Multi-Cell Monte Carlo Relaxation Method for Predicting Phase Stability of Alloys

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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. A combination of the Monte Carlo (MC) and energy minimization techniques is an effective approach to optimize the free energy: 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 due to the fact that 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 n parallel supercells of the initial phase and utilizes the Metropolis algorithm to optimize the total energy of all cells allowing for "intercell" as well as "intracell" atom exchanges. In order to allow for unconstrained compositional changes in all cells, we add weight coefficients to each cell based on the lever rule. This method can therefore predict phase formations at 0 K accurately. In addition, various approaches to consider entropic contributions are discussed to enable optimization of the free energy. This approach opens up the possibility of phase prediction for multicomponent alloys from first principles calculations.