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Multi-Cell Monte Carlo Relaxation method for predicting phase stability of alloys

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ABSTRACT

A Multi-Cell Monte Carlo Relaxation – $(MC)^2$ Relaxation – method, is introduced to predict stable phases of alloys, using *ab initio* energies. This method uses two parallel supercells for independent energy optimizations while allowing for atom swaps between/within the two supercells, and is particularly useful in predicting ordering or phase separation in multicomponent alloys. We predict the expected phases in the Au-Pt and Hf-Zr binary systems. In case of the HfNbTaZr "high-entropy" alloy, we predict separation into HfZr and TaNb phases, in agreement with recent experiments. Finally, we compare the method with other approaches that perform similarly unbiased searches.

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Predicting stable phases is a crucial step in understanding the thermodynamic behavior of alloys. Mathematically, these phases correspond to the minima of the free energy. The analogy between annealing in solids and optimization of a multivariable function was noted by Kirkpatrick et al. [1], resulting in the introduction of Simulated Annealing techniques, where the Metropolis algorithm [2] is used for optimization of complex systems. In addition, a combination of the Monte Carlo (MC) and energy minimization techniques have been used to optimize properties in a range of material systems [3–8]. Moreover, several structural prediction methods, with biased or unbiased sampling have been reviewed in [9].The advantage of a combined MC and energy minimization approach is that, while energy minimization searches for the nearest local minimum of the energy function, the MC algorithm allows for spanning configurations away from the local minima until a global minimum is reached. Application of the above approach to problems involving secondary phase formations becomes more challenging; the mismatch between regions of the two phases may introduce large strains at the interphase boundaries, capable of affecting the secondary phase formation and leading to fictitious finite size effects. Therefore, the cell size needs to increase accordingly such that the strain energy does not dominate the total energy. However, large simulation sizes are prohibitive when using computationally expensive *ab initio* methods that are essential to modeling multicomponent systems. Here, we propose an alternative Multi-Cell Monte Carlo Relaxation – abbreviated as $(MC)^2$ Relaxation method that avoids the strain due to internal interfaces, and consequently allows for efficient predictions of phase separation in alloys.

Our algorithm starts with two parallel supercells of the initial phase and utilizes the Metropolis algorithm to optimize the total energy of the two cells allowing for "intercell" as well as "intracell" atom exchanges as follows. A pair of atoms – from any of the supercells – are randomly selected. These atoms are then swapped. The sum of the total energies of the two cells, before and after the swap are calculated using density functional theory (DFT). The swap is then accepted with a probability P given by:

$$P = \begin{cases} 1; & (\text{if } \Delta E \le 0) \\ \exp\left(-\Delta E/(k_B T)\right); & (\text{if } \Delta E > 0) \end{cases}$$

where ΔE is the change in sum of the total energies of the supercells caused by the atom swap, k_B is the Boltzmann constant, and T is a temperature parameter. This procedure is repeated in search for a new, more energetically favorable state. The advantage of this method is that all degrees of freedom in cell volume and shape as well as atomic positions are optimized, allowing for an unbiased, strain-free condition for ordering or phase separation. We emphasize that the temperature parameter T is merely a control parameter which determines the acceptance rate of the energetically unfavorable atom swaps. These atom swaps are necessary to free the system from becoming trapped in a local metastable configuration. Other contributors to the free energy, such as configurational and

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vibrational entropy, need to be included in order to make predictions about the physical T at which the phase separation occurs.

Coexisting supercells in Monte Carlo simulations have previously been used within the *Gibbs ensemble Method* of Panagiotopoulos [10] for non-solids, where particles are free to move between two cells. In case of crystalline solids, accommodating the change in number of atoms in each cell requires excessive point defect concentrations, and is thus not feasible [11]. The (MC)^2 Relaxation method requires a fixed number of atoms in each cell, but this restriction can be overcome by considering several simulations with various combinations of cell sizes and compositions.

Ab initio calculations are performed with the Vienna *Ab initio* Simulation Package (VASP) [12,13], using the Projector Augmented Wave (PAW) method within the generalized gradient approximation of the exchange-correlation functional as determined by Perdew, Burke, and Ernzerhof (GGA-PBE) [14]. The valence electron configurations are Au:5d^{10}6s^1, Pt:5d^{9}6s^1, Hf:5d^{2}6s^2, Zr:4d^{2}5s^2, Ta:5d^{3}6s^2 and Nb:4p^{6}4d^{4}5s^1. Two settings for the DFT calculations are used, *accurate* and *fast*. The *accurate* DFT calculations use k-point meshes that ensure a total energy convergence of 1 meV/atom as well as energy cutoffs that are 30% higher than the default cutoff values in the potentials. Exact k-point meshes and energy cutoffs for individual examples are given below. The *accurate* DFT calculations also use a convergence criterion of 0.001 meV for electronic relaxations and a force convergence criterion of 10 meV/Å for ionic relaxation. The *fast* settings are used during the MC simulations to make the calculations feasible and have reduced k-point meshes and cutoff energies for MC simulations as given below. Electronic and ionic convergence criteria are 0.1 meV and 20 meV/Å, respectively. After the MC calculations are completed, initial, final and selected intermediate structures are recalculated with the *accurate* DFT settings. We quantify the errors caused by using less accurate settings during the Metropolis moves and verify that general trends and observations remain unchanged. All initial structures are *special quasi-random structures* (SQS) – periodic atomic supercells with near-neighbor radial correlation functions as similar as possible to a perfectly random solid solution [15]. SQS cells are generated by the ATAT package [16]. Pair correlation functions up to the second nearest neighbors (NN) are optimized during the generation of SQS. Binary SQS cells are perfectly random with respect to the first and second NNs; the quaternary SQS is perfect with respect to the first NN and its correlation function mismatch is below 0.05 for pairs of second NN. All atomic positions and cell volumes and shapes are optimized. This is necessary to separate the effect of strain energy from the formation energies in predicting the stable phases.

First, we study the binary Au-Pt alloy. The phase diagram of Au-Pt system shows a miscibility gap at equiatomic composition at low temperatures [17]. Therefore, an equimolar AuPt alloy is expected to decompose into Pt and an Au-enriched phases. We build a 16-atom $[-1, -0.5, 0.5] \times [1, 0.5, 1.5] \times [-1, 1.5, -0.5]$ equimolar fcc SQS where the reported lattice vectors are normalized by the lattice parameter. The energy cutoff and k-point mesh of the *fast* calculations are 230 eV and $3 \times 2 \times 2$, respectively. The MC calculations are performed with different values for the temperature parameter T at 100 K, 300 K, and 500 K. Intermediate structures from the MC search are re-used for *accurate* DFT calculations, in which the energy cutoff and k-points settings are 300 eV and $8 \times 6 \times 6$, respectively. Fig. 1 shows the change in energy and alloy composition during the three MC simulations of the AuPt alloy at $T = 500$ K. The accepted (black points) and rejected (red crosses) energies during the MC moves are relative to the initial step, while the accurate energies (blue squares) are relative to the accurate energy of the initial step. Fig. 1 also shows the composition of the two supercells during the (MC)^2 Relaxation. Lowest energy is achieved near complete phase separation and is predicted using all three T values. The *accurate* energies for the 20th, 40th, 60th, 80th, and 100th steps are also plotted in Fig. 1, showing small deviations from the accepted energies with *fast* settings. For the 20th and 40th steps in 500 K, the deviation is 3–7 meV/atom; for the other selected steps, where the separation of Au and Pt is nearly complete, the deviation is below 2 meV/atom. Compared to the total energy reduction of 46 meV/atom, these small errors confirm that the predicted phase separation is valid despite the use of *fast* DFT settings.

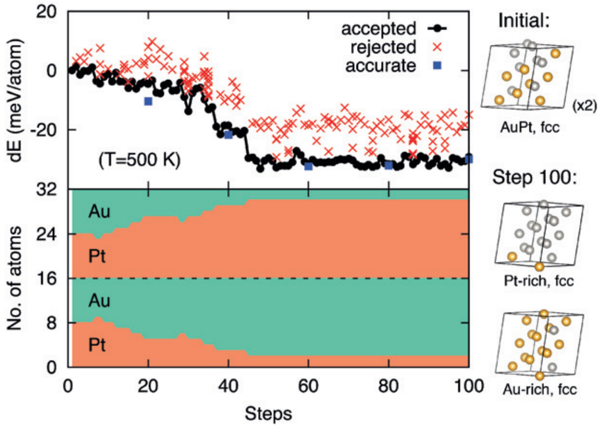

Fig. 1. Changes in energy and composition during MC searches for the stable phases of binary Au-Pt alloy. Energy values are relative to the total energy at the initial step. Top plot shows the energy change at the accepted (black dots) and rejected (red crosses) steps in each MC simulation with 500 K, and energies from accurate DFT calculations (blue squares) relative to the accurate energy of the initial steps. The horizontal axis shows the number of accepted steps. The rejected steps performed between accepted steps i and $i + 1$ are shown at the i-th accepted step. Bottom row shows alloy composition of the two supercells at each step. The simulation starts with a 50–50% random composition at step 0 and predict final separation of Au and Pt. The initial and final SQS supercells are also shown. The two initial cells are identical, and are marked by the supercell ×2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Next, we study the Hf-Zr binary alloy. Both elements have a stable hexagonal close-packed (hcp) phase at low temperature and remain completely soluble with each other [18]. A 16-atom $[2, 0, -1.633] \times [1, -1.732, -1.633] \times [-1.5, 0.866, -1.633]$ equimolar hcp SQS is generated where the lattice vectors are normalized by the lattice parameter. The energy cutoff and k-points for the MC calculations are 225 eV and $2 \times 2 \times 2$, respectively. The (MC)^2 Relaxation are again performed with $T = 100$ K, 300 K and 500 K, and several intermediate structures are recalculated with the *accurate* DFT settings for

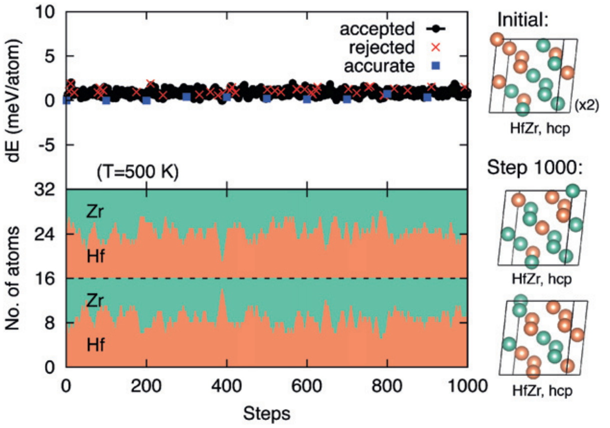

Fig. 2. Changes in energy and composition during MC searches for the stable phases of Hf-Zr hcp alloy. The MC calculations predict that the equimolar HfZr alloy maintains a solid solution phase. Initial and final SQS cells are shown with Hf and Zr atoms colored as blue and orange respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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