A derivation of the Ising model for the computation of phase diagrams

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The Ising model has been used very successfully in the computation of alloy phase diagrams. In this paper we show that this success is not coincidental by deriving the model from the full partition function of the alloy. In the process, the approximations that enter the Ising model description will be clarified.

1. Introduction

In recent years models in computational materials science have started evolving from the mere exhibition of well known phenomena to predictions about new structures or reaction mechanisms. This transition is slow though, as it requires the development of procedures that accurately map a complex quantum mechanical Hamiltonian onto the Hamiltonian of the model.

Inherent to every computation on a microscopic scale of materials is a many particle–many electron Schrödinger equation. Because of the enormous complexity in solving this quantum mechanical problem for systems with more than a few particles, most computations that are relevant for practical materials science have relied on more simplified descriptions. In molecular dynamics, for example, a material is simulated by particles that interact with a potential function and move according to the laws of Newtonian mechanics. Another example of a simplified model is the extended Ising model that is used in phase diagram calculations. It consists of particles that sit fixed at lattice sites and interact through “effective cluster interactions”. There are legitimate concerns over how accurately these models represent a real material, in which interactions cannot be represented with simple potentials or in which particles vibrate, and relax away from “ideal” lattice positions. In addition, it is often difficult to determine accurately the potential (or interactions) in these models. On many occasions the interaction potentials are determined by fitting to a few experimentally known properties of the material under investigation.

In this paper we will limit our concern to the applicability of the Ising model to the computation of alloy free energies and phase diagrams. We will place it on a more fundamental footing by showing how the exact partition function of an alloy can be cast into the partition function of an Ising lattice.

2. The Ising model

The Ising model was originally devised to study the ferromagnetic ordering of the magnetic moments in some solids. The model consists of a fixed lattice with a spin variable $\sigma_p$ defined on each lattice site $p$ (fig. 1). The spin has only one vector component that can either be up ($\sigma_p = +1$) or down ($\sigma_p = -1$). In Ising's original model only
nearest neighbor spins interact through an effective coupling constant. A model with more (longer range) interactions is sometimes referred to as an ‘extended Ising model’. We, however, will use the un-compounded term for the general case with arbitrary number and type of interactions. In the latter case, the Ising Hamiltonian is given by:

$$H = \sum_{\alpha} J_{\alpha} \sigma_{\alpha}. \quad (1)$$

A cluster, $\alpha$, is any collection of lattice sites and the cluster spin, $\sigma_{\alpha}$, is simply the product of all spins in cluster $\alpha$:

$$\sigma_{\alpha} = \sigma_i \sigma_j \ldots \sigma_l \quad \text{with} \; i, j, \ldots, l \in \alpha. \quad (2)$$

Greek and Latin indices will be consistently used to denote clusters or points, respectively. $J_{\alpha}$ is the effective interaction for cluster $\alpha$. The interactions depend on the lattice type (fcc, bcc, and so on). In principle, the summation in eq. (1) is performed over all clusters on the lattice. Since the spin on each lattice site can take on only two values, the Ising model lends itself very well to studying atomic configurations of a binary alloy in a periodic structure. The spin is then a representation of the occupation of a particular lattice site.

To make the model practical, the Ising Hamiltonian is truncated. Retaining only a few interaction constants in the Hamiltonian expansion can already lead to a rich variety of phase diagrams. Given the effective interactions $J_{\alpha}$ for an alloy, the stable superstructures as a function of composition can be found exactly out of an infinity of possible candidate structures [1]. This is one of the advantages of a linear energy parametrization like the Ising Hamiltonian (eq. (1)). Once the ground state structures have been found a number of techniques can be used to obtain the free energy of the Ising system at non-zero temperature and construct the temperature-spin (composition) phase diagram. The agreement with real alloy phase diagrams can be very close: Van Baal [2] was the first to compute a realistic Cu–Au phase diagram with only a repulsive nearest neighbor interaction on the fcc lattice. De Fontaine and Kikuchi [3] later showed that the solid state Cu–Au phase diagram could be accurately reproduced by using nearest neighbor pair and many-body interactions. Recently, it was shown [4] that even the ordering spinodal in this system could be matched if an accurate enough entropy expression is used in the free energy computation. All different types of phase diagrams that can be obtained with first and second neighbor interactions on the fcc lattice have been computed by Sanchez [5]. Similar work for the bcc coherent phase diagrams has been done by Sluiter [6]. The topologies of these phase diagrams show excellent agreement with what is found in real systems and obtaining quantitative agreements seems to be merely a matter of adjusting the interactions in the Ising Hamiltonian.

There is thus strong evidence that, with a set of suitable interactions, every coherent phase diagram (or part of it) can be closely reproduced with an Ising model. This may be surprising as it is commonly believed that the model is concerned with atoms sitting rigidly at fixed lattice sites. In the next section we will justify the use of an Ising model for phase diagram computations by arguing that the states of an alloy can be collapsed onto Ising model states. In the process, the nature of the Ising Hamiltonian for an alloy will be clarified.

3. Reduction of the alloy problem to an Ising model

The free energy $F(N, V, T)$ of a system at constant composition, volume and temperature is
related to the canonical partition function \( \Phi(N, V, T) \):

\[
F(N, V, T) = -\frac{1}{\beta} \ln \Phi(N, V, T),
\]

(3a)

with

\[
\Phi(N, V, T) = \sum_{\text{all states } j} \exp(-\beta E_j(N, V, T)).
\]

(3b)

\( N \) is a vector that specifies the number of atoms of all different chemical species and \( \beta \) has its usual meaning of \( 1/k_B T \). At this point we will focus on binary alloys only. The generalization to multi-component systems is straightforward.

Formula 3 for the free energy involves computation of the canonical partition function which, in turn, incorporates a sum over all possible microstates. Let us consider what these microstates are. At zero Kelvin (neglecting the zero point motion) all atoms of a binary alloy occupy well defined sites. To every site we can assign an occupation variable \( \sigma_p \) which can have value +1 or -1 depending on the type of atom that is present at that site. Together, these sites form the “Ising lattice”. The atomic positions at zero Kelvin do not need to coincide with a point of the Ising lattice. This is possible when the symmetry of the ordered structure allows for relaxation away from the lattice position. In that case we still take the ideal sites to form the Ising lattice. The procedure described in the last sentences defines the projection of an alloy state onto a configuration of the Ising lattice. Note that the Ising lattice is a collection of possible atomic sites and thus not necessarily a Bravais lattice. At non-zero temperature all kinds of excited states are possible, such as vibrations around the average site, intra-atomic excitations and substitutional excitations. Only the substitutional excitations in the alloy change the spin configuration on the Ising lattice that describes the alloy, and all other excitations keep the particular state of the Ising model unchanged. Let us illustrate this with the example in fig. 2. Fig. 2a shows the atoms of a two-dimensional alloy occupying “ideal” positions. In fig. 2b, some atoms are slightly displaced from these positions. Both microstates will be labeled by the same spin configuration on the Ising lattice. Many microstates of the alloy thus project onto the same Ising model configuration. If we assume that every microstate of the alloy can be projected unambiguously onto one Ising model state, then we can partition all microstates of a real alloy into groups of states that have the same Ising model configuration. We will denote an Ising model configuration by \( \{ \sigma \} \), and the collection of alloy states that projects onto that particular configuration by \( \text{CC}(\{ \sigma \}) \). It is now possible to separate the sum over all microstates in the partition function (3b) into a sum over all Ising model configurations and a sum over all the microstates of the atoms consistent with that Ising-configuration

\[
\Phi(N, V, T) = \sum_{\{ \sigma \}} \sum_{\text{CC}(\{ \sigma \})} \exp(-\beta E(\text{state})).
\]

(4)

The canonical partition function can then be rewritten as

\[
\Phi(N, V, T) = \sum_{\{ \sigma \}} \Lambda(N, V, T, \{ \sigma \}),
\]

(5a)

with

\[
\Lambda(N, V, T, \{ \sigma \}) = \sum_{i = \text{CC}(\{ \sigma \})} \exp(-\beta E_i(N, V, T)).
\]

(5b)

Fig. 2. Two microstates of the alloy that are represented by the same spin configuration on the Ising lattice. In (a) all atoms are located exactly at the lattice sites whereas in (b) some are slightly displaced from the ideal lattice sites (relaxation).
Because many microstates of the alloy project onto the same configuration on the Ising lattice we cannot "invert" the projection. This implies that an Ising model cannot specify an exact spatial arrangement of atoms. Rather, it specifies what we would like to call a "state of colored connectivity" (CC); that is, a state of connectivity between the atoms in which the atom type is taken into account. A CC state is only modified by a substitutional excitation in the alloy. \( \Lambda(N, V, T, \{\sigma\}) \) is thus simply the partition function of a new ensemble, an ensemble in which all microstates are in the same CC state. From this perspective, there is nothing special about eqns. (5). It is common practice in statistical mechanics to express the partition function of an ensemble as a sum over partition functions of subensembles. For example, the canonical partition function can be obtained by summing over the microcanonical partition functions for all possible energy values. In eq. (5), the canonical ensemble is partitioned into CC-ensembles, one for each possible configuration.

These considerations should make it clear that the Ising model is just a formalism to label the possible atomic connectivities and has nothing to do with atoms sitting at fixed lattice sites, as is usually believed. Actually, atomic displacements (relaxation), vibrational energy contributions, etc. can be included in an Ising model through the partition function \( \Lambda(N, V, T, \{\sigma\}) \). However, we will later see that, in practice, \( \Lambda(N, V, T, \{\sigma\}) \) is approximated.

We can associate a "free energy", \( H(\{\sigma\}, N, V, T) \), with the CC-ensemble. It is the characteristic function for a system with fixed \( \{\sigma\} \), \( N \), \( T \) and \( V \):

\[
H(\{\sigma\}, N, V, T) = -\frac{1}{\beta} \ln \Lambda(\{\sigma\}, N, V, T).
\]

The canonical partition function then becomes

\[
\Phi(N, V, T) = \sum_{\{\sigma\}} \exp(-\beta H(\{\sigma\}, N, V, T)),
\]

and the alloy free energy:

\[
F(N, V, T) = -\frac{1}{\beta} \ln \left[ \sum_{\{\sigma\}} \exp(-\beta H(\{\sigma\}, N, V, T)) \right].
\]

The computation of the free energy of a binary alloy is now formally reduced to computing the free energy of an Ising model in which the energy of each configuration \( \{\sigma\} \) (the Hamiltonian) is given by eqn. (6). The value of this Hamiltonian for a given \( \{\sigma\} \) is the "free energy" of the corresponding CC-ensemble, which represents a system in which no substitutional excitations occur. Other excitations, like phonons, are present in this ensemble. In practice, \( H(\{\sigma\}, N, V, T) \) is further approximated. In the next section we will discuss some of these approximations.

4. Additional approximations for \( H(\{\sigma\}, N, V, T) \)

4.1. Temperature dependence of \( H(\{\sigma\}, N, V, T) \)

In the previous sections we described how the alloy partition function can be mapped onto the partition function of an Ising model. The Hamiltonian of the Ising model is still temperature dependent as it contains the integrated effect of all excitations apart from substitutional excitations. All practical ab initio computations have so far made use of a much simpler temperature-independent Ising Hamiltonian. We will describe next what additional approximations need to be made to arrive at this simpler Hamiltonian.

\( H(\{\sigma\}, N, V, T) \) is the free energy of a subensemble of the canonical ensemble. After decoupling the electronic and nuclear coordinates (Born–Oppenheimer) we can write the Ising Hamiltonian as

\[
H(\{\sigma\}, N, V, T) = U^0(\{\sigma\}, N, V, T) + F_{\text{ex}}(\{\sigma\}, N, V, T).
\]

\( U^0(\{\sigma\}, N, V, T) \) is the energy of the static configuration in the CC-ensemble with the lowest
energy. It is not a real ground state energy, just the energy of a system with "frozen" nuclear coordinates. $U^0$ can be temperature dependent due to electronic excitations. $F_{\text{ex}}(\sigma, N, V, T)$ contains the excitation part of the internal energy in the CC-ensemble due to atomic motion as well as the entropy of this ensemble. It is expected that, in practice, $F_{\text{ex}}(\sigma, N, V, T)$ is largely dominated by the vibrational free energy.

The first approximation one needs to make to arrive at a traditional Ising Hamiltonian consists of making $F_{\text{ex}}(\sigma, N, V, T)$ configuration-independent

$$F_{\text{ex}}(\sigma, N, V, T) = F_{\text{ex}}(N, V, T).$$  \hfill (10)

This approximation permits us to factor $F_{\text{ex}}(\sigma, N, V, T)$ out of the canonical partition function (eq. (7)). Substituting eqs. (9) and (10) into eq. (8) gives

$$F = F_1(N, V, T) + F_{\text{ex}}(N, V, T),$$  \hfill (11)

with $F_1$ the free energy of an Ising model with Hamiltonian $U^0(\sigma, N, V, T)$

$$F_1 = -\frac{1}{\beta} \ln \left[ \sum_{\sigma} \exp(-\beta U^0(\sigma, N, V, T)) \right].$$  \hfill (12)

In the case of coherent phase diagram computations, i.e. phase diagrams that consist solely of superstructures on the same parent lattice, one usually makes the additional assumption that $F_{\text{ex}}(\sigma, N, V, T)$ is a linear function of the composition. For a binary alloy

$$F_{\text{ex}}(N, V, T) = N_a F_{\text{ex},A}(T) + N_b F_{\text{ex},B}(T).$$  \hfill (13)

Seeing that the term $F_{\text{ex}}(\sigma, N, V, T)$ in eq. (11) is now just a linear function of the composition, it can be left out completely for the purpose of computing phase diagrams. (Phase equilibria are determined by chemical potentials and any linear function of the composition in the free energy just changes the chemical potentials by a constant)

Omitting $F_{\text{ex}}(\sigma, N, V, T)$ for the study of incoherent phase diagrams may not be a good approximation at all, considering that, for example, some fcc-bcc transitions in elemental solids are known to be driven by vibrational entropy (which is the main contribution to $F_{\text{ex}}(\sigma, N, V, T)$).

The final approximation for the free energy usually involves computing $U^0(\sigma, N, V, T)$ at zero kelvin which is done by approximating the Fermi–Dirac distribution as a step function. This last assumption effectively makes $U^0(\sigma, N, V, T)$ temperature independent:

$$U^0(\sigma, N, V, T) = U^0(\sigma, N, V)$$  \hfill (14)

and the Ising free energy becomes:

$$F_1(N, V, T) = -\frac{1}{\beta} \ln[Z(N, V, T)],$$  \hfill (15a)

where $Z$ is the Ising partition function:

$$Z(N, V, T) = \sum_{\sigma} \exp(-\beta U^0(\sigma, N, V)).$$  \hfill (15b)

### 4.2. The expanded Ising Hamiltonian

To compute $Z$ one needs, in principle, the ground state energies of the alloy corresponding to all configurations in the Ising model. If the lattice has $N$ sites there are $2^N$ such configurations. This is where the general Ising Hamiltonian (eq. (1)) brings relief. Sanchez [7] showed that this Hamiltonian is in fact an exact expansion of the configuration dependent energy $U^0(\sigma, V)$ around the disordered state with spin zero. The expansion variables are the cluster functions $\sigma_n$ and form an orthogonal basis set [7] when the appropriate scalar product is defined. The effective cluster interactions $J_n$ are simply the expansion coefficients. Since the domain of the basis functions also covers changes in composition [8,9], the functional dependence of the energy on $N$ can be omitted, and the effective cluster interactions (ECI in short) will only depend on the volume. As an example, the effective pair interaction $J_{ij}$ is defined as [7]

$$J_{ij}(V) = \frac{1}{2} \left( \langle U^{0}_{AA}(V) \rangle + \langle U^{0}_{BB}(V) \rangle - \langle U^{0}_{AB}(V) \rangle - \langle U^{0}_{BA}(V) \rangle \right),$$  \hfill (16)

where $\langle U^{0}_{AA} \rangle$ stands for the average of $U^0(V)$ over all configurations in the Ising model that
have an A atom at site \( i \) and \( j \). Similar definitions hold for the third other terms in eq. (16).

Several techniques to compute the (ECI) have been advanced, all involving some kind of electronic band structure computation. Despite the significant progress that electronic structure methods have made in the last decade, the determination of the ECI from first principles is still the major source of error in ab initio phase diagram computations. In the Connolly–Williams method [10], the effective cluster interactions are determined by fitting a truncated form of the Ising Hamiltonian (eq. (1)) to the energies of a set of ordered structures

\[
J_a(V) = \sum_i a_{a_i} U^0(\sigma_i, V). \tag{17}
\]

Structure \( i \) is specified by \( \sigma \). The coefficients \( a_{a_i} \) depend both on the truncation of the Ising Hamiltonian and on the choice of structures \( \sigma \). Truncation is typically used after the fourth nearest neighbor for pair interactions and after a shorter distance for multibody terms. The values of \( U^0 \) for various structures can be computed by quantum mechanical methods. If \( U^0 \) is known for enough structures, the effective cluster interactions can be obtained from eq. (17).

In section 3 we mentioned that an Ising model state does not exactly specify the state of an alloy (location of the atoms etc.). This ambiguity has spurred some question as to what alloy state exactly needs to be used for the determination of \( U^0(\sigma_i, V) \). Should all atoms be fixed at lattice sites, as the nature of the Ising model seems to imply, or should local degrees of freedom be relaxed? From our derivation it is clear that the latter option should be chosen. \( U^0(\sigma_i, V) \) is the ground state energy of the CC-ensemble with \( \sigma = \sigma \). Hence, local degrees of freedom need to be relaxed so as to obtain the minimum energy for a given CC-state. Note that small structural relaxations do not affect the Ising model state onto which the alloy configuration projects.

5. Discussion

Equation (6) defines the Hamiltonian, \( H(\{a\}) \), that one should use in an Ising model so that it exactly reproduces the free energy of an alloy. Only one assumption needs to be made to arrive at this result, namely, that all microstates of the alloy can be partitioned into groups (CC states), each associated with a certain Ising model configuration. It is not clear whether this is always possible. One could, for example, imagine that there are phonons with large amplitude that make clusters of atoms resonate between two lattice structures. In that case this hypothesis might break down. All other approximations that are regularly made in Ising model computations concern the value of the Hamiltonian for a given Ising model state.

Projecting \( H(\{\sigma\}, N, T, V) \) onto the cluster functions \( \sigma \) results in an expansion for the Ising Hamiltonian with volume and temperature dependent cluster interactions. This additional temperature dependence brings, in principle, no new complexity to the statistical methods that are currently used for the computation of the free energy. The two most used methods for the computation of alloy phase diagrams, the Cluster Variation Method and Monte Carlo simulation, can be easily extended to include temperature dependent interactions. However, the determination of the ECI will need to be done at different temperatures. One way of doing this would be to perform a Connolly–Williams fit at several temperatures. The energy of a given structure in the Connolly–Williams method then has to consist of the total energy of the ground state in the corresponding CC-ensemble plus the vibrational free energy. The latter could be computed with a simple Einstein or Debye model.

The fact that coherent phase diagrams can be fitted with good accuracy by using interactions that do not depend on temperature indicates that, for these coherent systems, the variation of the ECI with temperature is small. This does not mean that the variation of \( H(\{\sigma\}, N, T, V) \) with temperature is small. But most of that temperature dependence will project onto the constant (empty lattice cluster) and linear term (point cluster) in the Hamiltonian expansion (eq. (1)). These two terms have little effect on a coherent ordering phase diagram. The ECI on clusters larger than the point, will be affected only by the part of
the vibrational free energy that varies with configuration. Based on the results of Moraitis and Gautier [11] we expect this contribution to be small.

The additional approximations, discussed in this paper, make the ground state energy in the CC-ensemble temperature independent, by assuming zero temperature for the electrons. The approximation of the Fermi–Dirac function as a step function should have little effect on results since at most temperatures where solids exist, the Fermi–Dirac distribution function goes from 1 to 0 in an interval that is negligible compared to the total electron energy.

6. Conclusion

An Ising model is a model to compute the entropy of a solid due to substitutional excitations (configurational entropy). It is not required that the substitutional excitations are between atoms at ideal lattice sites. Atomic relaxations only alter the value of the Ising Hamiltonian for a given configuration. It should now be clear that the association of the Ising model with atoms sitting fixed at lattice sites is incorrect. Taking the rigid lattice approximation will only alter the value of the Hamiltonian $H(\sigma)$ (or the effective cluster interactions in an expanded Hamiltonian like eq. (1)). This is especially important when computations are performed with interactions that are fitted to experimental data. Since we have shown that the form of the Ising Hamiltonian is essentially correct, one should be able to obtain very good results with a fitting Ising model. Ab initio phase diagram calculations with Ising models can be made more accurate by using temperature dependent “ground state” energies in the determination of the ECI. This requires the computation of the vibrational free energy of a solid with given CC state.

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