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Cluster expansions and the configurational energy of alloys

J. M. Sanchez

Center for Materials Science and Engineering, The University of Texas, Austin, Texas 78712 (Received 16 August 1993)

A formal description of configurational functions in alloys is presented. The approach introduces an infinity of orthogonal and complete basis sets in the configurational space of finite clusters, and leads naturally to generalized cluster expansions. In the present approach, the orthogonality of the basis functions is defined with respect to the scalar product given in terms of unrestricted sums over all possible configurations of the cluster. In the thermodynamic limit, this definition of the scalar product corresponds to sums in the canonical ensemble and, as such, the basis are well adapted to describe functions at any fixed concentration. A general relation between the expansion coefficients in different basis is derived.

A description of the configurational energy of alloys and, in general, of any function of configuration, was proposed by Sanchez, Ducastelle, and Gratias in terms of orthogonal discrete Chebyshev's polynomials.¹ In this representation, the configurational energy takes the form of a generalized Ising model with effective pair and manybody interactions. This Ising-like form of the configurational energy is well suited for finite temperature studies, especially when the range of the effective interactions is relatively short. In such cases, standard techniques in statistical mechanics, such as Monte Carlo simulations and the cluster variation method, can be used to compute thermodynamic properties of alloys.

The problem of calculating the effective interactions in this cluster expansion has received a great deal of attention during the last several years. Connolly and Williams² first applied the cluster expansion in conjunction with *ab initio* total-energy calculations in order to extract the effective interactions by means of a straightforward inversion procedure. In the Connolly-Williams method, effective cluster interaction (ECI's) are obtained by applying the truncated, but other wise exact, cluster expansion to the total energies for a set of ordered compounds. Several studies have shown that the cluster expansion converges relatively fast and, thus, provides an important link between *ab initio* electronic-structure and statistical-mechanics calculations.³⁻¹⁰

In view of the simplicity of the cluster expansion and its ease of implementation with electronic-structure calculations, the possibility of optimizing convergence by using other basis functions is a subject of considerable current interest. In particular, Asta *et al.*¹¹ have recently proposed a scheme based on a set of orthogonal cluster functions which, in these authors' terminology, leads to concentration-dependent effective interactions. This particular cluster expansion has been referred to as the canonical scheme since the scalar product is defined as concentration-restricted sums over configurations. The same authors have referred to the previously introduced expansion of Sanchez, Ducastelle, and Gratias,¹ as the grand canonical scheme and as leading to concentrationindependent interactions. The approach of Asta *et al.*¹¹ closely parallels the scheme proposed by Sanchez, Ducastelle, and Gratias.¹ For a binary alloy with concentration $c = \frac{1}{2}$, it has been shown that both schemes of computing effective interactions are equivalent in the thermodynamic limit.¹¹ An apparent difference between both schemes is the definition of the scalar product and their applicability to finite clusters. In particular, the definition of scalar product in terms of restricted sums proposed by Asta *et al.*¹¹ is meaningful only in the thermodynamic limit, whereas a scalar product defined in terms of unrestricted sums can be easily applied to any finite cluster.

Here we introduce an infinite family of orthogonal basis functions that are well adapted to describe functions in the configurational space of any cluster (finite or not). Although in the thermodynamic limit the scalar product is defined in terms of unrestricted sums, i.e., in the grand canonical ensemble, the basis are equivalent to those introduced by Asta et al.¹¹ and include, for all cluster sizes, the basis of Sanchez, Ducastelle, and Gratias.¹ With regard to the application of these and possibly other cluster expansions to the energy of alloys, the current definition of basis functions clearly shows that there are an infinite number of choices between equally valid ECI's. Further, the often quoted concentration dependence (or lack of it) of the ECI's reflects, in most cases, the choice of basis functions in configuration space. As such this "concentration dependence" is void of physical meaning and should not be confused with some explicit dependence due, for example, to the dependence of the ECI's on the volume of the alloy. It is clear that even this concentration dependence, arising from volume changes, can be fully renormalized into concentration independent ECI's. However, convergence of the cluster expansion may dictate that this type of concentration dependence be explicitly kept in the ECI's.

In close parallel to the method of Ref. 1, we begin by considering a "point cluster" for a binary system. The configurational variable σ is discrete, taking values 1 and -1 for each type of atoms, and the configurational space is one dimensional. Given two functions $f(\sigma)$ and $g(\sigma)$, we define their scalar product in this space by 14 014

$$\langle f,g \rangle_{\mu} = \frac{1}{2\cosh(\mu)} \sum_{\sigma=\pm 1} e^{\mu\sigma} f(\sigma) g(\sigma)$$
 (1)

where μ is an arbitrary constant. For each value of μ , a complete and orthonormal basis in the one-dimensional space spanned by the discrete variable σ is given by a set of two polynomials, $\varphi_{1}^{\mu}(\sigma)$ and $\varphi_{1}^{\mu}(\sigma)$, of order 0 and 1, respectively.¹ These are given by

$$\varphi_0^{\mu}(\sigma) = 1 , \qquad (2a)$$

$$\varphi_1^{\mu}(\sigma) = \cosh(\mu) [\sigma - \tanh(\mu)] = \frac{(\sigma - \overline{\sigma})}{\sqrt{1 - \overline{\sigma}^2}}$$
, (2b)

with $\overline{\sigma} = \tanh(\mu)$. We note that for $\mu = 0$, the scalar product, and therefore the basis, is identical to that introduced in Ref. 1. Furthermore, this basis can be extended to multicomponent systems by simply considering higher-order polynomials in the discrete multivalued variable σ .

Given the polynomials $\{\varphi_i^{\mu}, i = 0, 1\}$ for the point cluster, an orthogonal basis for any finite cluster, including the whole crystal with N lattice sites, can be easily constructed. Following Ref. 1, we note that the configurational space of a cluster $\alpha = \{p_1, p_2, \ldots, p_{n_{\alpha}}\}$, where p_i refers to the sites in the cluster, is given by the

direct product of the subspaces associated to each site.

Thus, an orthonormal basis in the spaces associated to each site. Thus, an orthonormal basis in the space spanned by the n_{α} -dimensional discrete vector $\boldsymbol{\sigma} = \{\sigma_1, \sigma_2, \dots, \sigma_{n_{\alpha}}\}$ is given by characteristic functions $\Phi_{\alpha}^{\mu}(\boldsymbol{\sigma}_{\alpha})$ which are obtained from all possible products of the polynomials defined in Eq. (2):¹

$$\Phi^{\mu}_{\alpha}(\boldsymbol{\sigma}_{\alpha}) = \prod_{i \in \alpha} \varphi^{\mu}_{1}(\boldsymbol{\sigma}_{i}) .$$
(3)

The corresponding scalar product between two functions $f(\sigma_{\gamma})$ and $g(\sigma_{\gamma})$ in the configurational space of cluster γ is defined by

$$\langle f,g \rangle_{\mu} = \frac{1}{\left[2\cosh(\mu)\right]^{n_{\gamma}}} \sum_{\sigma_{1}=\pm 1} \cdots \sum_{\sigma_{n}=\pm 1} e^{n_{\gamma}\mu x} f(\sigma_{\gamma})g(\sigma_{\gamma})$$

(4)

where n_{γ} is the number of sites in γ and

$$x = \frac{1}{n_{\gamma}} \sum_{i=1}^{n} \sigma_i \quad . \tag{5}$$

The orthogonality of the characteristic functions, which follows trivially from the orthogonality of the $\varphi_i^{\mu}(\sigma)$, is then expressed as

$$\langle \Phi^{\mu}_{\alpha}, \Phi^{\mu}_{\beta} \rangle_{\mu} = \frac{1}{\left[2\cosh(\mu)\right]^{n_{\gamma}}} \sum_{\sigma_{1}=\pm 1} \cdots \sum_{\sigma_{n}=\pm 1} e^{n_{\gamma}\mu x} \Phi^{\mu}_{\alpha}(\sigma_{\alpha}) \Phi^{\mu}_{\beta}(\sigma_{\beta}) = \delta_{\alpha,\beta}$$
(6)

(9)

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where both α and β are subclusters of the cluster γ . We note that the sums in Eqs. (4) and (6) are unrestricted.

All definitions remain unchanged when the cluster γ becomes the entire crystal with N sites. If the arbitrary constant μ is taken equal to 0, the definitions of the scalar product and of basis functions used here are identical, for both finite and infinite clusters, to that of Sanchez, Ducastelle, and Gratias.¹ Furthermore, in the thermodynamic limit, i.e., when $N \rightarrow \infty$, the *unrestricted sums* in Eq. (4) are equal to *restricted sums* in which only those configurations with $x = \overline{\sigma} \equiv \tanh(\mu)$ [see Eq. (5)] are involved. This can be seen by rewriting Eq. (4) as

$$\langle f,g \rangle_{\mu} = \sum_{n=-N}^{n=+N} [G(x,\overline{\sigma})]^{N} \left\{ \frac{1}{W_{n}} \sum_{\sigma}' f(\sigma) g(\sigma) \right\}$$
 (7)

where the first summation index is $n = xN = N_A - N_B$, with N_A and $N_B = N - N_A$ the number of A and Batoms, respectively. Furthermore, we note that in Eq. (7) the sums over σ are restricted to those configurations with $x = \overline{\sigma} \equiv \tanh(\mu)$, $W_n = (N!) / [(N_A!)(N_B!)]$ is the number of configurations in the canonical ensemble, and $G(x, \overline{\sigma})$ is given by

$$G(x,\overline{\sigma}) = \left\lfloor \frac{e^{\mu x}}{2\cosh(\mu)} \right\rfloor [W_n]^{1/N}.$$
(8)

In the thermodynamic limit, $G(x, \overline{\sigma})$ is given by

$$G(x,\overline{\sigma}) = \left[\frac{(1-\overline{\sigma}^2)}{(1-x^2)} \left[\frac{(1-x)(1+\overline{\sigma})}{(1-\overline{\sigma})(1+x)}\right]^x\right]^{1/2}$$

and, therefore, the factor $[G(x,\overline{\sigma})]^N$ in Eq. (7) becomes the Kronecker's delta $\delta(x-\overline{\sigma})$. Thus, in the thermodynamic limit, the scalar product defined by Eq. (4) involves only restricted sums over configurations in the canonical ensemble for all values of μ .

Consider the expansion of a function of configuration, such as the energy, in the basis $\Phi^{\mu}_{\alpha}(\sigma)$ for some value of μ :

$$E(\boldsymbol{\sigma}) = \sum_{\alpha} V^{\mu}_{\alpha} \Phi^{\mu}_{\alpha}(\boldsymbol{\sigma})$$
 (10)

where the coefficients V^{μ}_{α} , i.e., the ECI's, are given by

$$V^{\mu}_{\alpha} = \langle \Phi^{\mu}_{\alpha}, E \rangle_{\mu} . \tag{11}$$

It is perhaps worth noting that, in the scalar product of Eq. (11), the sums are restricted to configurations with an average concentration of A atoms, i.e., $\sigma = 1$, given by

$$c = \frac{1}{2} [1 + \tanh(\mu)] = \frac{e^{\mu}}{2\cosh(\mu)} .$$
 (12)

Thus, only configurations with concentration c participate in the determination of the V^{μ}_{α} and the corresponding ECI's have been referred as concentration dependent.¹¹ It should be noted that, although for a given value of μ the ECI's are obtained from configurations with fixed concentration c, the same ECI's can be used to describe, through Eq. (10), the energy for any alloy concentration. Thus, in the context of the cluster expansion, the concentration used to calculate the ECI's is not

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necessarily the same as the concentration of the system being studied in, for example, a canonical ensemble. This simply expresses the trivial fact that we can write the same energy $E(\sigma)$ using different basis. For example, taking any two arbitrary values μ and μ' we can write

$$E(\boldsymbol{\sigma}) = \sum_{\alpha} V^{\mu}_{\alpha} \Phi^{\mu}_{\alpha}(\boldsymbol{\sigma}) = \sum_{\beta} V^{\mu'}_{\beta} \Phi^{\mu'}_{B}(\boldsymbol{\sigma}) .$$
(13)

In view of their completeness, the basis functions $\Phi_{\beta}^{\mu'}(\sigma)$ and $\Phi_{\alpha}^{\mu}(\sigma)$ are related. Using the definitions of Eqs. (2)-(4), we can write

$$\Phi_{\beta}^{\mu'}(\sigma) = \sum_{\alpha \subseteq \beta} a_{\beta\alpha}^{\mu'\mu} \Phi_{\alpha}^{\mu}(\sigma)$$
(14)

where the sum is over all subclusters α of the cluster β , the latter included, and where the coefficients are given by

$$a_{\beta\alpha}^{\mu'\mu} = \frac{\left[\cosh(\mu')\right]^{n_{\beta}}}{\left[\cosh(\mu)\right]^{n_{\alpha}}} \left[\tanh(\mu) - \tanh(\mu')\right]^{(n_{\beta} - n_{\alpha})} \quad (\beta \supseteq \alpha)$$
(15a)

or, equivalently,

$$a_{\beta\alpha}^{\mu'\mu} = \frac{\left[1 - \overline{\sigma}'^2\right]^{n_{\beta}/2}}{\left[1 - \overline{\sigma}^2\right]^{n_{\alpha}/2}} \left[\overline{\sigma} - \overline{\sigma}'\right]^{(n_{\beta} - n_{\alpha})} \quad (\beta \supseteq \alpha) \tag{15b}$$

where $\overline{\sigma} = \tanh(\mu)$ and $\overline{\sigma}' = \tanh(\mu')$.

A relation between any two choices of ECI's then fol-

lows from Eqs. (13)–(15):

$$J^{\mu}_{\alpha} = \sum_{\beta \supset \alpha} J^{\mu'}_{\beta} (\overline{\sigma} - \overline{\sigma}')^{(n_{\beta} - n_{\alpha})}$$
(16)

where, in order to simplify the notation, we have defined new ECI's which include the normalization factor of the characteristic functions [see Eq. (2)]:

$$J^{\mu}_{\alpha} = \left[\cosh(\mu)\right]^{n_{\alpha}} V^{\mu}_{\alpha} = \left[1 - \overline{\sigma}^{2}\right]^{n_{\alpha}/2} V^{\mu}_{\alpha} .$$
 (17)

We note that Eq. (16) reduces to the equivalence equation between the so-called "concentration independent" (μ =0, i.e., $\overline{\sigma}$ =0) ECI's of Sanchez, Ducastelle, and Gratias¹ and the "concentration dependent" ECI's proven by Asta *et al.*¹¹

In summary, a family of complete and orthogonal basis in the configurational space of finite and infinite clusters was introduced. The applicability of these basis to finite clusters requires a definition of the scalar product that involves unrestricted sums over the cluster configurations. In the thermodynamic limit, these basis are equal to those introduced previously.^{1,11} The present approach shows that the so-called concentration dependence (or independence) of the ECI's simply reflects the choice of basis functions.

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