

Editor's Choice

A compound unit method for incorporating ordered compounds into lattice models of alloys



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ABSTRACT

Lattice models can be a basic tool for alloy design, due to their ability to capture the most important thermodynamic and kinetic phenomena of a wide-range of alloys at a low computational cost. However, in order to correctly treat ordered precipitates at off-stoichiometric compositions requires multi-body potentials, and these can be challenging to calibrate to known alloy behaviors. Here we introduce a simple means of capturing the multi-body terms needed to treat ordered compounds in a lattice model based on defining “compound units”. This approach is particularly designed for, and easily calibrated in, cases where the structure and formation energy of equilibrium compounds are already known. This is accomplished by defining a compound unit that derives its energy from the formation energy of the compound as an a priori input. The method is illustrated for a binary alloy with $D0_3$ and B2 stable compounds.

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1. Introduction

Lattice models provide a convenient framework for studying the evolution and stability of alloy microstructures [1–15]. These models typically focus on the mesoscale behavior of the system, describing the state of the alloy on a fixed lattice, with an interatomic potential that expresses the relative preference for different arrangements of species on the lattice. A pairwise potential is often used because of its simplicity for implementation and easy adaptability for conducting rapid surveys across many material systems [1–4,16–20]. The pairwise potential for a binary alloy can generally be written as:

$$H = \sum_{\{ij\}} J^{(k)} (1 - \delta_{\sigma_i \sigma_j}) \quad (1)$$

The summation is conducted over all pairs of lattice sites, where $\sigma_i = 1$ for a solvent atom and -1 for a solute atom located at lattice site i , and δ is a Kronecker delta, which is 1 for like bonds (solvent–solvent (AA) and solute–solute (BB)) and 0 for solute–solvent bonds (AB). $J^{(k)}$ is the pairwise interaction parameter describing the difference in pairwise bond energy, E , between like and unlike pairs at a neighbor distance of k : $J^{(k)} = E_{AB}^{(k)} - \frac{(E_{AA}^{(k)} + E_{BB}^{(k)})}{2}$. By varying $J^{(k)}$ many different alloy systems can be represented using this general description.

When considering only nearest neighbor interactions ($k = 1$), a shortcoming of the pairwise potential for modeling negative enthalpy of mixing alloys becomes apparent. For a positive enthalpy of mixing alloy ($J^{(1)} > 0$), the internal energy can be minimized by forming separate solute and solvent phases, and thus at 0 K the thermodynamic equilibrium state consists of two phases that are immiscible in one another. In a negative enthalpy of mixing alloy ($J^{(1)} < 0$), thermodynamically it is expected that an ordered compound will be formed to minimize internal energy such that at 0 K the equilibrium state again consists of two phases that satisfy the zero entropy requirement of the third law of thermodynamics. The pairwise model does not produce this result for negative enthalpy of mixing alloys, instead predicting a disordered alloy state (solid solution) to be thermodynamically stable. Moreover, this limitation is inherent to the pairwise potential, and thus exists regardless of whether the equilibrium state is determined via the cluster variation method [7–9] or a Monte Carlo simulation [1,6].

This anomalous behavior can be attributed to the insufficient description of ordering using a pairwise potential, which is illustrated in Fig. 1 for the case of a two-dimensional square lattice. In this schematic, one system contains an ordered compound, while the second system is disordered. According to Eq. (1), both of these systems have the same internal energy since each solute is bonded to only solvent atoms in both situations, which is also the lowest energy state possible for the system. Because the second system is disordered, it has higher entropy and is therefore found to be stable at all finite temperatures.

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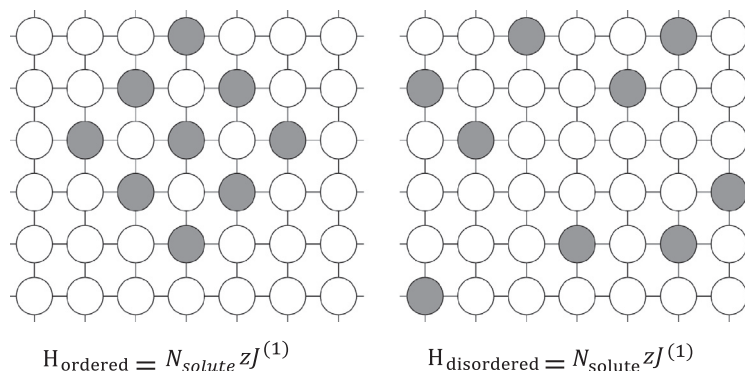


Fig. 1. The schematic shows two solute arrangements, ordered (on left) and disordered (on right). The internal energies calculated by Eq. (1) in the nearest neighbor approximation are equivalent in both cases, making ordered phases unstable at off-stoichiometric concentrations (N_{solute} is the number of solutes and z is the coordination number).

The repercussions of this shortcoming are not limited to the 0 K equilibrium. In a pairwise model, ordering only occurs when the solute concentration is large enough to impose a geometrical constraint, e.g. when a disordered phase requires forming solute–solute bonds at an energetic cost. For example, the nearest neighbor model exhibits an equiatomic compound in the 2D square lattice because at this stoichiometry the only way to attain all solute–solvent bonds is to form an ordered phase. While the above discussion mainly focuses on the nearest neighbor model to simplify the explanation, this behavior is expected to be present at absolute zero for any pairwise model with negative interaction parameters [1,7–9]. The inability to capture accurate ordering tendencies limits the usefulness of such a description for designing alloys, where it is often desirable to study the precipitation of an ordered compound at off-stoichiometric compositions, and in systems where ordering has additional energetic implications beyond merely the geometric ones.

The standard route to better incorporate an alloy’s ordering tendency is to include the interactions of multiple atoms, and thus allow ordered states to access a lower internal energy [21–25]. A general formulation for introducing the multi-body terms can be written as:

$$H = \sum_{\text{singlet}} J_i \sigma_i + \sum_{\text{pairs}} J_{ij} \sigma_i \sigma_j + \sum_{\text{triplets}} J_{ijk} \sigma_i \sigma_j \sigma_k \dots \quad (2)$$

where the J terms are now called effective cluster interactions. A typical procedure for predicting the bulk phase diagrams of different alloy systems is to calculate compound formation energies using density functional theory, and then using these to infer reasonable effective cluster interactions (called the Structure Inversion Method or Connolly–Williams method [21]). Generally, this requires consideration of 30–50 possible ordered compounds in order to determine a set of 10–100 interaction parameters that are deemed the most important for the interaction potential.

This method of including multi-body terms has been useful for developing bulk phase diagrams of alloys [26–29]. Increasingly, however, lattice models are being extended outside of classical bulk thermodynamic behavior, for instance to study the effects of interfaces [16–18,31–35]. In such cases, while using a cluster expansion to define the interatomic potential may still be feasible, it is not optimal because (i) the stability of compounds in bulk systems is already known [30], and thus “predicting” the stable compounds through simulation is unnecessary and (ii) the multi-body terms are calculated for each alloy system and thus too specific to probe a large number of alloy combinations and often not easily extendable to non-bulk environments. In some of our group’s work on nanostructured alloys we have found a need for a lattice-based

method that can be rapidly calibrated to known bulk thermodynamics and then used to explore, e.g., driven processing through ballistic mixing [34] or deposition [35], or simply to explore the space of accessible structures in nanostructured systems [18,36–38]. It is our purpose in this paper to present such a method that overcomes the limitations of the pairwise model in describing negative enthalpy of mixing systems, specifically for cases where the structure and formation energy of equilibrium compounds are already known, and a full cluster expansion would be redundant.

2. Compound unit model

In order to permit stable compounds in a pairwise model, a distinction has to be drawn between solute–solvent bonds in a solid solution and those in an ordered phase. Rather than add multiple higher order terms as in Eq. (2), we directly include an ordered compound with known structure and formation energy into a nearest-neighbor pairwise formalism by identifying its structure through a “compound unit”. A compound unit is defined here as a repeating group of atoms from which the entire superstructure of the compound can be formed. For example, we may define the compound unit shown in Fig. 2a to identify the compound shown in Fig. 1. Many potential compound units may be defined – the selection of appropriate compound units is discussed in Section 2.1, but the key feature of the unit is that when it appears in the structure, it will be assigned a lower enthalpy than what the pairwise

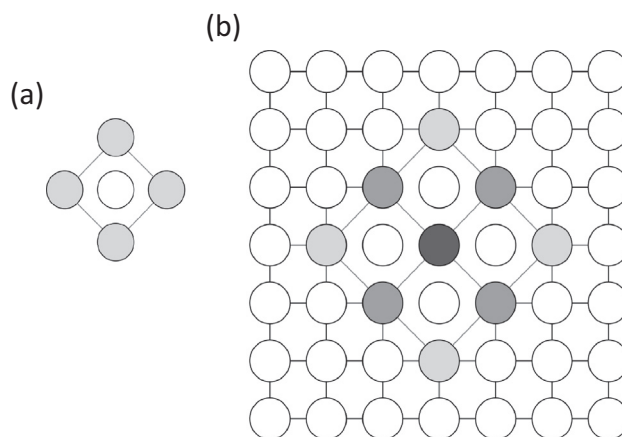


Fig. 2. (a) Shows a possible definition of a compound unit for the ordered compound pictured in Fig. 1, where dark atoms are solute. (b) Shows a schematic of how the energy of an atom is calculated in the compound unit model, where darker atoms have a larger compound unit contribution to their energy.

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