

# MCC Summer School 2005 — Coherency Strain Lab

Gus Hart, Dept. of Physics and Astronomy, Northern Arizona University

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## 1 Overview

Although the Ising expansion-based cluster expansion method for modeling alloys is remarkably powerful and has many strong successes to claim, it fails dramatically in cases where long-range strain fields dominate the behavior of the system. In other words, in any phase-separating system where the constituents are mis-matched (different lattice constants), or where a mis-matched ordered phase forms inside of a matrix, a truncated cluster expansion *cannot* accurately predict the energy. In fact, it will fail *qualitatively* in almost all cases.

The reason for this is simple: a truncated cluster expansion only describes relatively short range interactions. In systems where precipitates form, long range strain fields are present and will account for the majority of the energy in the system. Since a CE only describes short-range interactions, it does not correctly account for the resulting strain fields. For example, consider an  $A_nB_n$  superlattice. There are two contributions to the formation enthalpy of this superlattice:  $E_{CS}$ , the strain due to the *coherent* alignment of slabs of A and B atoms; and  $E_{\text{chem}}$ , the “chemical” interactions of A and B atoms at the interfaces.

Note that as the thickness of the layers in the superlattice increases, that is, as  $n \rightarrow \infty$ , the ratio of  $E_{\text{chem}}/E_{CS}$  approaches zero.  $E_{CS}$  approaches a finite value, while  $E_{\text{chem}}$  becomes vanishingly small. But the cluster expansion can only describe the interfacial contribution to the energy—large volumes containing only A or only B atoms (away from the interfaces) are predicted to contribute *zero* to the formation enthalpy. But note that, in fact, these large areas of pure A and pure B are coherently strained so they contribute a non-zero amount to the formation enthalpy (and are in fact, the only contribution to the formation enthalpy in the  $n \rightarrow \infty$  limit).

Thus, the generalized Ising model *by itself* cannot correctly describe the energetics of alloy system in many cases (i.e., whenever precipitate formation occurs). Note that in our example of an  $A_nB_n$  superlattice, *qualitative* errors occur in a typical cluster expansion even when  $n$  is small. Thus, the problem is not just a problem in principle, but is a problem in practice. Accordingly, we must face this problem head on.

Before we continue, there is one more point to realize. In the perfectly phase-separated case, that is, the  $n \rightarrow \infty$  case,  $E_{CS}$  approaches a finite value, as we said above. The total strain of course depends on the lattice constant mismatch of materials A and B. Higher mismatches result in larger strain energies. But the strain energy also depends on the crystallographic orientation of the interface. Thus the strain energy is “direction dependent.” This peculiar, non-analyticity in the strain has profound physical consequences on precipitate formation in alloys.

## 2 Treating the coherency strain explicitly

To overcome the difficulties of accounting for the energy contribution of coherency strain with the finite-ranged interactions of a truncated Ising expansion, we take a rather direct approach. We use the CE formalism to account for the “chemical” energy and treat the strain energy with a *separate model*. This means that the input energies we use in the Ising model must only be the “chemical” energies. In other words, the

strain energy part of the formation enthalpy must be removed before the resulting energies are fitted to the cluster expansion.

$$\Delta H = E_{\text{chem}} + E_{CS} \quad (1)$$

$$= J_0 + J_1 \sum \hat{S}_i + \sum_{\text{pairs}} J_{ij} \hat{S}_i \hat{S}_j + \sum_{ijk} J_{ijk} \hat{S}_i \hat{S}_j \hat{S}_k \quad (2)$$

$$(3)$$

In principle, this approach is *independent* of which strain model we choose to use. In the following, we consider one choice of strain model but other models are possible. In the spirit of our original cluster expansion report, we can use first-principles results to parameterize our model so that the entire approach (the entire strain+Ising-based cluster expansion) can be still be ab initio-based.

The particular form of the strain energy we use here is:

$$E_{CS}(\vec{\sigma}) = \frac{1}{4x(1-x)} \sum_{\mathbf{k}} \Delta E_{CS}^{\text{eq}}(x, \hat{k}) |S(\mathbf{k}, \vec{\sigma})|^2 \quad (4)$$

where  $\sum_{\mathbf{k}} |S(\mathbf{k}, \vec{\sigma})|^2$  is a lattice Fourier transform of the particular structure in question.  $\sigma$  is a vector representing the current configuration. Here,  $\Delta E_{CS}(x, \hat{k})$  is the coherency strain energy, defined as the energy change when the bulk solids A and B are deformed from their equilibrium cubic lattice constants  $a_A$  and  $a_B$  to a common lattice constant  $a_{\perp}$  in the direction  $\hat{k}$ :

$$\Delta E_{CS} = \min_{a_{\perp}} [(1-x) \Delta E_A^{\text{epi}}(\hat{k}, a_{\perp}) + x \Delta E_B^{\text{epi}}(\hat{k}, a_{\perp})] \quad (5)$$

where  $\Delta E_A^{\text{epi}}(\hat{k}, a_{\perp})$  is the energy required to deform A biaxially to  $a_{\perp}$ . Note that this formulation contains the necessary *non-analyticity* as  $\mathbf{k} \rightarrow 0$  ( $n \rightarrow \infty$ ).

### 3 Parameterizing the strain

To parameterize (based on DFT results) this formulation for the strain for a particular choice of elements A and B requires two steps: (i) calculate the epitaxial strain energy for both elements for a range of values of  $\{a_{\perp}\}$  and a number of different directions,  $\{\hat{k}\}$ , (ii) determine the minimum  $a_{\perp}$  for each direction and then interpolate the results over all directions.

The purpose of this lab is to practice these two steps. Note that for cubic systems, the ATAT code will handle this automatically. (A full generalization of the procedure has never been completed though some work has been done for extending it to hcp systems.) Note that the examples given in the lab use Mathematica but that the procedure can be performed in other packages as well: Matlab, MathCad, even Fortran or C++.

#### 3.1 Calculating the epitaxial strain energies

1. Calculate the equilibrium lattice constant (according for DFT) for two elements, e.g., Al and Cu. (In the interest of time, use a small cutoff and a coarse grid of k-points.)
2. Now calculate the “epitaxial strain energy” for one of the elements in the (100) direction. Use an in-plane lattice constant  $a_{\perp}$  that is halfway between the two equilibrium lattice constants of the end-points. In other words, fix the lattice constant in the x-y plane,  $a_{\perp}$ , and then vary the lattice constant in the z-direction,  $c$ .

In this lab, we will only calculate the epitaxial strain energy for a single value of  $a_{\perp}$ , but in general you will need to calculate the strain energy for 4–5 different in-plane lattice constants for each endpoint material. (And you will need to repeat this procedure for a number of different directions...)

If it's not already obvious, you should realize that for each value of  $a_{\perp}$ , you must calculate the energy for a series of  $c$  values, i.e., out-of-plane lattice constants. (In general, the equilibrium value for  $c$  is *not* the equilibrium volume-preserving one.) Then, the epitaxial strain energy for a given  $a_{\perp}$  is determined by finding the minimum as  $c$  is varied. So this requires some plotting and root finding in general.

Finally, here are some things to watch out for. Make sure that the DFT code you are using is *not set* to automatically optimize the volume or the cell shape. Second, if the range of values of  $c$  that you are using includes one that "accidentally" increases the symmetry of the system (e.g.,  $a_{\perp} = c$  recovering the full cubic symmetry), make sure that the DFT code *does not* use a different k-point set. The k-point set for each set of calculations (both for varying  $c$  for a given  $a_{\perp}$ , and for varying  $a_{\perp}$  for a given crystallographic direction) should be the same. It will be different, however, for strains along different crystallographic directions, obviously.

3. Plot the epitaxial strain energy as a function of  $c$  the out-of-plane lattice constant. Based on the plot, estimate the epitaxial strain energy, i.e., estimate the minimum in your plot.
4. In the interest of time, we calculated the epitaxial strain energy for only one value of  $a_{\perp}$  and only for one of the two endpoints, *and* for only one stacking direction. As mentioned above, in general we need 4–5 strain energies for each endpoint material, for each of several stacking directions.

Open the Mathematica file `epi_strains.nb` and execute the first three cells (by hitting `Shift+Enter` in each cell in turn.) If you don't know how to do this in Mathematica, ask one of the lab instructors for help. The first three cells set up the notebook, give DFT-derived data for  $E(V)$  for two elements  $A$  and  $B$ , and then plot the results. The results are interpolated with a simple polynomial fit. (Actually, we don't really need the isostatic strain but we include it here anyway.)

5. Execute the next cell.

This cell contains a series of epitaxial strain energies vs.  $a_{\perp}$ , determined using a DFT method known as LAPW. There are 10 sets data corresponding to 5 different crystallographic directions for both endpoint materials. This cell interpolates the data with simple polynomials and plots the results.

Note that the plots are different depending both on the material and the direction of distortion. Also note that because we have interpolated (just with simple polynomials) the results, we easily estimate the epitaxial strain energy in any of our 5 directions for *any value* of  $a_{\perp}$ .

### 3.2 The coherency strain

6. Next, we use the epitaxial strain fits to construct the *coherency strain energy*. This is the energy that is required to bring a slab of material  $A$  into contact with a slab of material  $B$  forming a *coherent* interface. Because the coherency requirement forces one of the materials to dilate and the other to contract in the plane of the interface, both materials will be strained.

Realize that the strain energy is concentration dependent. Thus thick slab of material  $A$  brought into contact with a thin slab of material  $B$  will result in a deformation of both, but the lattice constant will be close to that of material  $A$  and the strain will be relatively small. Roughly speaking, the strain is maximum at 50-50 concentrations where both materials are maximally deformed.

The coherency strain (for a particular direction,  $\hat{k}$ ) is simply a weighted average of the epitaxial strain energies for each material:

$$\Delta E_{CS} = (1 - x)E_A^{\text{epi}} + xE_B^{\text{epi}}$$

where  $x$  is the concentration of material  $B$ . But we've just left out one important detail: the epitaxial energies are also dependent on the in-plane lattice constant,  $a_{\parallel}$ . When a slab of material  $B$  is brought into coherent contact with material  $A$  (which in general has a different lattice constant than material  $A$ ) each will be deformed until the in-plane lattice constant is the same on both sides of the interface.

What will be the value of the in-plane lattice constant? The value that minimizes the coherency strain. So, for a given concentration  $x$ , we need to sweep through all values of  $a_{\perp}$  to find the value that minimizes the coherency strain:

$$\Delta E_{CS} = \min_{a_{\perp}} [(1-x)\Delta E_A^{\text{epi}}(\hat{k}, a_{\perp}) + \Delta E_B^{\text{epi}}(\hat{k}, a_{\perp})]$$

(Basically, this is just Eq. 5 again.) Also, note that everything is also  $\hat{k}$ -dependent, as we have mentioned several times before.

7. Return to the Mathematica notebook. Execute the next block of statements. This block defines the weighted average of the epitaxial strain energies (for each direction) and then plots the results as a surface plot. That is, the plots represent the average strain energies as a function of concentration  $x$  and in-plane lattice constant  $a_{\perp}$ .

### 3.3 The full strain energy

We can use any root-finding method that works to find the full coherency strain energy.

8. Execute the next 4 blocks of statements in the Mathematica notebook. At the end of the fourth block, two plots will appear, one is the full strain energy for our hypothetical superlattice as a function of concentration (and of course for a number of different  $\hat{k}$  directions). If you observe crossing in the plots for different directions, this tells you immediately that the strains in the system are anharmonic. Thus, typical, simple theories of elasticity, based on the elastic constants, for instance, such as harmonic elasticity theory are inadequate models for your chosen binary system. (Never fear, we are using a model that goes well beyond harmonic-only terms.)

The second is a plot of in-plane lattice constants. We don't actually need this for our cluster expansion but it can tell us a number of interesting things, such as the anisotropic nature of the alloy and how well Vegard's law is followed (or not). In large mis-match systems you typically will see a large deviation for Vegard's law. In fact, sometimes there will even be discontinuities in the equilibrium lattice constant vs.  $x$ . (When this is the case, extra care must be taken in performing the minimization over values of  $a_{\perp}$ .)

### 3.4 Interpolating over all directions

So at this point, we have the coherency strain energy, as a function of concentration, for a handful of directions  $\hat{k}$ . What we need to do next is to interpolate the data that we have generated from first-principles to all directions (1/48 of the unit sphere, in the case of cubic systems). Thus, we write down a direction-dependent expansion for the strain and then use our calculated data to determine the coefficients in that expansion.

The expansion we use is almost what one would guess—the most natural choice would seem to be an expansion in spherical harmonics. That is essentially what we will do with two exceptions. (i) Instead of using the “normal” spherical harmonics, which are complex-valued functions, we will take linear combinations of these to make them real. (The strain energy is real, not complex, so this is more intuitive.) (ii) We will explicitly leave out terms that don't match the symmetry of our lattice. In the case of cubic systems, we will combine the remaining terms to form Bethe's famous “Kubic Harmonics.” In principle, these exceptions are not really necessary and we do them only for convenience.

In math, we write the coherency strain as

$$\Delta E_{cs}(x, \theta, \phi) = \sum_{\{L,m\}} c(x)K(\theta, \phi) \tag{6}$$

Note that we have replaced our normal notation for direction,  $\hat{k}$ , with  $\theta, \phi$ . Also note that the coefficients of the expansion are concentration dependent, that is, they depend on  $x$ . In other words, we have a different expansion for each value of  $x$ .

9. Execute the next 5 blocks of statements in the Mathematica notebook. Pay attention to the two resulting plots. The left one plots the errors between the expansion and the actual input data. Compare the size of these errors to the magnitude of the input energies. The right plot shows the coefficients of the expansion as a function of  $x$ . Note the “decay” of higher order terms— $A_0$  is the largest, followed by the magnitude of  $A_4$ , etc. Note also the finite value for terms that go beyond harmonic elasticity theory,  $A_6$  and  $A_8$ . (Ask one of the lab instructors if you don’t understand this.)

We can visualize the full, direction-dependence of the strain energy by making a 3D surface plot (but this naturally suppresses the concentration dependence).

10. Execute the three cells in the Mathematica notebook. Two double plots are shown, one A-rich and the other B-rich. Which directions are hard? Which are soft?
11. Compare these plots to the initial epitaxial strain data. Is it consistent? Or does it seem backwards? When we put a small amount of material A in a matrix of material B, does the direction dependence of the resulting strain mimic that of material B? or material A? (Give this some thought! The answer is both obvious and surprising.)

## 4 Making a cluster expansion

Now that we understand why the strain cannot be treated in an Ising-like framework and how to handle it with a separate model, there is still one more small, but important, detail that we need to face. How does one construct a cluster expansion when it is coupled with an explicit strain model?

As we said earlier, the approach is to use the Ising model to fit the “chemical” energies and the explicit strain model to handle the “long-range part” of the energy. So after calculating the formation enthalpy of a given structure, instead of fitting it directly (ala Ising) you must first subtract off the part of the energy due to the strain and then fit the remainder. When using the resulting fit to make a prediction for a particular structure, one must add back on *ex post facto* the contribution to formation enthalpy due to strain.

Thus, our final problem is this, “How do we determine the strain part of the energy for a particular structure?” The answer is simple, use Eq. 4 to calculate the strain energy for a particular structure  $\sigma$ . All that is required is our 3D fit of the coherency strain and the “structure factors”  $S(\mathbf{k}, \vec{\sigma})$ . The last cell of the Mathematica notebook does this for a bunch of common CE fcc input structures.