

*Overview of The Cluster Expansion Method
Its Foundations and Use in “First Principles
Thermodynamics”*

Juan M. Sanchez

The University of Texas at Austin

A Bit of History and (lost?) Prehistory

- **Early 70's:** *Cluster Expansion introduced to study prototype order-disorder Phase Diagrams for “generalized” Ising models.*
 - **Early 80's:** *Connolly & Williams propose to use Total Energy calculations to fit the Effective Cluster Interactions (ECI).*
 - **1984:** *Formal development of the Cluster Expansion (SDG basis).*
 - **Early 90's:** *Development of a **general** CE formalism (totally ignored by CE “practitioners”)*
 - **Mid 90's:** *(Gonis et al.) Wait a minute: the physics of the CE in the SDG basis cannot be right; ECIs must depend on concentration! Community response: Total Silence...*
 - **2010:** *Rigorous Development of CE. Shown to be a MDFT and Introduction of VBCE to account for concentration dependence of ECI.*
 - **Now:** *ECIs depend on everything (i.e. all configurational variables). Sorry...*
- Thus, no one has done (or will ever do) a full Cluster Expansion from a finite number of compound energies*

The Cluster Expansion

Therefore

Some Basic Observations

or

So, why use any basis other than SDG?

Less Obvious Observations

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Cluster expansion and the configurational theory of alloys

J. M. Sanchez

Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, USA

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In other words: in the presence of non-linear terms in concentration, a “truncated” CE in the SDG basis will not work, specially in the implementation of the Connolly-Williams method

A Partial Solution (to account for non-linear concentration dependence)

In this representation (VBCE), the expansion coefficients are function of concentration

Periodic Systems

Thus:

With:

Thermo 101

By Euler's homogeneous function theorem, the total energy $F = N E$ is given by:

Or,

Thus, for a converged CE (in whatever basis) we should have:

Which shows that the ECIs will not only depend on concentration but also on all the higher order correlations (i.e. SRO)

Pair Potential Model At constant volume the Cluster Expansion in the SDG basis is EXACT

Energies of 627 fcc compounds

Exact Euler Derivatives

SDG Basis (Variables are z_{n0})

Variable Basis: (Variables are z_{nx})

*CE in SDG Basis vs **Exact** Euler Derivatives*

Variable Basis Cluster Expansion

Comparison of *SDG CE* , *VBCE* and *Exact Euler Derivatives*

SDG Basis

Variable Basis

The Bottom Line

What is a *truncated* CE in the SDG basis?

- A Taylor expansion to *first order* in the configurational variables (x and z_{n0}) about the random state at $x=0$!

What is a *truncated* VBCE?

- A Taylor expansion to *first order* in the configurational variables z_{nx} about the random state at concentration x !

Can we do better?

- *Yes! Include higher order terms in the Taylor expansion*

Taylor Expansion: SDG vs Variable Basis

Taylor Expansion in the SDG Basis

Taylor Expansion in VB

Taylor Expansion of the Euler Derivatives compared to Exact values

SDG Basis

Variable Basis

Fe-Co (Original Fit) Published: A. Díaz-Ortiz et al., *Phys. Rev B*, 73, 224208, (2006)

- DFT (PAW)
- CE (SDG)

Variational CE (VCX) _____

Fe-Co Phase Diagram: CVX with 14 clusters CVM Approximation: 15Points + 4 Octahedra

bcc

• Exp.
CE (SDG)

B2

Issues

- Energy Scale: 50 K \square 4.3 meV
 - Probable Cause: using wrong thermodynamic variables for relaxed structure
 - Solution: All-electron calculations (LAPW) with Volume relaxation ONLY
- Shape
 - Probable Cause: SDG CE
 - Solution: Taylor Expansion in the VB

Fe-Co Revisited

- *Unpublished Data (A. Díaz-Ortiz)*
 - *Un-relaxed energies for the 70 Structures*
 - *Plus the energies of an additional set of 23 un-relaxed structures*

Next

1. *Do the Taylor Expansion in the Variable Basis using 70 un-relaxed structures. Does the PD change?*
2. *Use the CE (TVB) to calculate the energies of the 23 un-relaxed structures not used in the fitting. Is there agreement with the DFT energies?*

Second order Taylor Expansion
First and Second neighbor pairs

The Energy and the ECIs (Euler Derivatives) in the VB

The Fe-Co Phase Diagram

bcc

B2

bcc

B2

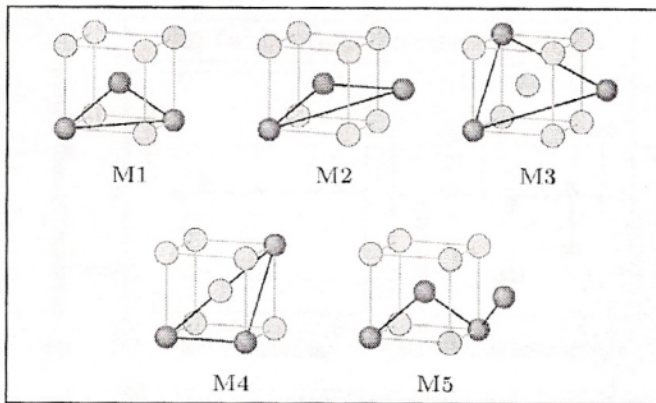
“Predicted” Energies for 23 un-relaxed Structures

Mo-Ta

Published: V. Blum & A. Zunger, *Phys. Rev. B*, 70, 155108 (2004)

Converged “Mixed Base” CE:

Empty, Point, 8 Pairs
Plus



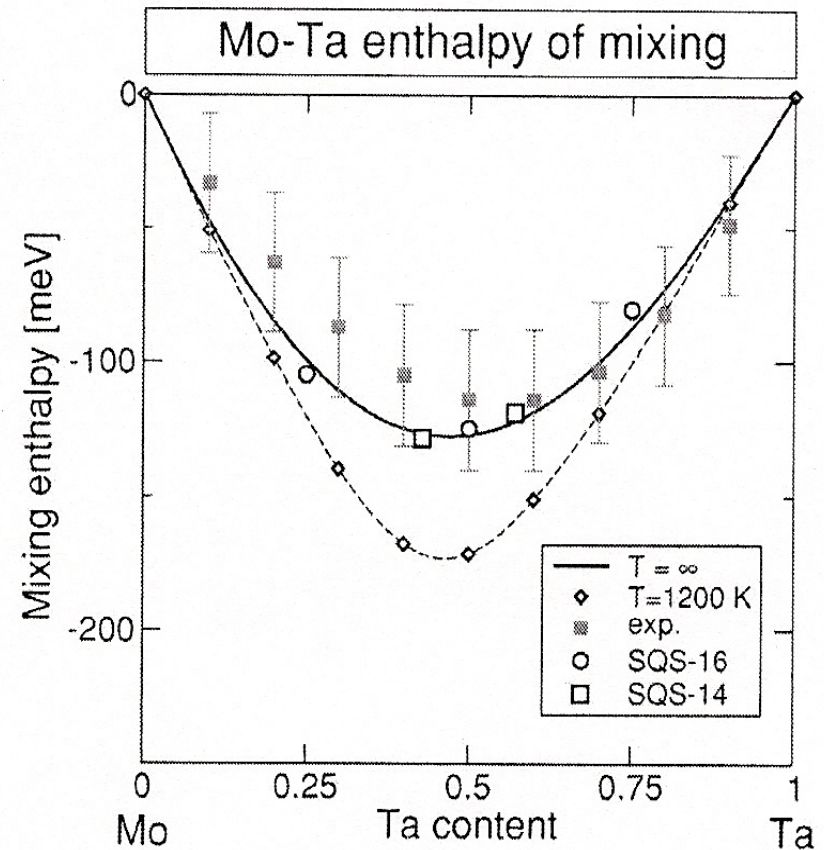
Fitting Error ≈ 2.5 meV

B2 Structure

ELAPW = -195 meV
EVASP = -205 meV

C11b Structure

MoTa₂: $\delta E_{rel} = -7.1$ meV
Mo₂Ta: $\delta E_{rel} = -23.4$ meV



“underestimating the truth”

The Four Issues with the Mo-Ta Calculations:

1. *Accuracy of Projector Augmented Wave Potentials (VASP): Not a major issue unless accuracies below 10 meV are required.*

Solution: All-electron calculations: LAPW (WIEN)

1. *Description of the energies of fully relaxed structures using a CE with the space group symmetry of the disordered phase: Major conceptual problem (i.e. uses the wrong thermodynamic variables for the relaxed structures!)*

Solution: DO NOT relax the structures (except for volume relaxation)

1. *Use of a truncated CE in the SDG basis: CE does not converge. Assumes constant Euler derivatives or ECIs. Equivalent to a Taylor expansion to first order about the 50/50 random state.*

Solution: Use a higher order Taylor expansion about the random state at each concentration x (a high order Variable Basis CE)

1. *Number of structures (56) is not enough for a meaningful VB Taylor expansion.*

Solution(s): Calculate more energies or overdimension the LSF and “regularize”

Addressing Issues 1) and 2)

The Art of Fitting

- *Basic Principles:*

- *Use as many clusters as you can afford: 6 pairs + all clusters in the octahedron (17 clusters in all)*
- *Control non-linear terms through regularization (**but with minimum bias**)*

Mo-Ta: 2nd order Taylor expansion in the VB

Mo-Ta Enthalpy @ 1200 K

□ Experimental

-□- Taylor VBCE
Random (TBVCE)

-□- Blum & Zunger

Conclusions

- *The most important result of the CE: Gives all configurational variables for an alloy with a given space group symmetry.*
- *At least three approximate versions of the CE:*
 - *SDG Basis ($\mu = 0$): MDFT, ECIs are constant, good phenomenological model.*
 - *VBCE (μ matched to concentrations): Wavelet Transform ECIs depend on concentration, better phenomenological model?*
 - *Taylor expansion in the VB: ECIs depend on all configurational variables. Might lead to a quantitative First Principles Thermodynamic Theory*

Issues that need to be considered (re 30 years of use of the CE):

- *The configurational variables typically used in the CE are the wrong variables to describe fully relaxed structures*
- *A truncated CE in the SDG basis is a good phenomenological model (but*