

Robustness of the cluster expansion: Assessing the roles of relaxation and numerical errorAndrew H. Nguyen,¹ Conrad W. Rosenbrock,¹ C. Shane Reese,² and Gus L. W. Hart^{1,*}¹*Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602, USA*²*Department of Statistics, Brigham Young University, Provo, Utah 84602, USA*

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Cluster expansion (CE) is effective in modeling the stability of metallic alloys, but sometimes cluster expansions fail. Failures are often attributed to atomic relaxation in the DFT-calculated data, but there is no metric for quantifying the degree of relaxation. Additionally, numerical errors can also be responsible for slow CE convergence. We studied over one hundred different Hamiltonians and identified a heuristic, based on a normalized mean-squared displacement of atomic positions in a crystal, to determine if the effects of relaxation in CE data are too severe to build a reliable CE model. Using this heuristic, CE practitioners can determine a priori whether or not an alloy system can be reliably expanded in the cluster basis. We also examined the error distributions of the fitting data. We find no clear relationship between the type of error distribution and CE prediction ability, but there are clear correlations between CE formalism reliability, model complexity, and the number of significant terms in the model. Our results show that the *size* of the errors is much more important than their distribution.

DOI: [10.1103/PhysRevB.96.014107](https://doi.org/10.1103/PhysRevB.96.014107)**I. INTRODUCTION**

Increases in computational power and algorithmic advancements are making many computational materials problems more tractable. For example, density functional theory (DFT) is used to assess the stability of potential metal alloys with high accuracy. However, the computational costs of DFT prevents exhaustive exploration of all possible configurations of a system. In certain cases, one can map first-principles results on to a faster Hamiltonian, the cluster expansion (CE) [1–3]. Over the past 30 years, CE has been used in combination with first-principles calculations to predict the stability of metal alloys [4–16], to study the stability of oxides [17–21], and to model interaction and ordering phenomena at metal surfaces [22–26]. Numerical error and *relaxation* effects decrease the predictive power of CE models. The aim of this paper is to demonstrate the effects of both and to provide a heuristic so one can know when a reliable CE model can be expected for a particular material system.

CE treats alloys as a purely configurational problem, i.e., a problem of decorating a fixed lattice with the alloying elements [1,2]. However, CE models are usually trained with data taken from “relaxed” first-principles calculations where the individual atoms assume positions that minimize the total energy, displaced from ideal lattice positions. Unfortunately, cluster expansions of systems with larger lattice relaxation converge more slowly than cluster expansions for unrelaxed systems [27]. In fact, CEs with increased relaxation may fail to converge altogether. No rigorous description of conditions for when the CE breakdown occurs exists in the CE literature.

A persistent question in the CE community regards the impact of relaxation on the accuracy of the cluster expansion. Some proponents of CE argue that the CE formalism holds even when the training structures are relaxed because there is a one-to-one correspondence in configurational space between relaxed and unrelaxed structures. This is an assumption.

Independent of whether or not it is true, the relevant issue is not the correspondence but the sparsity of the expansion. In this paper, we demonstrate a relationship between relaxation and sparsity in the CE model. As relaxation increases, CE sparsity and the accuracy of CE predictions decreases.

In addition to the effects of relaxation, we also examine the impact of numerical error on the reliability of the CE fits. There are several sources of numerical error: approximations to the physics of the model, the number of k points, the smearing method, basis set sizes and types, etc. Most previous studies [28–30] only examine the effect of Gaussian errors on the CE model, but Arnold *et al.* [28] also investigated systematic error (round-off and saturation error). They showed that, above a certain threshold, the CE model fails to recover the correct answer, that is, the CE model started to incorporate spurious terms (i.e., sparsity was reduced). A primary question that we seek to answer is whether the shape of the error distribution impacts predictive performance of a CE model.

In this study, we quantify the effects of: (1) relaxation, by comparing CE fits for relaxed and unrelaxed data sets and (2) numerical error, by adding different error distributions (i.e., Gaussian, skewed, etc.) to ideal CE models. We study more than one hundred Hamiltonians ranging from very simple pair potentials to first-principles DFT Hamiltonians. We present a heuristic for judging the quality of the CE fits. We find that a small mean-squared displacement is indicative of a good CE model. In agreement with past studies, we show that the predictive power of CE is lowered when the level of error is increased. We find that there is no clear correlation between the shape of the error profile and the CE predictive power. It is possible to decide whether the computational cost of generating CE fitting data is worthwhile by examining the degree of relaxation in a smaller set of 50–150 structures.

II. RELAXATION

Relaxation is distinct from numerical error—it is not an error—but it has a similar negative effect. When relaxations are significant, it is less likely that a reliable CE model

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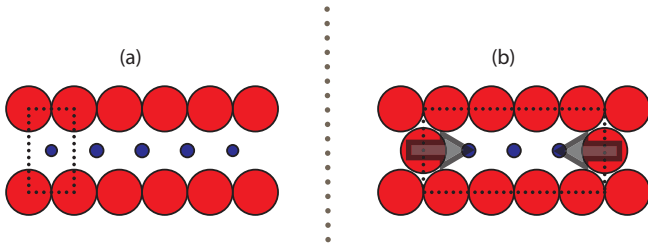


FIG. 1. Symmetry-allowed distortions for two different unit cells. The atomic positions of the cell on the left do not have any symmetry-allowed degrees of freedom, but the aspect ratio of the unit cell is allowed to change. For the unit cell on the right, the horizontal positions of the atoms in the middle layer may change without destroying the symmetry. (The unit cell aspect ratio may also change.)

exists. Relaxation is a systematic form of distortion, the local adjustment of atomic positions to accommodate atoms of different sizes. Atoms “relax” away from ideal lattice sites to reduce the energy, with larger atoms taking up more room, and smaller atoms giving up volume. The type of relaxations (i.e., the distortions that are possible) for a particular unit cell are limited by the symmetry of the initially undistorted case, as shown in Fig. 1. In the rectangular case (left), the unit cell aspect ratio may change without changing the initial rectangular symmetry. At the same time, the position of the blue atom is *not allowed* to change because doing so would destroy rectangular symmetry. In contrast, the two blue atoms in the similar structure shown in the right panel of the figure can move horizontally without reducing the symmetry.

Conceptually, the cluster expansion is a technique that describes the local environment around an atom and then sums up all the “atomic energies” (environments in a unit cell) to determine a total energy for the unit cell. For the cluster expansion model to be sparse—to be a predictive model with few parameters—it relies on the premise that any specific local neighborhood contributes the same atomic energy to the total energy regardless of the crystal in which it is embedded. For example, the top row of Fig. 2 shows the same local environment (denoted by the hexagon around the central blue atom) embedded in two distinct crystals. If the contribution of this local environment to the total energy is the same in both cases, then the cluster expansion of the energy will be sparse.

The effect of relaxation on the sparsity becomes clear in the bottom row of Fig. 2. In the left-hand case [panel (a)], the crystal relaxes dramatically and the central blue atom is now *fourfold coordinated* entirely by red atoms. By contrast, in the right-hand case [panel (b)], a collapse of the layers is not possible and the blue atoms are allowed by symmetry to move closer to each other. From the point of view of the cluster expansion, the local environments of the central blue atom are the same for both cases. This fact, that two different relaxed local environments have identical descriptions in the cluster expansion basis, leads to a slow convergence of cluster expansion models. The problem is severe when the atomic mismatch is large and relaxations are significant (i.e., when atoms move far from the ideal lattice positions.)

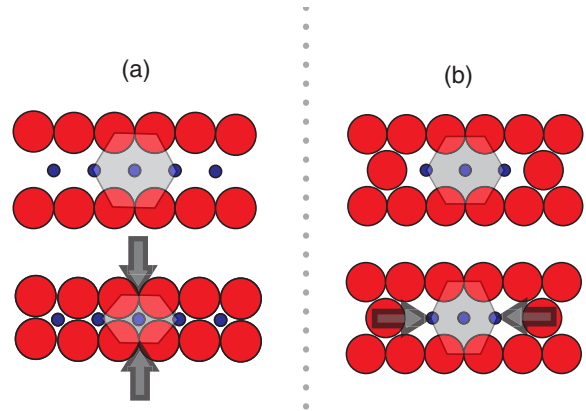


FIG. 2. Relaxation scheme. The top images show the original unrelaxed configurations, while the bottom figures show the relaxed configuration. The left images (a) shows the relaxation where the hexagon is contracted as shown by the black arrows in the bottom left figure. The relaxation in the right images (b) is restricted to displacement of the blue atoms as shown by the black arrows in the bottom right figure.

A. Methodology

We investigated the predictive power of cluster expansions using data from more than one hundred Hamiltonians generated from density functional theory (DFT), the embedded atom method, Lennard-Jones potential, and Stillinger-Weber potential. To investigate the effects of relaxation, we examined different metrics to measure the degree of atomic relaxation in a crystal configuration.

1. Hamiltonians

First-principles DFT calculations have been used to simulate metal alloys and for building cluster expansion models [7,9–14]. However, DFT calculations are too expensive to extensively examine the relaxation in many different systems (lattice mismatch). Thus, we examine other methods such as the embedded atom method (EAM) which is a many-body potential derived from first-principles calculations. EAM potentials of metal alloys such as Ni-Cu, Ni-Al, and Cu-Al have been parameterized from DFT calculations and validated to reproduce their experimental properties such as bulk modulus, elastic constants, lattice constants, etc. [31]. EAM potentials are computationally cheaper, allowing us to explore the effects of relaxation for large training sets; however, we are limited by the number of EAM potentials available.

Therefore, we also selected two classical potentials, Lennard-Jones (LJ) and Stillinger-Weber (SW), to adequately examine various degrees of relaxation, which can be varied using free parameters in each model. The Lennard-Jones potential is a pairwise potential. Using the LJ potential, we can model a binary (A_xB_{1-x}) alloy with different lattice mismatch and interaction strength between the A and B atoms by adjusting the σ parameter in the model. Additionally, we also examined the Stillinger-Weber potential which has a pair term and an angular (three-body) term. In attempting to determine the conditions under which the CE formalism

breaks down, we implemented a set of parameters in the SW potential where the angular dependent term could be turned on/off using the λ coefficient [32]. For example, depending on the strength of λ , the local atomic environment in a relaxed, two-dimensional structure switches between three-, four- and six-fold coordination. When the system relaxes to a different coordination, the CE fits would no longer be valid or at least not sparse.

All first-principles calculations were performed using the Vienna *ab initio* simulation package (VASP) [33–36]. We used the projector-augmented-wave (PAW) [37] potential and the exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) [38]. In all calculations, we used the default settings implied by the high-precision option of the code. Equivalent k -point meshes were used for Brillouin zone integration to reduce numerical errors [39]. We used 1728 (12^3) k points for the pure element structures and an equivalent mesh for the binary alloy configurations. Each structure was allowed to fully relax (atomic, cell shape, and cell volume).

Relaxation was carried out using molecular dynamics simulations for EAM, LJ, and SW potentials. Two molecular dynamics packages were used to study the relaxation: GULP [40,41] and LAMMPS [42]. Details for the LJ, SW, and EAM potentials and the DFT calculations can be found in the Supplemental Material [43].

2. Cluster expansion setup

The universal cluster expansion (UNCLE) software [44–46] was used to generate 1000 derivative superstructures each of face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal closed-packed (HCP) lattice. For the DFT calculations, we used only 500 structures instead of 1000 due to the computational cost. We generated a set of 1100 clusters, ranging from two-body up to six-body interactions. 100 independent CE fits were performed for each system (Hamiltonian and lattice).

We briefly discuss some important details about cluster expansion here, but for a more complete description, see the Supplemental Material [43] and past works [1,4,10,13,47–50]. Cluster expansion is a generalized Ising model with many-body interactions. The cluster expansion formalism allows one to map a physical property, such as E , to a configuration ($\vec{\sigma}$):

$$E_i^{\text{CE}} = \sum_i J_i \Pi_i(\vec{\sigma}), \quad (1)$$

where E is energy, Π is the correlation matrix (basis), and J is coefficient or effective cluster interaction (ECI).

When constructing a CE model, we are solving for the effective cluster interactions or J s. We used the compressive sensing (CS) framework to solve for these coefficients [13,50]. The key assumption in compressive sensing is that the solution vector has few nonzero components, i.e., the solution is sparse [51,52]. The CS framework guarantees that the sparse solution can be recovered from a limited number of DFT energies. Using the J s, we can build a CE model to interpolate the configuration space.

Each CE fit used a random selection of 25% of the data for training and 75% for validation. Results were averaged over the 100 CE fits with error bars computed from the standard deviation. We defined the percent error as a ratio

of the prediction root mean squared error (RMS) over the standard deviation of the input energies, percent error = $\text{RMS}/\text{STD}(E_{\text{input}}) \times 100\%$. This definition of percent error allowed us to consistently compare different systems.

3. Relaxation metrics

Currently, there is no standard measure to indicate the degree of relaxation. We evaluated different metrics as a measure of the relaxation: normalized mean-squared displacement, Ackland's order parameter [53], difference in Steinhardt order parameter (D_6) [54], SOAP [55], and the centrosymmetry parameter [56]. We compared the metrics across various Hamiltonians to find a criterion that is independent of the potentials and systems [43]. We found that none of these metrics are descriptive/general enough except for the normalized mean-squared displacement.

4. Normalized mean-squared displacement (NMSD)

To measure the relaxation of each structure/configuration, we used the mean-squared displacement (MSD) to measure the displacement of an atom from its reference position, i.e., the unrelaxed atomic position. The MSD metric is implemented in the LAMMPS software [42], which also incorporates the periodic boundary conditions to properly account for displacement across a unit cell boundary. The MSD is the total squared displacement averaged over all atoms in the crystal:

$$\text{MSD} = \frac{1}{N_{\text{atom}}} \sum_{\text{atom}} \sum_{X=x,y,z} (X[t] - X[0])^2, \quad (2)$$

where X represents the Cartesian components of each atom position, t is the final relaxed configuration, and 0 is the initial unrelaxed configuration. Additionally, we defined a normalized mean-square displacement (NMSD) percent:

$$\text{NMSD} = \frac{\text{MSD}}{V^{2/3}} \times 100\% \quad (3)$$

which is the ratio of MSD to volume of the system. This allows for a relaxation comparison parameter that is independent of the overall scale.

B. Results and discussions

To explore the effects of relaxation on CE predictability, we examine relaxation in various systems from very high accuracy (DFT) to very simple, tunable systems (LJ and SW potentials). We examine more than one hundred different Hamiltonians and we find several common trends among the different systems.

In most cases, we find that the relaxed CE fits are worse (higher prediction error and higher number of coefficients) than the unrelaxed ones. For example, Fig. 3 shows the cluster expansion fitting for unrelaxed and relaxed data sets of Ni-Cu alloy system using DFT and EAM with two different primitive lattices, FCC and BCC. Because Ni-Cu alloys are naturally FCC-like and the lattice mismatch is small, the training structures for the FCC-based training structures have small relaxations, whereas BCC-based training structures have large relaxations. The contrast between the two cases demonstrates the effect of atomic relaxations. As Fig. 3 shows, Ni-Cu alloy

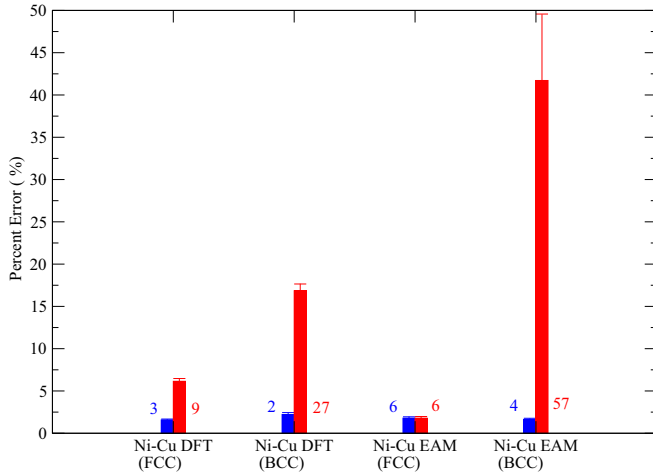


FIG. 3. Cluster expansion fits for Ni-Cu alloy using DFT or EAM potential. Each bar represents the average percent error and error bar (standard deviations) for 100 independent CE fits. The blue bars represent the unrelaxed CE fits, while the red bars represent the relaxed CE fits. The colored number represents the average number of coefficients used in the CE models. When the configurations are relaxed, we find that the CE fits are often worse (higher prediction error and higher number of J s) than the unrelaxed system. However, we show that in one case (Ni-Cu EAM) the unrelaxed and relaxed CE fits are identical (same error and same number of coefficients) and this is due to a small relaxation.

fitting for a FCC lattice is below 10% error, while BCC fitting result in more J s and higher percent error (above 10%) [57]. We find similar results in the relaxation of Ni-Cu alloy using first-principles DFT and EAM potential. The difference between relaxed and unrelaxed CE fits are negligible when relaxations are small. This is shown in Fig. 3 for the relaxation of FCC superstructures using a Ni-Cu EAM potential.

Figure 3 shows that relaxation is often associated with reduced sparsity (increased cardinality of J s) [58]. One possible implication is that a number of coefficients (J) could be used to evaluate the predictive performance of the CE fits. The number of coefficients used in the fits (such as in Fig. 3) is a simple way to determine whether or not a CE fit can be trusted. Figures 4(b) and 4(f) show similar clusters across the 100 independent CE fittings; thus, vertical lines indicate the presence of the same cluster across all CE fits. When the fit is good, only a small subset of clusters is needed [Fig. 4(b)]. On the other hand, Fig. 4(f) shows some common clusters in all of the CE fits with several additional clusters. Figure 5(a) shows the correlation of the percent error with the number of terms in the expansion. We find that as the number of coefficients increases the percent error increases. However, this is not a sufficient metric as shown in Fig. 5(a) where the number of coefficient varies a lot. Nonetheless, the number of coefficients may be used as a general, quick test.

The degree of relaxation is crucial to define whether or not the CE model is accurate or not. However, there is no standard for *when* cluster expansion fails due to relaxation. Thus far, we have made some remarks about relaxation and CE fits. But the question of how much relaxation is allowed has not been addressed. By examining a few metrics: NMSD, SOAP

[55], D6 [54], Ackland [53], and centrosymmetry [56], we find that there is a relationship between degree of relaxation and the quality of CE fits. As shown in the Supplemental Material, we have used these metrics to investigate over 100+ systems (different potentials, lattice mismatches, and interaction strengths). Here, we present a heuristic to measure the degree of relaxation based on the NMSD.

In general, cluster expansion will fail when the relaxation is large. Figure 5(b) shows that a small NMSD weakly correlates with a small number of coefficients. However, Fig. 6 highlights the correlation between degree of relaxation and prediction error. There is a roughly linear relationship between the degree of relaxation and the CE prediction. We partition the quality of the CE models into three regions: good (NMSD < 0.1%), maybe ($0.1\% \leq \text{NMSD} \leq 1\%$), and bad (NMSD > 1%). The “maybe” region is the gray area where the CE fit can be good or bad. This metric provide a heuristic to evaluate the reliability of the CE models, i.e., any systems that exhibit high relaxation will fail to provide an accurate CE model.

III. NUMERICAL ERROR

As we have shown in the previous section, greater relaxation results in worse CE fitting. In addition to the effects of relaxation, we now investigate the effects of numerical error on reliability of CE models. The distinction between relaxation “error” and numerical error is that the former is inherent in the data used to train the CE model. Numerical error can be completely eliminated, in principle. Numerical error arises from various sources such as the number of k points, the smearing method, minimum force tolerance, basis set sizes and types, etc. These errors are not stochastic errors or measurement errors; they arise from tuning the numerical methods. We assume that the relaxation-induced change in energy for each structure is an *error term* that the CE fitting algorithm must handle. The collection of these “errors” from all structures in the alloy system then form an error profile (or distribution). Using the simulated relaxation error profiles from the previous section together with common analytic distributions, we built “toy” CE models with known coefficients. We then examined whether or not the shape of the error distribution affects the CE predictive ability.

A. Methodology

The numerical errors in DFT calculations are largely understood, but it is difficult to disentangle the effects of different, individual error sources. Instead of studying the effects of errors separately, we added different distributions of error to a “toy” model in order to imitate the aggregate effects of the numerical error on CE models. Hence, we opt to simplify the problem by creating a “toy” problem for which the exact answer is known. To restrict the number of independent variables, we formulated a “toy” cluster expansion model by selecting five nonzero values for a subset of the total clusters. Using this toy CE, we predicted a set of energies y for 2000 known derivative superstructures of an FCC lattice. These y values are used as the true energies for all subsequent analysis. We added error to y , chosen from either: (1) “simulated”

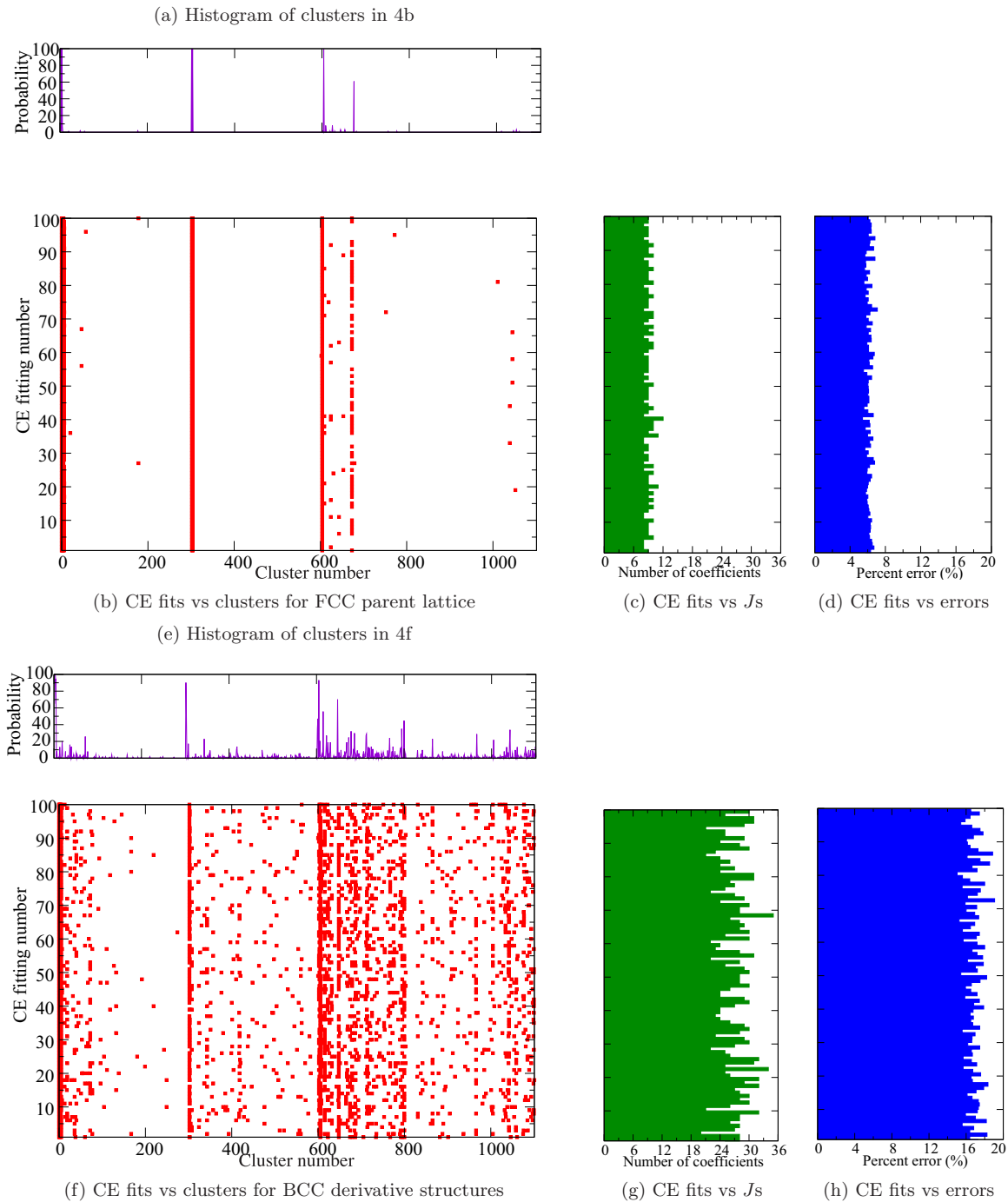


FIG. 4. CE fitting and relaxation of Ni-Cu alloys (DFT calculations) using FCC derivative superstructures and BCC derivative superstructures. Shown in Figs. 4(b) and 4(a) are the 100 CE fits and the histogram of the clusters used for the FCC lattices, while plots 4(f) and 4(e) are for the BCC lattice. The errors and coefficients are shown in 4(c) and 4(d) for the FCC structures and in 4(g) and 4(h) for the BCC lattice. The plot shows that the number of clusters used in fitting is small when cluster expansion fitting is good (error is on average 6.03% for FCC derivative structures). However, the CE fitting of the BCC parent lattice is worse at 16.70% compared to FCC at 6.03%. More coefficients are used when CE fails. The increased number of J_s and error indicate a bad CE fitting model as shown by plots 4(g) and 4(h). Figure 4(e) shows only a few significant terms with many other clusters used sparingly in the fits.

distributions obtained by computing the difference between relaxed and unrelaxed energies predicted by either DFT, EAM, LJ, or SW models (Fig. 7) or (2) common analytic distributions (Fig. 8).

To generate the simulated distributions, we chose a set of identical structures and fitted them using a variety of classical

and semiclassical potentials, and quantum mechanical calculations using VASP. For each of the potentials we selected, we calculated an unrelaxed total energy y for each structure and then performed relaxation to determine the lowest energy state \tilde{y} . The difference between these two energies ($\Delta y = \tilde{y} - y$) was considered to be the “relaxation” error.

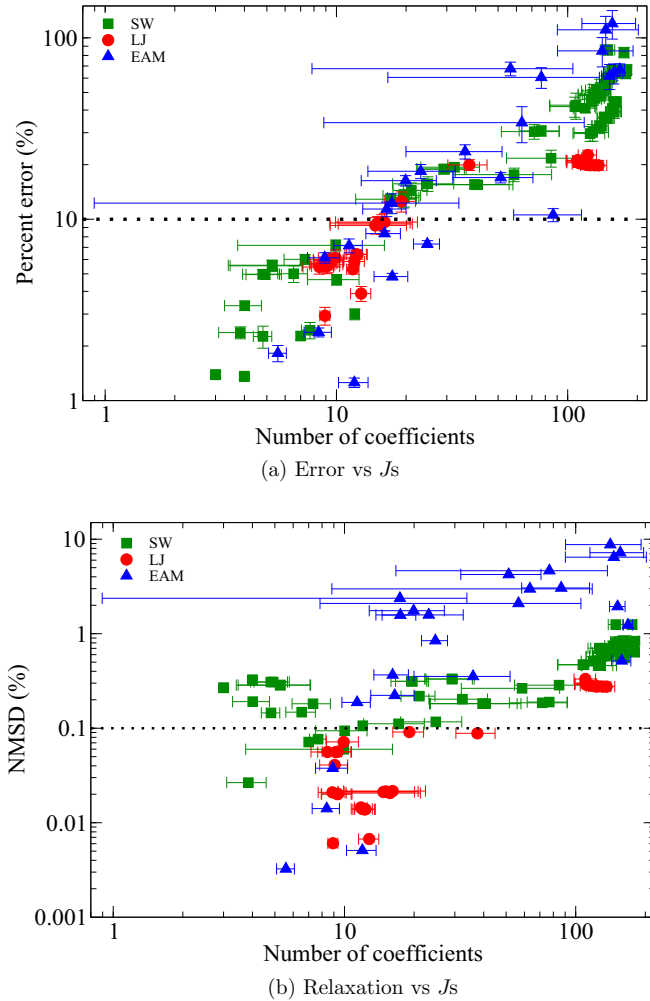


FIG. 5. Plot 5(a) displays the CE fitting error vs the number of coefficients, while plot 5(b) highlights the relationship between number of coefficients and relaxation. The dashed line approximates what we consider as the maximum acceptable error for a CE model (10%). The dashed line in Fig. 5(b) marks the estimated threshold for acceptable relaxation level. Each symbol represents 100 independent CE fittings for each Hamiltonian. Higher error correlates with a higher number of coefficients.

Certain assumptions are usually made about the error in the signal, namely that it is Gaussian. The original CS paradigm proves that the ℓ_2 error for signal recovery obeys [52]:

$$\|x^* - x\|_{\ell_2} \leq C_0 \cdot \|x - x_S\| / \sqrt{S} + C_1 \cdot \epsilon, \quad (4)$$

where ϵ bounds the amount of error in the data, x^* is the CS solution, x is the true solution, and x_S is the vector x with all but the largest S components set to zero. This shows that, *at worst, the error in the recovery is bounded by a term proportional to the error.* For our plots of this error, we first normalized Δy so that $\epsilon \equiv \text{normalized}(\Delta y) \in [0, 1]$ using

$$\epsilon = \frac{y - \min(y)}{\max(y) - \min(y)}. \quad (5)$$

Not surprisingly, the various potentials produced different error profiles.

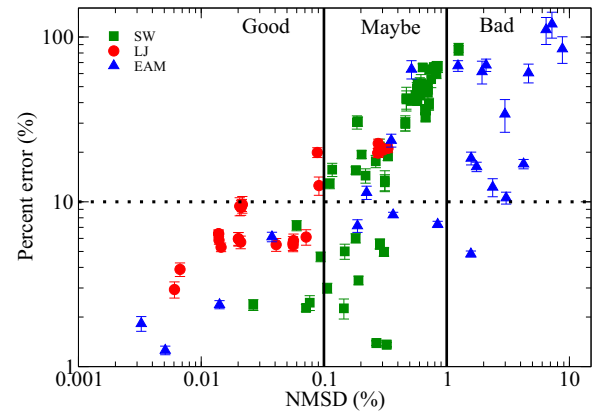


FIG. 6. Relationships between relaxation and CE fitting reveal a heuristic for determining the quality of a CE model. This graph shows the CE fitting error vs normalized mean square displacement (NMSD). Each mark represents 100 individual CE fittings for each system (potentials and parameters). As the NMSD (relaxation) increases, the CE fitting error increases for various systems and potentials. Using the relaxation metric, the quality/reliability of the CE fits can be divided into three regions: good, maybe, and bad CE model. The solid black lines indicates these three areas.

The expectation value of the distributions was set to be a percentage of the average, unrelaxed energy across all structures. Thus, “15% error” means that each unrelaxed energy was changed by adding a randomly drawn value from a distribution with an expectation value of 15% of the mean energy. We performed CE fits as a function of the %-error added (2, 5, 10, and 15%) for each distribution. Although we only present the 15% error results in the next section, all results at different error levels can be found in the supporting information [43]. For each data point, we performed 100 independent CE fits and used the mean and standard deviation to produce the values and error bars for the plots.

B. Results and discussions

As shown in Fig. 9, the error is weakly uniform across all (analytic and simulated) distributions, implying that there is no correlation between specific distribution and error. None of the normal quantifying descriptions of distribution shape (e.g., width, skewness, kurtosis, standard deviation, etc.) show a correlation with the CE prediction error. The error increased proportionally with the level of error in each system (2, 5, 10, and 15% error). We therefore turn to the compressive sensing (CS) formalism for insight.

The theorems of Tao and Candés [51] guarantee that the solution for an underdetermined CS problem can be recovered *exactly* with overwhelming probability provided:

- (1) The solution is sparse within the chosen representation basis.
- (2) Sufficient data points, sampled independent and identically distributed (i.i.d).
- (3) The sensing and representation bases are maximally incoherent.

If all of these conditions are met, we know that CS will provide a solution that is very close to the true answer. Conversely, if CS cannot converge to a good solution, it means that one of

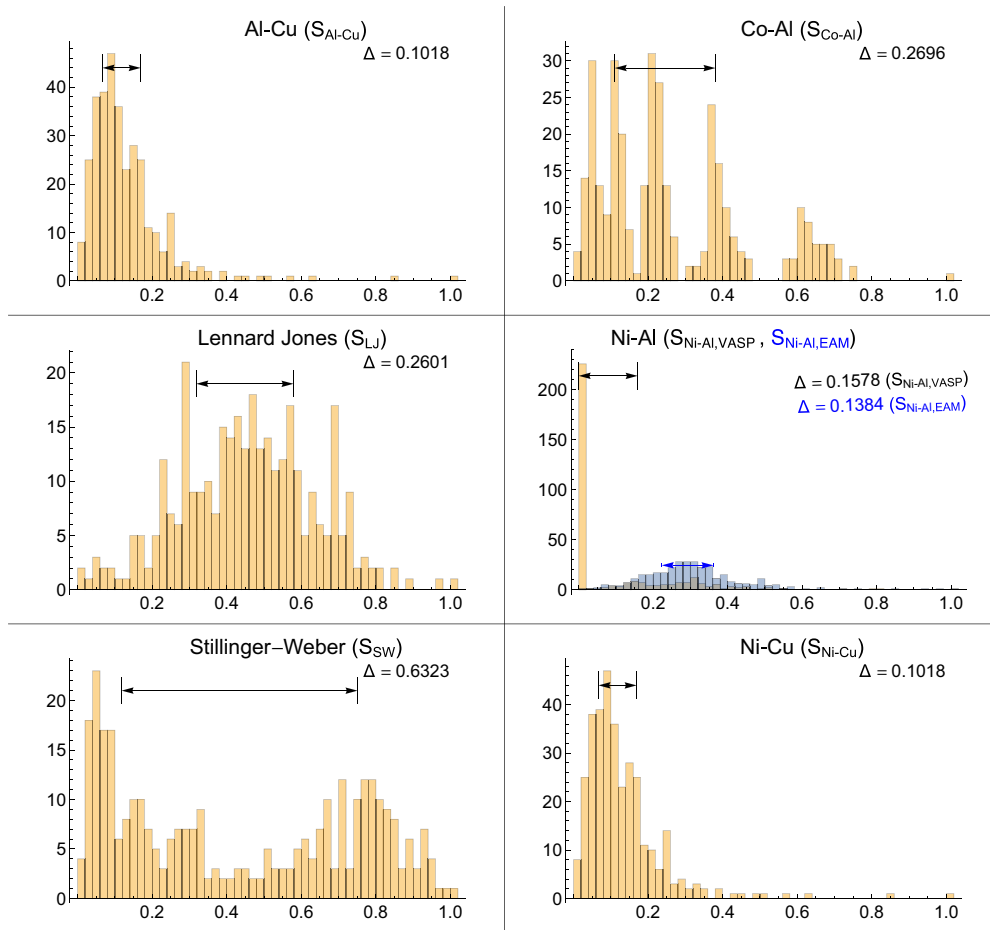


FIG. 7. Distributions from real relaxations using classical and semiclassical potentials, as well as DFT calculations. The distributions are all normalized to fall within 0 and 1. The widths Δ were calculated by taking the difference between the 25th and 75th percentiles.

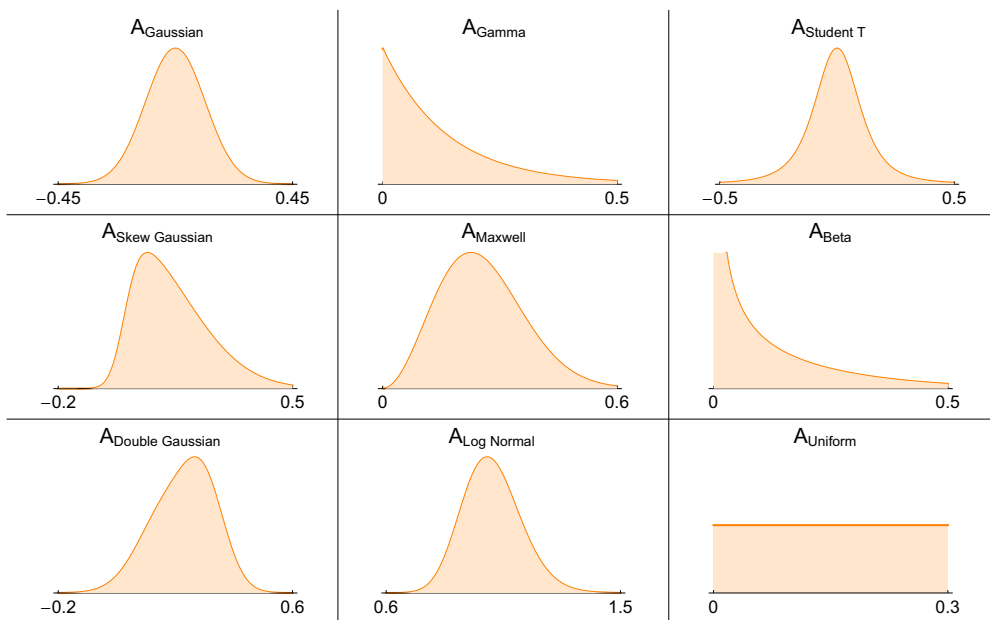


FIG. 8. The analytic, equal width distributions used for adding error to the toy model CE fit.

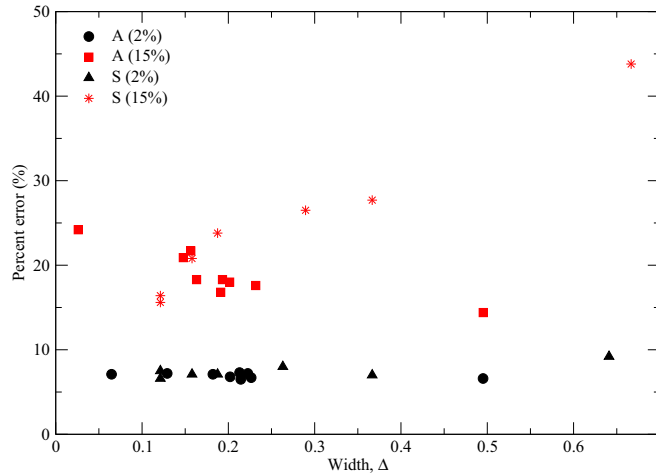


FIG. 9. Comparison of the predictive error in CE fits as the shape of relaxation error changes. (A) refers to the analytic distribution while (S) refers to simulated distribution. The fits are ordered from lowest to highest distribution width. Fits were averaged over 100 randomly selected subsets with 500/2000 data points used for training; the remaining 1500 were used to verify the model’s predictions. The black and red colored symbols represent 2% and 15% error levels, respectively. The circles and triangles represent the analytical and simulated distributions, respectively. Higher error produces higher prediction errors.

these conditions has been violated. We have control over the number of training points, and the incoherence of the sensing-representation bases. However, we *cannot* control whether the true physical solution is sparsely represented for relaxed systems. This suggests a useful connection between the CS framework and the robustness of CE: if CS cannot reproduce a good CE fit (quantified below), then sparsity has been lost.

In the CS framework, the foundational assumption is that of sparsity, meaning that the compressed signal (or cluster expansion) requires only a few terms to accurately represent the true signal (physics). Thus, the number of terms recovered by CS to produce the CE is a good measure of the quality of the CS fit. This begs the question: Can we use the number of terms within the CS framework to heuristically predict *in advance* whether the CE fit will converge well?

In answering the question of predictability for a good CE fit, we define three new quantities:

- (1) Ξ : total number of unique clusters used over 100 CE fits of the same dataset. We also call this the model complexity.
- (2) ζ : number of “exceptional” clusters. These are clusters that show up fewer than 25 times across 100 fits, implying that they are not responsible for representing any real physics in the signal, but are rather included because the CE basis is no longer a sparse representation for the relaxed alloy system. They are sensitive to the training/fitting structures.
- (3) Λ : number of *significant* clusters in the fit; essentially just the total number of unique clusters minus the number of “exceptional” clusters, $\Lambda = \Xi - \zeta$.

In the relaxation section, we showed that the average number of coefficient is not sufficient to determine the quality of the CE model. Here, we decompose the number of J s into three new quantities to provide additional insights into the

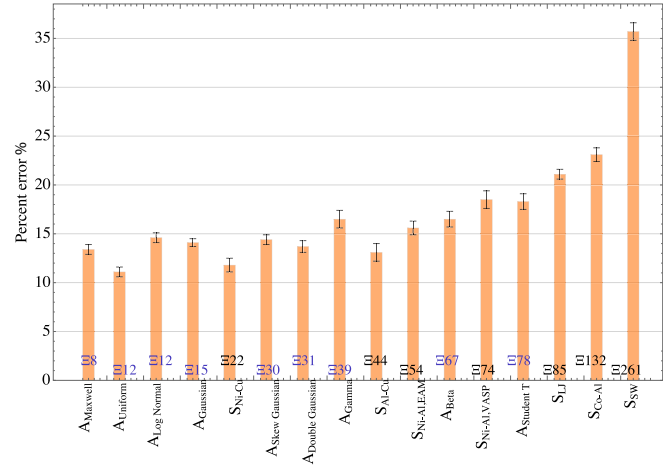


FIG. 10. Prediction error over 65% of the structures for the “toy” cluster expansion (at 15% error added). The systems are ordered by Ξ , which is the total number of unique clusters used by any of the 100 CE fits for the system. This ordering shows a definite trend with increasing Ξ .

reliability of the CE fits. In Fig. 10, we plot the CE error, ordered by model complexity and show that it reproduces the trend identified by the number of coefficients (indeed they are intimately related, Ξ being the statistically averaged number of coefficients across many fits). An ordering by the number of exceptional clusters ζ produces an identical trend, showing that it may also serve to quantify a good fit [43].

As indicated earlier, all these experiments were performed for a *known* CE model that had five nonzero terms. Additional insight is gained by plotting the errors, ordered by Λ , the number of significant clusters (Fig. 11). Figure 11 shows that in almost all cases, once we remove the exceptional clusters ζ , the remaining model is almost *exactly* the known CE model that we started with. The CS framework provides a rigorous mathematical framework for this statement because it guarantees to

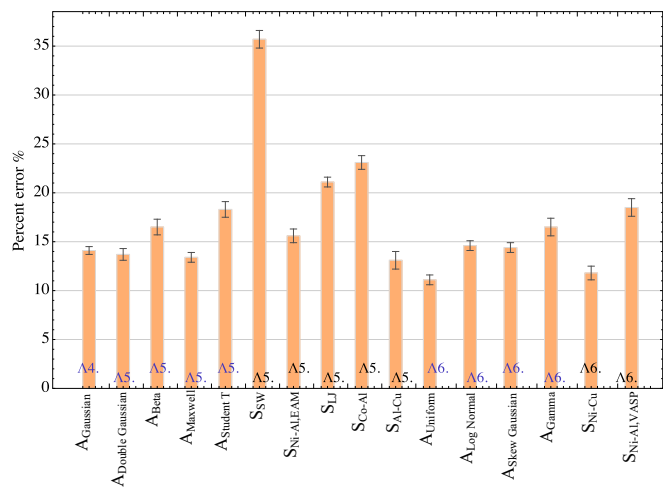


FIG. 11. Prediction error over 65% of the structures for the “toy” CE model (at 15% error added). The errors are ordered by Λ , the number of significant terms in the expansion. As expected, the values are close to the known model complexity (5 terms) and the ordering once more appears random.

exactly recover the original function with high probability as long as we have enough measurements and our representation basis is truly sparse. Once the cluster expansion stops converging, we lose sparsity and CS fails. This gives us confidence to use the CS framework as a predictive tool for CE robustness.

Provided the training structures are independent and identically distributed, we do not necessarily need hundreds of costly DFT calculations to tell us that the CE will not converge. Using our toy CE model, we discovered that for all error distributions, a training set size of 50 data points was sufficient to recover the actual model complexity (five terms) [43]. For actual DFT calculations, where relaxation was known to disrupt CE convergence, we saw a similar trend with about 100 data points needed to identify whether the CE would converge with more data or not.

We conclude that CE robustness for relaxed systems can be predicted with a *much* smaller number of data points than is typically needed for a good CE fit (on the order of 5–10% from our experience) [59]. The proposed heuristic to verify convergence of the relaxed CE, when trained with a limited dataset, is to examine the values of Λ and Ξ over a large number of independent fits. If the number of the exceptional clusters \notin is significant compared to Λ , then it is likely that the CE will *not* converge on a larger dataset as shown in Fig. 12. Figure 13 highlights the CE fitting as a function of training set size. We observe small relaxation (black curve) correlates with a small number of coefficients; thus the CE can fit using a small number of J s even with 5% (25) to 10% (50) of the structures. On the other hand, red and blue curves, which have high relaxation, do not converge. By using a small relaxed dataset (50 to 100 structures), we can predict whether or not the computational cost of relaxing *many* structures is fruitful.

IV. CONCLUSIONS

Relaxation and error decrease the reliability of the cluster expansion fit because the CE model is no longer sparse. Never-

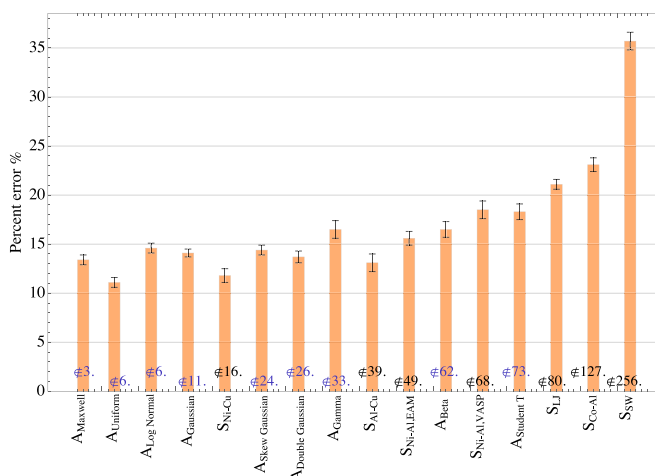


FIG. 12. Plot of predictive error over 65% of the structures for the “toy” problem (at 15% error added). The systems are ordered by \notin the number of clusters that were used less than 25 times across all 100 CE fits. These are considered exceptions to the overall fit for the system. As for Fig. 10, there is a definite trend toward higher error for systems with more exceptional clusters.

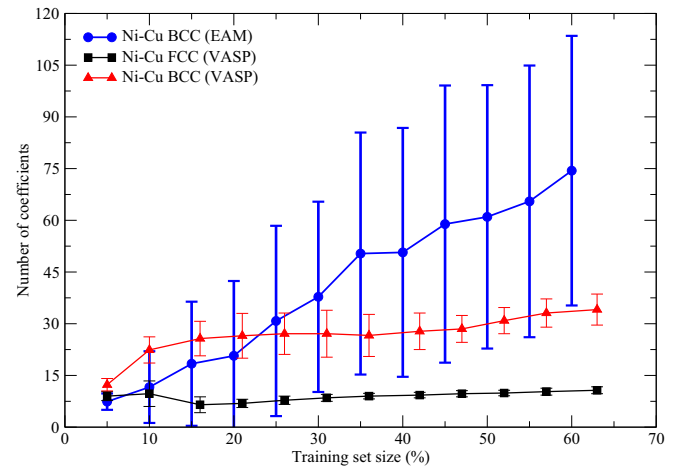


FIG. 13. For a reliable CE model, the number of coefficients converges as a function of the training set size. A total of 500 structure were available for training. The number of coefficients in a fit and its error bars give us an indication of the predictive power of CE with only a small training set. The black curve represents a good CE fit; only 25 to 50 (or 5 to 10%) of training structures were needed. On the other hand, the red and blue curves show that CE fails to fit the data due to a slowly converging expansion. The error bars on the blue points indicate extremely bad fitting.

theless, until now, there has been no measure of relaxation that provides a heuristic as to when the CE fitting data is reliable. Using four different Hamiltonians (first-principles, Lennard-Jones, Stillinger-Weber, and embedded atom method), we show that the normalized mean-squared displacement of alloy configuration is a good measure of relaxation and CE predictability. A small displacement percent, e.g., less than 0.1%, will usually generate a reliable CE model. The number of cluster terms in the CE models can be an indicator of how well cluster expansions perform; we find that models with a large number of parameters have poor predictive capability and tend not to converge, even with more training data. CE tends to fail when the number of J s exceeds 80.

In our error analysis, we investigated the ability of the compressive sensing framework to obtain fits to a toy, cluster expansion model as the energy of relaxation changes in a predictable way. We used 16 relaxation error distributions (both analytic and simulated) and compared the prediction errors of the resulting CE fits for the relaxed vs unrelaxed case. No clear correlation appears between the statistical measures of distribution shape and the predictive errors. However, there are clear correlations between the predictive error, the complexity of the resulting CE model, and the number of significant terms in that model.

We cannot use the relaxation distributions alone to determine the viability of a CE fit in advance. However, the analysis does reveal that the majority of the clusters used by the unrelaxed CE fit will also be present in the relaxed case (albeit with adjusted J values) if the CE fit is viable. This suggests that it may be possible to decide whether the computational cost of full CE is worthwhile by making predictions for a few relaxed systems (50–100) and determining whether the error remains small enough.

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