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# Alloy design as an inverse problem of cluster expansion models

Peter Mahler Larsen [a, b], Arvind R. Kalidindi [a], Søren Schmidt [b], Christopher A. Schuh [a, *, 1]

[a] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[b] Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

Central to a lattice model of an alloy system is the description of the energy of a given atomic configuration, which can be conveniently developed through a cluster expansion. Given a specific cluster expansion, the ground state of the lattice model at 0 K can be solved by finding the configuration of solutes that minimizes the energy of the system. In this paper, we develop a method for solving the inverse lattice problem, where, given a broad class of potential, we find the ground states for *all possible* values of the effective cluster interaction energies. To do so, we formulate the inverse problem in terms of energetically distinct configurations, using a constraint satisfaction model to identify constructible configurations, and show that a convex hull can be used to identify ground states. To demonstrate the approach, we solve for all ground states for a binary alloy in a 2D hexagonal lattice both with and without an interface, based on pairwise interactions.


## 1. Introduction

Statistical mechanics models of alloys assign probabilities to the possible configurations of alloying elements and, based on a Maxwell-Boltzmann distribution, determine the equilibrium state of the alloy. Describing the configuration space of the alloy inevitably requires some approximation. The simplest models rely on assumptions of random distributions of each alloying element, either in the entire system, as in an ideal solution model, or within any phase as in a regular solution model. A major improvement to capturing configurational degrees of freedom is a lattice model, also known as the generalized Ising model [1] or Cluster Expansion [2] (CE) model, where each lattice site represents a single atom of a particular element with a pseudo-spin occupancy variable $\sigma_i$ that, for the binary case, is $-1$ or $+1$ for a solute or solvent atom, respectively. The energy of an alloy configuration, $\boldsymbol{\sigma}$, in the lattice model with a cluster expansion interatomic potential$\mathbf{V}$, can generally be defined by the Hamiltonian [3]:

$$H(\boldsymbol{\sigma}, \mathbf{V}) = V_0 + \sum_{c \in \mathbf{C}} V_c \boldsymbol{\sigma}_c \tag{1}$$

where $\mathbf{C}$ is the set of clusters for which effective cluster interactions (ECIs), $V_c$, are prescribed. $\boldsymbol{\sigma}_c$ is a generic cluster function defined as the product of $\sigma_i$ over all sites in a cluster and captures the solute configuration of the cluster. While a fixed site geometry still constrains the configuration space considered, lattice models are a remarkably accurate tool for developing phase diagrams of alloys, where a cluster expansion can be performed from ab-initio calculations [2–13].

The 0 K phase diagram is determined by the alloy configurations that minimize Equation (1) at different solute concentrations. The problem of merely solving for the minimum energy configurations we term the 'forward problem'. Conversely, the much more complex 'inverse problem' is the one underlying alloy design, where, given a desired alloy configuration the objective is to determine which alloy systems, if any, possess this configuration as an equilibrium state. The possible ground states of the alloy model are those for which there exists a parameter set $\mathbf{V}$ that minimizes energy according to Equation (1). While the relationship between energy and the cluster functions is linear, finding all possible ground states is difficult due to the constraints imposed on the cluster functions by the lattice, namely the integrality constraint of equalling $-1$ or 1.

Allen and Cahn were able to solve this inverse problem for body-centered cubic and face-centered cubic lattices where the interatomic potential is constrained to nearest-neighbor and next-nearest-neighbor pairwise bonds [14]. Their approach and the more general polytope method [15–18] circumvent the integrality

* Corresponding author.
*E-mail address:* schuh@mit.edu (C.A. Schuh).
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constraint by first selecting one base cluster (e.g. an octahedron for the body-centered cubic lattice), and then determining all possible ways in which the alloying elements can occupy sites in this cluster, assigning each configuration on the cluster a probability weight from 0 to 1. Since probability is a continuous function, this problem can be solved by standard linear programming techniques to determine all possible equilibrium states.

However, not all combinations of probabilities for each cluster are constructible in a larger lattice, and thus additional rules must be defined to ensure that a ground state determined in this way represents a physical system. In a crystalline phase with short range interactions, these rules can be reasonably simple, but in more complex systems constructibility can be a cumbersome problem [18]. Inverse problems in certain disordered systems, such as hyperuniform glasses, have been studied to determine the interatomic potentials that lead to disordered ground states [19,20], but are beyond the scope of a standard cluster expansion representation. There has been growing interest in studying chemical ordering at interfaces, such as grain boundaries, and constructing phase diagrams (also known as complexion diagrams) of the segregation and ordering at these interfaces [21–30]. Such problems have an inhomogeneous cluster expansion, since clusters at an interface have different energies than ones in the crystal, which makes use of the polytope method more challenging. Even in crystalline phases, considering clusters with longer range interactions can be challenging within the polytope method as a larger base cluster must be chosen leading to a larger number of potential configurations and more complex constructibility considerations.

The forward problem of finding ground states in complex systems has recently been formulated by Huang et al. [31] as a class of problem known as pseudo-Boolean optimization [32] (PBO). PBO models, which consist of an objective function to be optimized and a set of constraints to be satisfied, greatly improve the generality and speed of solving lattice models given a cluster expansion. In this paper, we present a framework for solving the inverse problem of the lattice model directly in the configuration space of the lattice using a constraint satisfaction model. We then investigate the ground state ordered states in a 2D hexagonal lattice both with and without an interface to demonstrate how all possible configurations with a given potential form can be calculated.

## 2. The inverse problem in lattice models

The forward problem asks: for a specified $\mathbf{V}$, what is the ground state configuration? A configuration $\boldsymbol{\sigma}$ is a ground state if it has a lower energy than all other configurations:

$$H(\boldsymbol{\sigma},\mathbf{V}) < H\left(\boldsymbol{\sigma}',\mathbf{V}\right) \quad \forall\, \boldsymbol{\sigma}' \neq \boldsymbol{\sigma} \tag{2}$$

Then, the inverse problem asks: for a specified configuration $\boldsymbol{\sigma}$, does there exist a set $\mathbf{V}$ for which $\boldsymbol{\sigma}$ is the ground state? Here, the space of interactions being considered (e.g. nearest neighbor, next-nearest neighbor, etc.) is constant. We denote such a configuration as *minimizing*. It must satisfy the condition:

$$\exists \mathbf{V} \quad \text{s.t.} \quad H(\boldsymbol{\sigma},\mathbf{V}) < H\left(\boldsymbol{\sigma}',\mathbf{V}\right) \quad \forall\, \boldsymbol{\sigma}' \neq \boldsymbol{\sigma} \tag{3}$$

Thus, to solve the inverse problem, all possible ECIs as well as all possible configurations must be considered in order to find the ground states. In order to make this tractable, we will first reduce the configuration space to a smaller, abstract space, and then use arguments based on principles of convexity to identify minimizing configurations.

In order to reduce the configuration space, we note that the Hamiltonian in Equation (1) can be expanded to lattice-gas [33] form:

$$H(\mathbf{x},\mathbf{E}) = E_0 + \sum_j \sum_{\mathbf{c}\in\mathbf{C}_j} \prod_{i\in\mathbf{c}} E_j x_i \tag{4}$$

where spin variables $\sigma_i \in \{-1,1\}$ of the cluster function have been replaced by a binary variable $x_i \in \{0,1\}$ using the relation $\sigma_i = 2x_i - 1$, and $\mathbf{E}$ is the equivalent set of ECIs. For each cluster instance we can then define a binary variable $y_\mathbf{c} = \prod_{i\in\mathbf{c}} x_i$ which denotes *cluster instance activity*, where 0 and 1 denote an inactive and active cluster instance respectively. Using Equation (4), the Hamiltonian can then be rewritten in the number of active cluster instance (ACI) counts:

$$H(\mathbf{x},\mathbf{E}) = \langle \mathbf{E},\mathbf{N}\rangle \tag{5}$$

where $\mathbf{N} = \{ \sum_{\mathbf{c}\in\mathbf{C}_1} y_\mathbf{c}, \sum_{\mathbf{c}\in\mathbf{C}_2} y_\mathbf{c}, \sum_{\mathbf{c}\in\mathbf{C}_3} y_\mathbf{c}, \ldots\}$ is the vector of ACI counts (ACI vector). Representing a configuration as an ACI vector is a much more compact description and permits a simpler expression of the Hamiltonian. Using this parametrization, we define the 'energy space' $V(\mathbf{N})$ of a configuration as the region of ECI space for which it is a ground state:

$$V(\mathbf{N}) = \{\mathbf{E} |\ \langle \mathbf{E},\mathbf{N}\rangle < \langle \mathbf{E},\mathbf{N}'\rangle \ \forall\ \mathbf{N}' \neq \mathbf{N}\} \tag{6}$$

where $\mathbf{N}$ and $\mathbf{N}'$ denote constructible bond count vectors with the same number of solute atoms.

Determination of the minimizing configurations proceeds by identifying the convex hull [34] of configurations. The *maximum principle* [35] states that the maximum (or equally, minimum) of any convex function on a compact convex set is attained at the boundary of the set. Thus, in order to exploit the maximum principle, we require a convex function of a convex compact set. If we relax the implicit integrality constraints on $\mathbf{N}$, the inner product in Equation (5) is a sum of linear functions, which is a convex function. Next, let $\mathbf{S} = \{\mathbf{N}_1, \mathbf{N}_2, \mathbf{N}_3, \ldots\}$ be the set of all constructible ACI vectors for a given set of clusters. Then, the convex hull of S is by definition a compact convex set. By restricting the domain ($\mathbf{N}$) of the Hamiltonian in Equation (5) to the convex hull of $\mathbf{S}$, we satisfy the necessary conditions of the maximum principle. As such, we can state that all possible ground states for a given $\mathbf{E}$ must lie on the boundary of the convex hull of $\mathbf{S}$. For practical reasons we can tighten the definition: any minimizing configuration must lie on a vertex of the convex hull of $\mathbf{S}$. We can do this since any configuration which lies on a plane of the convex hull has a zero energy space according to Equation (6).

What the above means is that solving the inverse problem amounts to finding all states that lie on the vertices of the convex hull of cluster space, which is a space where each axis is the number of counts of a given cluster. We illustrate this concept with a 1D example. Fig. 1 shows a periodic lattice in $\mathbb{R}^1$, with bonds between adjacent sites only, and whose sites are occupied by either A-type or B-type atoms. Given this energetic model, there are two types of clusters: 1-body and nearest-neighbor 2-body clusters. For a fixed concentration of B-type atoms, though, the contribution of 1-body clusters is the same in each case, meaning there is only one linearly independent cluster. The ACI vector of any configuration in this model can therefore be written as a 1D vector, $\mathbf{N} = \{k_1\}$ where $k_1$ is the number of nearest-neighbor B–B bonds. As such, the convex hull of all constructible ACI vectors consists of two points. These states, which constitute the minimizing configurations of the lattice, correspond to preferences for heteroatomic bonds (Fig. 1a) and