prediction and the design of functional materials from first principles continue to present a major challenge to the theoretician [1, 2, 3, 4]. It is unfortunate that the presence of imperfections and disorder make these problems even harder. Nevertheless, taking explicitly into account disorder (both impurities and defect concentrations far from the dilute limit), rather than resorting to various mean-field approaches and simple crystallographic models, is of key importance in order to understand material properties at their working temperature and pressure [5, 6].

Many materials with defect concentrations far from the dilute limit have a substitutional disordered structure. Prime examples involve metallic and semiconductor alloys as well as many ceramics, all of which are of tremendous technological importance within numerous fields as electric-, magnetic-, and optical components or devices. However, substitutionally disordered materials are in general not well understood from an atomistic point of view, and describing the preferential arrangements of the atoms and defects is essential in order to help searching for materials with target properties [7]. Identifying the local structural variations within disordered compounds is not only essential for designing new materials, but the disorder provided by the solid solution of atoms in minerals is also essential for understanding the dynamics in the earth’s interior and of particular importance to assess computationally since these compounds often only exist at conditions (high pressure and temperature) which are difficult to reproduce experimentally [8].

Taking explicitly into account the variation in the local structure is not only important for understanding disordered bulk materials, but also essential for understanding many surface phenomena. For example, simulations of the deposition of small organic molecules on various metal surfaces [9], and locating the surface-configurations which are likely to influence the powder morphology of, e.g., UO₂ [10] are not trivial due to the multitude of different possible atomic arrangements. Also, the ability to position atoms at will using a STM-tip [11] or the opportunities provided by various atomic vapour deposition techniques open the way to efficient material design in search for configurations/superstructures with certain target physical properties which may be difficult to guess by chemical intuition.

In a first attempt to attack substitutionally disordered materials by simulation in search for, e.g., low energy configurations and superstructures, one could carry out an exhaustive and unbiased enumeration of all likely candidates. Alas, such a procedure allows only the smallest simulation cells to be investigated. Consider, for example, the archetypal binary fcc alloy of gold and copper, AuCu. Although the smallest simulation cells can be investigated by means of brute force enumerations (for instance the small 4 atom unit-cell has only 12 distinct arrangements), the number of arrangements explodes rapidly with the size of the simulation box. Within a 2 × 2 × 2 simulation cell there are 6 × 10⁷ ways of arranging the 16 Au and 16 Cu, whereas a 4 × 4 × 4 (256 atom) supercell contains 6 × 10⁷⁵ configurations. Sadly, often much larger cells (> 1000 atoms) are needed for the accurate calculation of many alloy and mineral properties. Although symmetry can be used to reduce the search space [12], the combinatorial explosion of the number of potential energy minima cannot be overcome by conventional means, and other strategies are required.

Finding low energy minima (including the ground state) or configurations with “key properties” for alloys are in general nondeterministic polynomial-time hard in which heuristics such as for instance genetic algorithms (GA) have the potential to be particular suitable [13]. Indeed, Smith has demonstrated [14], in probably the first application of GA for the study of disordered materials, that GA are highly efficient in finding low en-
energy configurations for several simple alloy-models. It was shown that GA typically outperform the popular Metropolis Monte Carlo algorithm (MC).

Several contributions have demonstrated how GA can be applied successfully for the study of crystalline materials with substitutional disordered structure. Kim et al. as well as Dudiy and Zunger applied GA for the study of semiconductor alloys via the use of an inverse band structure approach in which alloy-configuration with particularly large band-gaps were searched for. Applications of GA in search for low energy configurations of simple binary oxide solid solutions have also been successful.

However, despite these promising attempts, the dynamics of genetic algorithms for the study of strongly disordered materials is not well understood and problems of choosing a suitable representations as well as the role of the different GA-operators require further investigations. In particular when bearing in mind that recent global energy minimisations of very simple 1D Ising models are very similar to that of finding low energies of alloys have shown that conventional GA are hampered by slow convergence at the late stage of the evolution due to the presence of inherent symmetry. We shall therefore take the opportunity to investigate very simple alloy models via GA, in an attempt to provide a solution to problems which appear to hamper the use of conventional GA for the study of substitutional disorder and related problems in which the underlying symmetry may explain the slow convergence of conventional GA.

We follow closely Smith, who carried out detailed tests on several different simple alloy models and compared the performance of conventional GA with that of MC. First, we give a general introduction to conventional GA within the field of alloy modelling. The basic ingredients are briefly discussed. Then, having identified and analysed the synchronisation problem which appear to hamper conventional GA, we briefly describe an efficient and general GA for finding alloy-configurations with target physical properties, e.g. low energy minima, using a simple 1D Ising model as an example. We discuss the algorithm for two simple 2D alloy models with non-trivial representations (genetic encoding), and compare with previously reported GA and MC simulations. The first model is a simple 2D periodic binary “Ising alloy” with nearest neighbour interactions. This model is an important benchmark for testing and analysing the performance of GA since exact analytical solutions exist and since the thermodynamic behaviour is well understood. The second test is also a 2D alloy model, where the atoms now interact via a Morse potential with parameters chosen such as to mimic the BiCu alloy. This test is particular challenging for conventional GA as demonstrated by Smith who found that GA actually perform worse than MC in locating low energy minima. We finally compare results from simulations using Ising models and Morse potentials such as to analyse the influence of the shape of the potential (the distribution of fitness) on the performance of GA.

**THEORY**

**The alloy models**

**Ising alloy**

The first case is a simple periodic 2D Ising model where the atoms are distributed on a square lattice. The potential, originally introduced for the study of ferromagnetism in 1925 by Ising, is given as (ignoring external fields)

$$V = -\frac{1}{2} \sum_{<ij>} J \sigma_i \sigma_j.$$  

The “spins”, $\sigma_i$, are either +1 (spin up) or −1 (spin down) and J is the (exchange) coupling constant between the spins. The summation is carried over the nearest neighbours only. For the study of binary alloys using a potential of the form of equation, $\sigma_i$ now represent an atom located at site i and J is associated with the bond energy. We choose $J = -1$, such that bonds between unlike atoms contribute −1 to the total energy and bonds between like pairs contribute +1 to the total energy. The potential is thus designed to promote a high degree of mixing between the different species. For the study of alloys, the summation in equation is *constrained* to maintain the overall composition (or magnetisation). That is

$$m = \sum_i \sigma_i = \text{constant},$$

throughout the evolution.

**Morse alloy**

Our second test is also a periodic 2D alloy model with atoms distributed on a square lattice with lattice constant 2.56 Å. The interactions are modelled using a Morse potential of the form

$$V_{ij}(r_{ij}) = D_{ij}[\exp(-2\alpha_{ij}(r_{ij}-\beta_{ij})) - 2\exp(-\alpha_{ij}(r_{ij}-\beta_{ij}))].$$

Here, $r_{ij}$ is the interatomic distance between atoms i and j. $D_{ij}, \alpha_{ij}$ and $\beta_{ij}$ are parameters which are kept fixed for a given interaction (see table). The parameters were chosen such as to model the binary BiCu bulk alloy and were employed by Smith for benchmarking his genetic algorithm.

In this work we carry out energy calculations using equation 2.3 including either only the nearest neighbour interactions, or up to the fourth nearest neighbours.
Conventional GA for the study of alloys

Genetic algorithms, originally introduced by Holland in the 1960s [13], are searches for finding good solutions to hard problems. In contrast to the popular Metropolis Monte Carlo algorithm where changes to a single solution are carried out, a population of solutions is evolved. Better solutions are found by allowing the “fitter” members of the populations to recombine and produce offspring. Random, usually small, changes (mutations) can be allowed for, such as to introduce “fresh blood” in the population and hence avoid problems with premature convergence. The advantage of GA over other optimisation algorithms is that large swaps can be carried out in the configuration space, which is particular useful within the field of global optimisations of, e.g., nano-clusters due to the roughness of the fitness landscape. Within this field, there exist reasonable consensus regarding the basic ingredients constituting efficient GA [22]. However, these are slightly different compared to those used for the study of periodic alloys and related problems such as ferromagnetism. We will therefore discuss the GA operations for modelling alloys with emphasis on the roles of crossover, mutation, encoding (choice of representation), population sizing, fitness etc., and compare in some details the present implementation with those of Smith [14] and Kim et al [16].

Encoding: For the purpose of genetic encoding it is useful to distinguish between the “real-space” solution (phenotype) and the “encoded” solution (genotype). A convenient choice of representation for modelling binary alloys is a binary string, \( x = x_1 x_2 ... x_k ... x_N \), where \( x_k \) is either 0 (if an atom of type A occupy lattice position \( k \)) or 1 (if an atom of type B occupy lattice position \( k \)), and \( N \) is the number of atoms in the simulation box. Intuitively, one expect GA to be sensitive on how the real structure is mapped to the form of \( x \). Smith [14] analysed the sensitivity of the performance of GA in the choice of different representations on simple binary alloys, by comparing runs where the atoms were mapped in major column form with those of mapping the lattice entirely at random. It was thought that GA may slow down if the positions of the atoms in the string does not reflect the actual spatial arrangement of the atoms. Although slower, GA were found to perform surprisingly well even if a “random binary representation” is used. Indeed, Kim [16] argue that a non-biased GA should not include any information of the spatial arrangements and successfully applied a “random binary representation” for the study of bulk alloys. By contrast, in ref [18] a binary representation that strongly reflects the spatial arrangements of the crystal structure was successfully used for finding low energy configuration of a binary oxide solid solution (the CaO:MgO system). This choice of representation seems reasonable due to the presence of strong Coulomb forces and the localised nature of the ionic bond. In this context, it is worth mentioning that for the optimisation of nano-clusters it is widely accepted that a real-space representation (which is isomorphic to the phenotype) performs better than a binary representation, see e.g. [23], and work is in progress to address these issues in further detail for the optimisation of substitutionally disordered materials. However, for the optimisation of 2D alloy models we have chosen to use the same representation as Smith [14] to allow for direct comparison. That is, the 2D lattice is mapped to a 1D binary string in major column form, which clearly reflect the spatial arrangements of the atoms although more “compact” binary representations exists [18].

Population-size: In GA, the initial population is constructed by selecting configurations at random. A sufficiently large initial population is in general crucial in order to avoid premature convergence. However, if the (initial) population is too large, the efficiency of the GA may slow down. On the other hand, GA are often quite tolerant to changes in the population-size. We will discuss the influence of population-size on the performance of GA below.

Fitness: The members of the population are assigned a “fitness” which measures the quality of the trial solution. Parents with high fitness are preferentially selected for, thereby the popular phrase “survival of the fittest”. The fitness in our work is the total energy (with opposite sign), taken either from the simple Ising model (equation 0.1) or from the Morse potential (equation 0.3). However, as discussed above any physical property can be used.

Selection: There are many different schemes for the selection of parents. Popular schemes are the roulette wheel-, the Boltzmann- and tournament selections. In this work we use a binary tournament selection in which two pairs are randomly chosen, and where the “fittest” member in each pair is allowed to mate. The binary tournament is convenient, since it does not require any choice of parameter that controls the selection pressure other than the population-size. It is worth mentioning that we have carried out checks with different schemes and found that GA are fairly insensitive to the choice of selection method but sensitive to the amount of selection [18].

Crossover: After a pair of parents has been selected, the parents are allowed to mate. Several types of mating operations (crossover) exist, which are either applied

| Pot     | D/eV | α/A\(^{-1}\) | β/Å |
|---------|------|--------------|-----|
| Cu–Cu   | 0.357| 1.386        | 2.82|
| Cu–Bi   | 0.154| 1.216        | 3.18|
| Bi–Bi   | 0.412| 1.136        | 3.54|

TABLE I: Parameters used with the Morse potential.
on the genotype or directly on the phenotype (the real solution). For the 2D alloy models, we use a standard binary representation where the parents are encoded in binary form. We use a two-point (TP) crossover, $O_{TP}: B \otimes B \rightarrow B \otimes B$ ($B$ is the configurational space) where two different integers $k < l \in [1, N]$ are chosen at random, and parents, $x = x_1 x_2 \ldots x_k x_{k+1} \ldots x_{l} x_{l+1} \ldots x_N$ and $y = y_1 y_2 \ldots y_k y_{k+1} \ldots y_l y_{l+1} \ldots y_N$ are cut between the points $x_k$ and $x_{k+1}$, and between $x_l$ and $x_{l+1}$ and spliced as follows

$$O_{TP}(x, y) = \begin{cases} x_1 x_2 \ldots x_k y_{k+1} \ldots y_l x_{l+1} \ldots x_N = v \\ y_1 y_2 \ldots y_k x_{k+1} \ldots x_l y_{l+1} \ldots y_N = w. \end{cases}$$

One of the children, e.g. $v$, is chosen at random, possibly mutated (see below), and added to the population by replacing the least fitted member. Note that the points where the parents are cut are chosen at random, but constrained such as to maintain the overall fixed composition. This is a severe constraint, and provides a major challenge in designing efficient GA for alloy modelling constrained such as to maintain the overall fixed composition (or magnetisation if viewed as a spin-problem). In all these cases, we found, in agreement with ref [19], that conventional GA (without mutations) are unable to find global minima of a 100 spin Ising model, even with huge population sizes.

To visualise the dynamics of a typical conventional genetic algorithm with emphasis on the role of the crossover when solving Ising-like problems, we show in figure 1 snapshots of an evolution using a 100 spin Ising model with $J = 1$ and fixed overall composition as an example. A steady state genetic algorithm, where the child replaces the worst fit member in the population, is used. The population-size is 30 and no mutations were applied.

Although the crossover is very efficient in finding low lying minima rapidly, the efficiency slows down very early in the evolution. After only 50 generations the diversity of the population is lost and the crossover has become

Conventional GA and synchronisation

Although GA have been highly successful for the study of alloys and has the potential to outperform the popular Metropolis Monte Carlo method [14, 16, 18], the optimisation of various Ising models via evolutionary algorithms have shown that conventional GA are hampered by slow convergence [19]. Simulations carried out in refs [14, 19] have shown that the use of highly specialised GA with modified mating schemes and rather “brutal” mutations (where large blocks of atoms were exchanged or scrambled with high probabilities ($> 0.1$)) were necessary to find global minima. It was argued [14], that such mating operations and mutations are required due to the constraint of fixing the overall chemical composition which severely limits the search-space of the genetic algorithm and leaves very little flexibility for the crossover to work properly. However, van Hoyweghen et al [19] carried out a detailed analysis of the dynamics of GA for finding low energy minima of an Ising ferromagnet without any such constraints and observed a similar slow convergence.

Following van Hoyweghen et al [19], we have analysed the convergence of a genetic algorithm for 1D Ising models with periodic boundary conditions. Tests were carried out with $J = 1$ and $J = -1$ with and without the constraint of fixing the overall composition (or magnetisation if viewed as a spin-problem). In all these cases, we found, in agreement with ref [19], that conventional GA (without mutations) are unable to find global minima of a 100 spin Ising model, even with huge population sizes.

FIG. 1: The populations at three stages using a conventional genetic algorithm applied to a 1D 100 spin Ising model with a fixed 50:50 composition of species A and B. Black and white squares are used to represent the different species. Top figure shows the initial population, the middle figure is the population after 50 generations (80 fitness evaluations), and the bottom figure shows the population after 100 steps (130 fitness evaluations).
useless. As can be seen, there are no recombinations which enables the building blocks within the population to combine to form higher order building blocks of an optimum.

The failure of conventional GA in finding a global minimum by means of recombinations is explained by the loss of a driving force due to the high degeneracy of symmetrically equivalent low energy configurations which in general are far away from one another in configuration space. A modest sized population does not contain sufficient diversity to “differ” between the building blocks of the low energy minima and the global minima because the high order building blocks (schemata) of the global minima are very similar compared to those of all other low energy minima. That is, the schemata of the global minima and low energy minima contain all high order building blocks such as **1100**, **1111** and **0000***. However, since the number of global minima are outnumbered by the low energy excited states and since furthermore symmetrically equivalent low energy minima (including the global minima) are far away from one another in the configurational space (in terms of Hamming distance), the conventional GA are unable to find global minima, and are stuck in a local optimum.

As can be seen in figure 1 the lack of synchronisation is manifested in the representation as domains of **00** and **11** at fixed spin-positions when conventional GA are used. The solutions found are low lying minima indeed, but clearly far away from the global minima in Hamming distance. Although the performance of conventional GA for attacking different Ising models can be improved using specialised operators [14], the strength of the crossover, which should play a major role in designing efficient GA, is not fully utilised.

**Symmetry adapted GA-operators**

Assume that the phenotype possesses some symmetry associated with a group, say $\mathcal{G}$, of order $K$, and that the representation chosen is isomorphic to the phenotype. Applying a random element $G_a \in \mathcal{G}$ on an arbitrary configuration, $\mathbf{x}$, leaves the fitness, $f$, invariant

$$f((G_a(\mathbf{x})) = f(\mathbf{x}) \quad (0.6)$$

without affecting the “schemata” of $\mathbf{x}$. At this point, it is worth emphasising, that $\mathbf{x}$ now represents the real-space configuration rather than the genotype (binary string). Replacing, at each generation, the population $(\mathbf{x}, \mathbf{y}, ...)$ with $(G_a \mathbf{x}, G_a \mathbf{y}, ...,)$, where the symmetry operations $G_a, G_b, ...$ are chosen at random allows all symmetrically equivalent configurations of the members in the current population to be accessible with equal probability at any step (generation). Thus, problems due to synchronisation is avoided, allowing the building-blocks of the optima to form also when the evolution is governed by genetic drift [13, 24].

Turning to our 1D periodic Ising model introduced above, we show how the symmetry can be incorporated in a straightforward manner within a conventional genetic algorithm scheme. Note that the 1D Ising problem, due to periodic boundary conditions, does not have the geometry of a string, but of a circle

$$\mathbf{x} = x_1x_2...x_1...x_N \text{ with } x_{N+1} = x_1, \quad (0.7)$$

and hence the encoded representation (genotype) can be trivially chosen isomorphic to the phenotype. Furthermore, when the overall composition is fixed, the genotype possesses the point-symmetry of an $N$-sided polygon and transforms according to the irreducible representations of the dihedral group, $D_N$ of order $2N$.

Having identified the symmetry of the problem, we now introduce a symmetry-adapted crossover (SAC) as follows. After applying the crossover (equation (0.4)), we act with a randomly chosen element $G_a \in D_N$ on the child, $\mathbf{x}$

$$\mathbf{x'} = G_a(\mathbf{x}), \quad (0.8)$$

and add, instead of $\mathbf{x}$, $\mathbf{x'}$ to the population.

To visualise the dynamics of utilising SAC, we return to our 100 spin Ising model showing in figure 2 a typical scenario. As can be seen by comparing the populations after 300 and 1000 steps, the use of symmetry adapted mating operations clearly enables the building blocks of good solutions (e.g. ****1100**** and ****0011****) to combine to form higher order building blocks of even better solutions (e.g. **11110000** and **00001111**). Since the operations $G_a(\mathbf{x})$ leaves the energy of $\mathbf{x}$ invariant without altering the order in which the atoms occur in the representation, large swaps can still be carried out in the configurational space when the diversity using conventional GA would have been lost (see figure 1). That is, the synchronisation problem is solved by the use of a phenotype representation and symmetry-adapted operators by means of inheriting the symmetry of the problem within the genetic algorithm. Sufficient diversity is therefore added, which enables the schemata of good solutions to combine to from schemata of even better solutions.

Now, having presented the use of symmetry-adapted operators, we turn our attention to the design of SAC for the study of 2D alloy models. Since the atoms are distributed on a square lattice, the underlying symmetry of the primitive unit-cell is that of the plane-group $p4m$. Symmetrically equivalent children are thus formed by applying the combined operations $G_a T_a$ where $G_a \in p4m$ and $T_a$ is a translation operation. Using a representation which is isomorphic to the phenotype involves the use of real-space operations. That is, cut-and-splice-type operators which are applied directly on the configurations rather than via the use of binary encodings. However, in
FIG. 2: The populations at three stages during the evolution using a genetic algorithm in conjunction with SAC applied to a 1D 100 spin Ising model with a fixed 50:50 composition of species A and B. Black and white squares are used to represent the different species. Top figure shows the initial population, the middle figure is the population after 300 generations (330 fitness evaluations) and the bottom figure shows the population after 1000 steps (1030 fitness evaluations).

order to compare with that of Smith [14], we have chosen to use a representation where the atoms were mapped in major column form to a binary ring. Since this representation is not isomorphic to the phenotype, the act with a symmetry operations on the children $x'$ may alter the order in which the atoms are arranged in the representation. However, since this representation strongly reflects the positions of the atoms in the phenotype the act of a symmetry-operation will only alter very few atoms in the encoded solution and the crossover will work properly.

RESULTS AND DISCUSSION

Finding low energy minima of a 2D Ising model

Results from GA calculations using a 100 atom Ising alloy with a square unit-cell and equal concentrations of species A and B are shown in figure 3. Results from calculations with and without the use of symmetry adapted crossover is reported. In this test $J = -1$ which promotes a high degree of mixing between the different species. 1000 independent runs were carried out, and the mean value of the best energies at each step is displayed in figure 3. A steady state genetic algorithm, where the child replaces the worst fit member in the population, is used. The population-size is 30. The conventional GA runs were carried out both with and without a mutation of exchanging a pair of atoms (using equation 0.5) with probability 0.05, whereas no mutations were used during the SAC runs.

As can be seen from the figure, the use of symmetry-adapted operators clearly outperform the conventional GA which fails in all attempts to find the global minimum, in agreement with previous studies [14,19]. Even with huge population sizes (> 500) the conventional genetic algorithm is unable to find a global minimum without the use of mutation operations. However, as can be seen, the convergence when using a simple mutation such as exchanging a pair of atoms is slow. By contrast, in all 1000 SAC optimisations, less than 1500 fitness evaluations were required. We find that SAC is very robust even when very small populations-sizes (20 members) are used, finding global minima in all 1000 GA runs, although the use of larger populations (> 40 members) slows down the performance. By contrast, if the population size is too small (< 10 members) GA have the tendencies of being hampered by premature convergence. Using small populations (20 members) is particular advantages when the
fitness evaluation is expensive since a coarse tuning of the parameters can be carried out at relative low cost.

A few test calculations using SAC were also carried out with mutations. Results from these tests indicate that the use of mutations slows down the performance, although marginally, which is not surprising since the diversity of the population is maintained with SAC.

It is worth mentioning that Smith [14] is able to find a global minimum using a conventional specialised genetic algorithm with a modified mating scheme and large mutations. However, more than 5000 fitness evaluations were typically required, which is about an order of magnitude slower than that of using SAC, and attempts to solve larger problems (e.g. a 2D Ising alloy with 400 atoms) failed. By contrast, we were able to locate the global minimum of a 400 atom Ising alloy in less than 2000 steps. Attempts to find the global minimum of Ising alloys with more than 10 000 atoms were successful!

Finding low energy minima of a 2D Morse alloy

Having compared the performance of a conventional genetic algorithm with that of using SAC for finding low energy minima of a simple Ising model, we now turn to discuss the second model where the atoms interact via a Morse-potential (equation 0.3) with parameters taken from table I and cutoffs, $E_{\text{cut}}$ in equation (1.3) chosen such as to include either nearest neighbour interactions or up to the fourth nearest neighbours. Again, a periodic $10 \times 10$ atom cell is considered where 50 Bi and 50 Cu atoms are distributed on a square lattice with lattice constant 2.56 Å. 1000 runs were carried out, and the mean value of the best energies at each step are displayed in figure 4. Results from calculations with and without the use of symmetry adapted crossover is reported, and no mutations were used.

Again, rapid convergence is achieved using SAC, and less than 1100 steps were necessarily in all 1000 runs to reach the global minima. The conventional genetic algorithm fails in all attempts, hampered by premature convergence. Smith [14] showed that specialised conventional GA when applied for finding low energy minima in a Morse potential performed worse than a Metropolis Monte Carlo algorithm. It was argued that the specialised crossover, which was successful when applied to simple Ising alloys, fails to work properly when there is a marked difference in the bond energies. If the atoms were allowed to relax in space the specialised mating operation would work properly because of the similar Cu–Cu and Bi–Bi bond energies. Since, in the present work, we do not resort to the use of specialised operators, it is of interest to compare the performance of SAC with that of Metropolis MC [14]. Comparing the MC values in figure 7 in ref [13] with that of SAC, we find that the MC runs appear to converge faster than SAC early in the evolution. However SAC clearly outperforms MC in finding the global minima rapidly. The high efficiency is due to a properly working crossover throughout the evolution which is reflected in a steep, roughly linear, decay in the mean energy, followed by an exponential decay near the groundstates. By contrast, in Metropolis MC changes to a single solution is being made which is manifested in a different functional form of the mean energy which progress at a much slower rate in the latter part of the evolution.

We also carried out test calculations by increasing the cutoff distance in the Morse-potential such as to include up to the fourth nearest neighbours. Interestingly, as can be seen in figure 4 the performance of the genetic algorithm is not very sensitive to changes in the cutoff of the Morse-potential which is encouraging for the application of the presented genetic algorithm for modelling substitutionally disordered compounds with long-range interactions. In addition, the robustness of the presented genetic algorithm in handling different alloy models (i.e., with different functional form) without having to redesign the algorithm, is particular promising for the study of complex minerals and alloys as well as related problems (e.g. magnetism).
CONCLUSIONS

We have presented a novel genetic algorithm for finding configurations with target properties of substitutionally disordered materials (i.e. alloys and minerals) as well as surfaces in which premature convergence hampering conventional GA is avoided. The presence of a large number of symmetrically equivalent low energy configurations, which in general are far away from one-another in configuration space, is a challenge to conventional GA since there is no selection in the direction of a single global minimum. The conventional genetic algorithm has a synchronisation problem and the crossover fails to work properly when the diversity of the population is lost, leaving the the problem of finding a global minimum to the mutation operator alone.

We solve the synchronisation problem using a symmetry-adapted crossover in combination with representations which reflect the spatial arrangements of the atoms, by replacing the offspring with a symmetrically equivalent configuration. The use of symmetry-adapted mating operators allows one to carry out large swaps in configuration space, enabling the building blocks of good solution to combine to form higher order building blocks of even better solutions.

Calculations on simple 2D alloy models (i.e. an Ising alloy and a Morse alloy) show that the use of symmetry-adapted operators outperform a conventional genetic algorithm, which fails in all attempts to find a global minimum even with huge population sizes (i.e. with very little amount of selection). Although Smith [14] is able to find the global minimum of a 100 atom Ising model using a specialised genetic algorithm designed to solve simple Ising models, the use of this genetic algorithm fails to outperform Metropolis Monte Carlo algorithm when applied to Morse alloys. By contrast, we have shown that genetic algorithms in combination with SAC outperform Metropolis Monte Carlo–, and specialised GA methods in both cases, and global minima of large systems (e.g. alloys with more than 10 000 atoms) were found.

The robustness of the presented algorithm in handling alloy models with different interactions without the need for any redesign, is particular promising for future applications.

ACKNOWLEDGEMENTS

This work was funded by Norges Forskningsråd.

[1] G. M. Day, W. D. S. Motherwell, H. L. Ammon, S. X. M. Boerrigter, R. G. Della Valle, E. Venuti, A. Dzyabchenko, J. D. Dunitz, B. Schweizer, B. P. van Eijck, P. Erk, J. C. Facelli, V. E. Bazzerra, M. B. Ferraro, D. W. M. Hofmann, F. J. J. Leusen, C. Liang, C. C. Pantelides, P. G. Karamerzanis, S. L. Price, T. C. Lewis, H. Nowell, A. Torrisi, H. A. Scheraga, Y. A. Arnautova, M. U. Schmidt, and P. Verwer. A third blind test of crystal structure prediction. Acta Cryst., B61:511, 2005.
[2] F. C. Hawthorne. Crystal from 1st principles. Nature, 345:297, 1990.
[3] C. Mellot-Draznieks, S. Girard, G. Feray, J. C. Schon, Z. Cancarcievic, and M. Jansen. Computational design and prediction of interesting not-yet-synthesized structures of inorganic materials by using building unit concepts. Chem-A Eur. J, 8:4103, 2002.
[4] S. M. Woodley, P. D. Battle, J. D. Gale, and C. R. A. Catlow. The prediction of inorganic crystal structures using a genetic algorithm and energy minimisation. Phys. Chem. Chem. Phys., 1:2535, 1999.
[5] M. F. Thorpe. Local Structure From Diffraction. Springer, Berlin, 2002.
[6] I. T. Todorov, N. L. Allan, M. Yu. Lavrentiev, C. L. Freeman, C. E. Mohn, and J. A. Purton. Simulation of mineral solid solutions at zero and high pressure using lattice statics, lattice dynamics and Monte Carlo methods. J. Phys.: Condens. Matter, 16:2751, 2004.
[7] S. Stolen, E. Bakken, and C. E. Mohn. Oxygen-deficient perovskites: linking structure, energetics and ion transport. Phys. Chem. Chem. Phys., 8:429, 2006.
[8] M. Y. Lavrentiev, J. A. Purton, and N. L. Allan. Ordering in spinels - a Monte Carlo study. Am. Mineral, 88:1522, 2003.
[9] J. C. Campuzano. The Chemical Physics of Solid Surfaces and Heterogeneous Catalyses. Elsevier, Amsterdam, 1990.
[10] G. M. Day, W. D. S. Motherwell, H. L. Ammon, S. X. M. Boerrigter, R. G. Della Valle, E. Venuti, A. Dzyabchenko, J. D. Dunitz, B. Schweizer, B. P. van Eijck, P. Erk, J. C. Facelli, V. E. Bazzerra, M. B. Ferraro, D. W. M. Hofmann, F. J. J. Leusen, C. Liang, C. C. Pantelides, P. G. Karamerzanis, S. L. Price, T. C. Lewis, H. Nowell, A. Torrisi, H. A. Scheraga, Y. A. Arnautova, M. U. Schmidt, and P. Verwer. A third blind test of crystal structure prediction. Acta Cryst., B61:511, 2005.
Z. Phys, 31:235, 1925.

[21] H. K. Chang, J. K. Lee, and D. F. Stein. Interatomic Potentials and Crystalline Defects. The Metallurgical Society of AIME, Warrendale, PA, 1981.

[22] B. Hartke. Application of evolutionary algorithms to global cluster geometry optimization. Struc. and Bond., 110:33, 2004.

[23] R. L. Johnston. Evolving better nanoparticles: Genetic algorithms for optimising cluster geometries. Dalt. Trans., 2003.

[24] D. E. Goldberg. Genetic Algorithms in Search, Optimization and Machine Learning. Addison Wesly, Reading, 1989.