Building effective models from sparse but precise data

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Abstract
A common approach in computational science is to use a set of of highly precise but expensive calculations to parameterize a model that allows less precise, but more rapid calculations on larger scale systems. Least-squares fitting on a model that underfits the data is generally used for this purpose. For arbitrarily precise data free from statistic noise, e.g. ab initio calculations, we argue that it is more appropriate to begin with a ensemble of models that overfit the data. Within a Bayesian framework, a most likely model can be defined that incorporates physical knowledge, provides error estimates for systems not included in the fit, and reproduces the original data exactly. We apply this approach to obtain a cluster expansion model for the CaZr$_{1-x}$Ti$_x$O$_3$ solid solution.
A common approach in computational science is the use of a small number of highly
decise but expensive calculations to generate data to fit the parameters of a less accurate
but more computationally tractable “effective model” enabling larger-scale simulations.[1, 2] A
typical example is the fit of a simplified energy model to accurate quantum mechanical
calculations.[3, 4, 5, 6, 7, 8, 9, 10, 11] Although least-squares minimization is traditionally
used for this purpose, it is not commonly recognized that this approach implicitly and
incorrectly assumes that the uncertainty lies in the data rather than in the effective model.

Here we show that the fact that the model is less accurate than the data can be properly
taken into account within a Bayesian[12] framework where the “prior” probability distribu-
tion of the model parameters characterizes the range of physically plausible models. The
model parameters are obtained by maximizing the “posterior” distribution provided by
Bayes rule, given the accurate data and the prior. This approach enables a perfect fit to
the input noiseless data, while avoiding the usual artifacts of overfitting[10] and enables the
seamless inclusion of physical knowledge into the fitting procedure via the prior. Although
Bayesian methods have a long history in the statistical sciences, (including recent interest
in Bayesian learning techniques[13, 14]), the unexpectedly well-behaved limit of completely
noiseless data we report here has, to our knowledge, not been noted, perhaps because existing
methods have historically been motivated by the need to fit noisy experimental data rather
than noiseless calculated data. However, the latter setting clearly deserves more attention.

While our general theoretical approach should have broad applicability in numerous fields
of computational sciences, in this Letter, we focus on the specific but broadly applicable
example of the construction of an efficient energy model for a crystalline alloy.[3] This task
has immediate applications to thermodynamic modeling of alloys and the determination of
their phase diagrams, a crucial component of alloy design and optimization.

In this context, the accurate total energy data are provided by ab initio electronic struc-
ture methods based upon density functional theory (DFT),[15, 16] whose accuracy has
been thoroughly validated in a wide range of solid-state systems.[17] (Although such ab
initio calculations may not provide the exact quantum mechanical result, they are pre-
cise in that they are virtually free of random errors, as numerical noise is well-controlled
in modern ab initio software.) The effective model is a so-called cluster expansion
(CE),[3, 4, 5, 6, 7, 8, 9, 10, 11, 18] that takes the form of a polynomial in occupation
variables (described in detail below) indicating which atom lies on each lattice site. The
unknown parameters of CE to be determined are the coefficients of this polynomial. The CE has been previously shown [18] to be able, in principle, to exactly represent any possible configurational-dependence of the energy, provided that all terms the expansion are included, which unfortunately amounts to an infinite number of terms.

Typically, such CE models are created through a least squares fit to a database of \textit{ab initio} structural energies obtained using a CE truncated to a finite number of terms, so that the number of input configurations is larger than the number of unknown parameters. This leads to a “truncation problem”, where the terms to be retained in the model must be determined. Approaches for optimizing the truncation in this context have included the cross-validation score minimization\[3, 10, 19\], sometimes combined with regularization techniques\[20, 21\] and conventional Bayesian approaches.\[22, 23\]

These approaches treat systematic errors (due to model truncation) and statistical errors (due to numerical noise in the data) on an equal footing without exploiting the knowledge that statistical errors are, in fact, negligible in this context. In the large sample limit, truncation selection methods would eventually “discover” that the statistical noise is zero, but considerable improvements are possible if this known fact is explicitly taken into account from the start.

In this Letter, we avoid truncation problems by including many more terms in the effective model than the number of \textit{ab initio} calculations performed. Although the fitting problem is underdetermined, it can nonetheless be solved by using Bayesian inference with a physically based prior probability distribution for the model coefficients.

A configuration $i$ in a binary alloy is defined by the occupation of each site $k$ of a lattice by one of two species, indicated by a spin-like variable $s_{ik} = \pm 1$. Each configuration $i$ has an associated \textit{ab initio} energy $E_i$. These energies can be written in terms of effective cluster interactions\[6, 18\]:

$$\sum_{\alpha} \xi_{ia} J_{a} = E_{i},$$

where $\xi_{ia} = \langle \prod_{k \in \alpha} s_{ik} \rangle$ is the translationally and rotationally averaged multibody spin correlation for each symmetry-independent cluster $\alpha$, while $J_{a}$ is the associated effective interaction parameter to be determined.

Bayes’ theorem\[12\] states that given a prior probability distribution $P^{(0)}(J)$ of the unknown parameter vector $J$ and one energy observation $E_{i}$, the posterior probability of $J$
FIG. 1: (Color online) The ellipsoids schematically represent equiprobability surfaces of a many-dimensional prior probability distribution for $P^0(J)$. The plane represents the constraints on $J$ given by the results of an \textit{ab initio} total energy calculation. The $(N - 1)$-dimensional ellipsoid sliced by the plane gives an equiprobability surface for the posterior distribution of $P^{(1)}(J)$; the point marked $J^{(1)}$, represents the most likely solution for $J$.

given $E_i$ is

$$P(J|E_i) \propto P(E_i|J)P^{(0)}(J).$$

Since $E_i$ is precisely known, the conditional probability reduces to a delta function

$$P(E_i|J) = \delta(\xi_i J - E_i),$$

where $\xi_i$ denotes the row vector of all values of $\xi_{i\alpha}$ for a fixed $i$. As a result, $P(J|E_i)$ is trivially proportional to $\delta(\xi_i J - E_i)P^{(0)}(J)$. By induction, the posterior probability of $J$ based on all the energy information $E_i$, $i = 1, \ldots, n$ is

$$P^{(n)}(J) \propto \prod_{i=1}^{n} \delta(\xi_i J - E_i)P^{(0)}(J).$$

The difference between prior and posterior probabilities is represented geometrically in Fig. 1. Each new data point selects a cross-section of the prior distribution corresponding to sets of
parameter values that agree perfectly with this data point. Within the intersection of these cross-sections, each point has a different posterior probability that is dictated by the prior. The most likely model parameters $J^{(n)}$ can be determined by maximizing $P^{(n)}(J)$ (see Key methodological details, at end). This approach selects a unique solution from an otherwise underdetermined system of equations, based on the “physical” information provided by the prior.

The width of the posterior provides a measure of the uncertainty remaining in the fitted parameter after the data has been incorporated, which can be used, for instance, to access the accuracy of predicted energies for any structure not included in the fit. For a Gaussian prior, the posterior is Gaussian as well and the most likely parameter values are also the expected parameter values, which implies, given the linearity of the cluster expansion, that the predicted energies from the CE model will also be expected values.

![FIG. 2: (Color online) (a) Representative CZT structure; (b) Common 80-atom supercell for CZT energy calculations highlighted in bold.](image)

The above procedure was applied to modeling total energies in the CaZr$_{1-x}$Ti$_x$O$_3$ (CZT) system, a perovskite solid solution with tilted oxygen octahedra. The structures studied were constrained to a common 80-atom supercell shown in Fig. 2 which has 16 perovskite “B” sites that contain either Zr or Ti. Local density functional theory calculations were performed on specific CZT configurations using the VASP code and ultrasoft pseudopotentials, with semicore p electrons treated as valence electrons for Ca, Zr, and Ti. A 375 eV plane wave energy cutoff and a 1500 eV cutoff for augmentation charges were used. The $k$-point mesh was equivalent to an $8 \times 8 \times 8$ Monkhorst-Pack grid for a primitive
perovskite cell. The number of symmetrically distinct possible arrangements of Zr and Ti and the number of terms in the full cluster expansion are both 2386; all terms are retained in the fitting.

Based on simple physical considerations, the following Gaussian prior was selected

\[ P^{(0)}(J) = \prod_\alpha (\sqrt{2\pi}w_\alpha)^{-1} \exp \left( \frac{(-J_\alpha)^2}{2w_\alpha^2} \right), \]

with \( w_\alpha = Ab^{n_\alpha} \Pi \{ (r_{ij}/r_{\min})^{-2} \}. \) Clusters with more sites \( n_\alpha \) are expected to have smaller coefficients (i.e. \( b < 1 \)), and clusters with pairs \( \{i,j\} \) of atoms at larger separations \( r_{ij} \) are expected to have smaller coefficients. The exponent of \(-2\) is motivated by the observation that Zr and Ti have the same charge, so interactions cannot be mediated by differences in monopole coupling, leaving only dipolar leading terms. We set \( b = 0.17 \), based on the ratio of the quadratic to linear terms in a Taylor expansion to the energies of three trial structures (pure CaZrO\(_3\), pure CaTiO\(_3\), and rocksalt-ordered CaZr\(_{1/2}\)Ti\(_{1/2}\)O\(_3\)), and \( A = 1.58 \) eV per atom, based on scaling the error estimates for all 30 structures included in the final fit (see Key methodological details).

Our Bayesian approach is embedded in an iterative scheme where, at each step, a most likely solution \( J \) is found and error estimates for the other configurations not included in the fit are calculated. The configuration with the highest estimated error is then added to the fit, after its \textit{ab initio} total energy is calculated (see Key methodological details). This procedure is repeated until a sufficient predictive accuracy has been reached, as illustrated in Fig. 3. A monotonic, rapid improvement of the fit is found as the number of structures included in the fit increases. For calculation efficiency purposes, one may truncate the terms to be retained in the solution to those whose \( J_\alpha \) exceeds some small threshold value, with little effect on the results (as suggested in [20] in a related context); in our methodology, these terms can be retained in estimating errors on predicted energies.

For thermodynamic applications, such as phase diagram calculations, it is crucial that the lowest lying energies have the proper order and energy differences. The least-squares fitting procedure does not guarantee this, \textit{even if these states were included in the fitting procedure}. By reproducing the energies of all states included in the fit exactly, our procedure avoids this problem.

While the need to specify a prior in Bayesian methods is often criticized, it should be realized that a conventional least-squares fit is not free of \textit{a priori} assumptions either. In
FIG. 3: Convergence of the mean and maximum predicted errors on energies of configurations not included in the fit, as a function of the number of configurations included in fit.

The cluster expansion example, a conventional fit with a user-specified truncation distance amounts to a prior which is uninformative (flat) for the included interactions coefficients but entirely concentrated at zero for the excluded coefficients. This incorporates physical knowledge into the problem, but with a complete certainty that far exceeds what a researcher could plausibly know. A smoother prior which gradually concentrates the probability towards zero coefficient values as the range of interaction increases appears a more appropriate description of a priori information.

If the data does contain some error (for instance, significant numerical noise), then the delta function in (1) must be replaced by a smooth density and a conventional Bayesian methodology would result (as in [22, 23]). If that density is Gaussian, then one recovers a so-called ridge regression or Tikhonov regularization [27], a penalized least-squares estimator, which has been previously used in the context of CE construction [20, 21].

One possible way to select a prior is to estimate a range of likely coefficient values on the basis of analogous systems. Good theoretical knowledge of the physics governing the
interactions is also useful. Another possibility is to use the data itself to optimize the choice of the prior. Although this is not appropriate in a strict Bayesian context, it is conceivable that some type of cross-validation approach could be a valid prior-selection method in a hybrid Bayesian/frequentist context. This scheme is the noiseless limit of an existing variational cross-validation method. Our preliminary results in this vein indicate that the method does have the ability to rule out clearly unphysical priors in favor of more physically plausible priors. Formally quantifying this method’s discriminating power represents a fruitful avenue of future investigation.

The construction of multibody interatomic force fields based upon quantum mechanical data represents an important possible application of the methodology proposed here. It differs from the alloy problem in that the energy is a function of a continuous set of distance variables, rather than a discrete set of spacings on a lattice. While force fields are often selected to be nonlinear in the unknown parameters, energy models that are linear in the parameters (such as splines) are probably preferable in our context, as they make the interaction optimization problem numerically stable and efficient. The lack of physical basis for spline functions is alleviated by the possibility of including many more parameters than data points and the ability to favor physically plausible interaction shapes via the prior. Such an approach could lead to successful force fields models, with defined uncertainties and with broad applications in computational physics.

**Key methodological details:** With a zero-mean Gaussian prior for the vector $J$ containing all interactions $J_{\alpha}$, the posterior maximum is given by $J^{(n)} = W\xi^T(\xi W \xi^T)^{-1}E$, where $W$ denotes the variance-covariance matrix of the prior while $\xi$ denotes the matrix with elements $\xi_{i\alpha}$ and $E$ denotes the vector of all $n$ known structural energies $E_i$. An equivalent approach is to perform the changes of variables $\xi' = \xi W^{1/2}$ and $J'^{(n)} = W^{-1/2}J^{(n)}$ (where we use the symmetric square root matrix), and find the minimum Euclidean norm solution $J'^{(n)}$ to $\xi' J'^{(n)} = E$ using, for instance, standard singular value decomposition techniques.

The expected energy of any additional configuration $i = n + 1$ (with correlations equal to the row vector $\xi_{(n+1)}^{(n)}$) is given by $\xi_{(n+1)}^{(n)} J^{(n)}$. The root mean square error in this energy is simply given by $|\text{Pr}_\perp^{(n)} \xi'_{n+1} |$, where $\text{Pr}_\perp^{(n)}$ is a projector in the prime space that simultaneously projects $\xi'_{n+1}$ orthogonal to all $\xi'_{i \leq n}$.

If all terms $w_{\alpha}$ in a Gaussian prior are scaled by the same value $x$, then: (1) $J^{(n)}$ remains unchanged; (2) all predicted errors are scaled by $x$. In an analogous way to the leave-one-out
cross validation method\cite{10}, one can take the set of structures used to obtain $J^{(n)}$, omit each single structure $i$ one-at-a-time, and calculate the estimated and actual errors for $E_i$ based on fitting the model to all the other structures. A self-consistent value for $x$ is then obtained by scaling the mean square estimated errors to equal the actual errors.

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