

PART 2: Reliable and not-so Reliable Cluster expansions and Monte Carlo

In Part 1, you learned to calculate reliable alloy formation energies. Then you constructed a cluster expansion, by hand, by getting correlations and solving a system of linear equations with equal number of unknown interactions and known formation energies. (By definition this direct inversion methods has no fit error. The least-square error is zero and the cross-validation (remove 1) score is infinite! You have no predictive power.)

But, what happens when you include more structures (in order to include more physics: configurations and correlations) and try to get finite predictive error (i.e., CV1)?

There are many ways to construct a cluster expansion, some obviously wrong from a physical point of view, with others not so clear. With a limited set of (noisy) data, one must truncate the interactions both in range and in multi-bodies. Therefore, a cluster expansion is not necessarily unique when truncated and fit to finite set of data.

For our point of view, the cluster expansion is nothing more than a basis set expansion just like in quantum mechanics. Therefore, as with any Rayleigh-Ritz minimization of basis set, ***the basis should be compact and contain no “holes”*** (i.e., no missing interactions, J_n , that are shorter ranged or more compact than the others contained within the basis).

Such a *compact basis* we refer as *optimal* when predictive error is minimized, i.e. CV1 Score is minimal for given truncation of clusters.

(1) How to do Cluster Expansion correctly: the case of fcc Ni₃V.

You saw earlier today that results of first-principles calculations can be intelligently stored for use, not only for seeding future calculations, but for performing cluster expansions. One may download formation energies for this system from “***the structural database***”, but we already did that for you (as a tar file). The subdirectories provided contain over 50 structures for fcc-based Ni₃V.

The ground-state is DO₂₂, ***two fcc cells*** stacked in z-direction with an *antiphase boundary* in central layer caused by (1/2, 1/2, 0) shift of the atoms within that plane. There are over 20 structures between DO₂₂ and the “usual suspect” L1₂, which means that really L1₂ is not easy to distinguish from the DO₂₂ structure with only short-range interactions.

(A) From DIRECTORY ~/mcc-adm/public_html

- i) If not already done so, source the ***mcc.cshrc*** from admin directory:
cat /nmnt/home2/m/mc/mcc/mcc-adm/mcc.cshrc >> .cshrc
source .cshrc
- ii) Copy ***ttk_input.tar*** and unpack in your local ***/tmp*** directory
cp /nmnt/home2/m/mc/mcc/mcc-adm/public_html/ttk_input.tar ./
- iii) Untar input files: ***tar -xvf ttk_input.tar***
- iv) Run CE/MC code, type: ***ttk >! out.ce &***

(B) While the code is executing, view the *input.txt* file (e.g., *less input.txt*). Within the file there are controls for Monte Carlo and Cluster Expansion.

- i) *structural inversion* (SINV) set as **ON**. (This is done quickly!)
- ii) Monte Carlo controls have several options:
 - size of MC lattice (CELLSIZE) set to **8 8 8**
 - number of passes through lattices for sampling (NPASS) set to **2000**
 - number of equilibration steps (NEQUIL) set to **100**
 - increment for temperature sweep (TEMPERATURE) in same units as interactions (e.g., eV). Values **0.125 0.1 -0.004** are for *cooling*.

Note that for good *specific heat vs. temperature* the box of 8x8x8 fcc cells is not large enough and will have finite-size effects, nor is the NPASS good enough (should be at least twice more). While better, CELLSIZE 16x16x16 will take 8 times longer, and good enough is 32x32x32, which is 64 times longer. Too long for lab today! But result should be convincing

In the file *inclus.txt*, you can find that the above CE/MC is running for a truncated CE containing 2 near-neighbor pairs and 2 smallest triplets (see lectures). Extending to 3 pairs and 3 triplets (the optimal CE) will change results very little, but will increase the Monte Carlo time ~50%. (Later, if you wish to check optimal CE, copy */backup/inclus.3p3t.txt* to *inclus.txt* in main directory and re-run SIM and CE/MC.)

Critical question: Why should CELLSIZE be in increments of 4?

(C) Structural Inversion should have completed in a few seconds and Monte Carlo is running (~11 minutes to complete).

- i) In meantime view results of SIM: *less out_struct.txt*, where you can find the CE-energy of fully disordered state (D) and CE-DO₂₂-energy (O) in the file. (The CE fit is in the third column.) Estimate transition temperature by $(\Delta H_D - \Delta H_O) \sim k_B T_{o/d}$. Compare to the experimental order/disorder temperature for DO₂₂-Ni₃V of 1318 K.
- ii) Also in “*out_struct.txt*” are the Least-Squares and CV1-score for the SIM. Write these values down as they estimate the error. What is error in temperature that you should expect in Monte Carlo?
- iii) When MC has completed view *Specific Heat vs. Temperature* (both in eV, as were the energies). Energy (C_v) is in the second (fourth) column.
Type: *gnuplot*
Type: *plot “output.txt” u 1:4 w linespoints*
 - (a) Where is CE/MC transition temperature? Estimate from peak of C_v.
 - (b) Convert estimate from eV to Kelvin (multiple by 1 eV ~ 11,600 K).
 - (c) How do both simple estimate in (i) and MC estimate in (ii) compare to experiment?

Optimal (or almost optimal) CE does very well.

(2) How NOT to do Cluster Expansion.

We have attempted to prevent people from doing the CE incorrectly. Nonetheless it is still quite possible to have a “*very good*” CV1 Score and a *very bad* CE.

As an example, we provide you a smaller set of structures (~10) and a set of clusters based upon the same 2 pairs and 2 triplets used in part (1). However, we have arbitrarily removed the smallest triplet, so the basis has a “hole”. And, now you will perform a similar exercise as in part I.

(A) We need to replace the previous inputs used in the working **/tmp** directory.

- i) **cp /select/inclust.select.txt inclus.txt** (contains the cluster info)
- ii) **cp /select/directories.select.txt directories.txt** (prevents MC run)
- iii) **cp /select/input.select.txt input.txt**
(Do Structural Inversion Method (SIM) only, prevents MC run, *i.e.*
 - NPASS set to **0**
 - NEQUIL set to **0**.
- iv) Again run CE/MC code, type: **ttk.exe > /out.ce2 &**
This takes almost no time.
- v) Also in **out_struct.txt** are the Least-Squares and CV1-score for the SIM. Write these values down as they estimate the error. Do these appear to be better than in part 1? What is error in temperature that you should expect in Monte Carlo?
- vi) Again, view results of SIM: **less out_struct.txt** where you can find the CE-energy of fully disordered energy (D) and the CE-DO₂₂-energy (O) in the file. (The CE fit is in the third column.) Estimate transition temperature by $(\Delta H_D - \Delta H_O) \sim k_B T_{o/d}$. Compare to the experimental order/disorder temperature for DO₂₂-Ni₃V of 1318 K, and the value in part 1.
- vii) Why is the CV1-score so much better and the CE so much worse (or, in this case, the disordered energy)?

(B) A possible extension. Run MC with this CE and see that it indeed gets the same estimate as the simple one – but this seems really unnecessary.

**Our answers to the exercises appear in the following 2 pages.
NO PEEKING!**

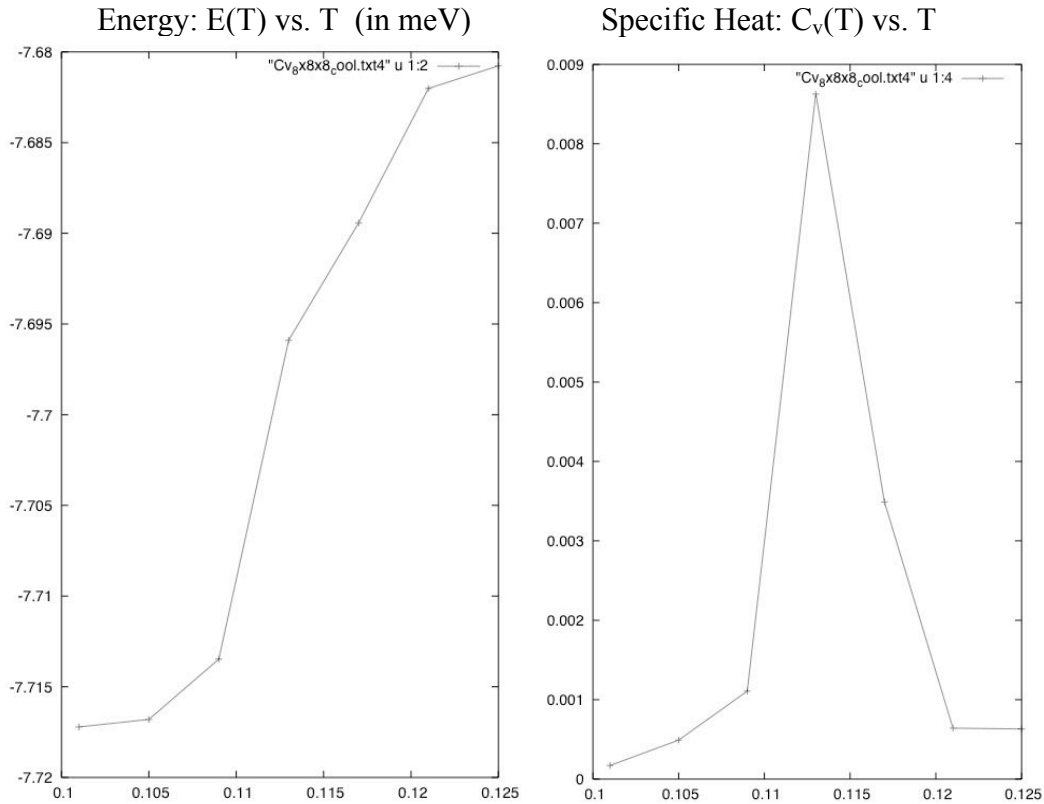
ANSWERS: Rudiments of CE

Part 1:

(C) (i) Simple estimate: From the output, the CE-fit energies for fully disordered and DO₂₂ are -7.5939 eV and -7.7038 eV, respectively. $(\Delta H_D - \Delta H_O) = 0.11$ eV. So the $k_B T_{o/d} \sim 1280$ K. The MC estimate should come out to be approximately this, within the CV1-score error bars.

(ii) $LS\text{-error} = 13$ meV and $CV1\text{-score} = 16$ meV. The 16 meV says that the temperature error is ± 197 K, even though the MC average (part iii) is very good. And, indeed, your predicted transition temperature should be within the error bars of experiment. Note that your MC average could be anywhere within the error estimate, so 1310 K is just lucky!

(iii) Estimated for coarse CE/MC result, the C_v peak in T is 0.113 eV (~ 1310 K), but $CV1\text{-score}$ is ± 197 K. Our runs are here:



Our Cluster Expansion toolkit will be made available on the MCC Software Archive.

Part 2: (A) (v) LS error = 3 meV, while CV1-score = 5 meV. Seemingly excellent. So, yes, these appear to be much better.

(vi) Simple estimate: From output, the CE-fit energies for fully disordered and DO₂₂ are **-7.5581 eV** and **-7.7076 eV**, respectively. ($\Delta H_D - \Delta H_O$) = 0.15 eV. So $k_B T_{o/d} \sim 1740$ K. A much higher temperature (~35% higher) arises because the *disordered state* is poorly represented by non-compact cluster basis. Basically, most ordered states do not have contributions from the nearest-neighbor triplet that was thrown away, while the disordered state does. Hence “holes” in the CE basis resulted in the wrong disordered state energy, raising the transition temperature. (In some previous publications, a much too high order/disorder temperatures originated from such an effect – i.e., bad CE.)

Take-home messages from this computational lab

Now you know: Do not choose longer-ranged clusters at the expense of shorter-ranged ones. They re-weight the interactions within the cluster expansion, and often can lead to a *smaller* CV1-score but *worse* thermodynamics due to ill-described energetics.

Briefly,

1) ***Selectively removing (or adding) structures can make CV smaller, but usually gives bad disordered energy.*** Hence, you will get wrong temperature and phase diagram.

2) ***Throwing away clusters arbitrarily usually results in the wrong disordered energy. So do not make “holes” in the basis.***

3) Make sure that you consider what you have learned when you read and try to assess published results.

This lab was based upon recent publication that sort out discrepancies between previous cluster expansions, KKR-CPA direct calculations with disorder, and experiment:

Nikolai Zarkevich and D.D. Johnson, "Reliable Alloy Thermodynamics from Truncated Cluster Expansions," Phys. Rev. Lett. 92, 255702 (2004).

All the results now agree, as you saw in lecture.

Also the cluster expansion may be used for surfaces. There are several examples. Our recent example, although not couched in the CE framework, is a prediction of new surface defects:

Nikolai Zarkevich and D.D. Johnson, "Energy Scaling and Surface Patterning of Halogen-Terminated Si(001) Surfaces," Surf. Sci. Lett., to appear.

These surface defects were recently observed experimentally:

G.J. Xu, N.A. Zarkevich, A. Agrawal, A.W. Signor, B.R. Trenhaile, D.D. Johnson, and J.H. Weaver, "Cross-over Energetics for Halogenated Si(100): Vacancy Line Defects, Dimer Vacancy Lines, and Atom Vacancy Lines" Phys. Rev. B 71, 115332-7 (2005).