



## Multicomponent multisublattice alloys, nonconfigurational entropy and other additions to the Alloy Theoretic Automated Toolkit

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### ABSTRACT

A number of new functionalities have been added to the Alloy Theoretic Automated Toolkit (ATAT) since it was last reviewed in this journal in 2002. ATAT can now handle multicomponent multisublattice alloy systems, nonconfigurational sources of entropy (e.g. vibrational and electronic entropy), Special Quasirandom Structures (SQS) generation, tensorial cluster expansion construction and includes interfaces for multiple atomistic or ab initio codes. This paper presents an overview of these features geared towards the practical use of the code. The extensions to the cluster expansion formalism needed to cover multicomponent multisublattice alloys are also formally demonstrated.

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### 1. Introduction

The Alloy Theoretic Automated Toolkit (ATAT) [1–3] is a suite of software tools facilitating the determination of thermodynamic properties of solid state alloys from first-principles calculations. It relies upon the cluster expansion formalism [4–11] to build a simplified effective Hamiltonian that accurately reproduces quantum mechanical calculation results for an alloy system of interest and that can be used to efficiently calculate their thermodynamic properties. ATAT is freely distributed and open-source, thus encouraging users to contribute [12].

ATAT's basic functionalities have been described in an earlier issue of the CALPHAD journal [1]. Since then, a number of new features has been added and the purpose of the present paper is to describe these additions and provide a concise “user guide” for these new features. The most significant additions to ATAT are

- (1) extensions to multicomponent multisublattice systems;
- (2) the inclusion of nonconfigurational sources of entropy (vibrational and electronic entropy);
- (3) Special Quasirandom Structures (SQS) generation;
- (4) tensorial cluster expansion construction;
- (5) support for multiple atomistic (ab initio) codes;
- (6) various new conversion and analysis utilities.

The features presented here are not exhaustive and new features are continuously being added. Hence, the reader is invited

to consult the manual supplied with the ATAT distribution or posted on the ATAT web site (<http://alum.mit.edu/www/avdw/atat>) for the most up-to-date information.

### 2. Multicomponent multisublattice systems

#### 2.1. The cluster expansion in multicomponent multisublattice systems

The traditional *cluster expansion* represents the relationship  $q(\sigma)$  between a *configuration*  $\sigma$  and some scalar intensive quantity  $q$ . While multicomponent alloys have been covered since the original introduction of the cluster expansion [4], handling multisublattice systems (in which different sites in the unit cell can host different binary sets of atoms) is a more recent extension [13]. ATAT implements a superset of these two formalisms, allowing different sites to host an arbitrary (and potentially different) number of elements, some of which may be common across sublattices. These sublattices may or may not consist of sets of symmetrically equivalent sites. To fix the ideas, refer to Table 1 for an example exploiting all of these extensions. The multicomponent multisublattice features of ATAT have been used, for instance, in [14–16].

The remainder of this section introduces the requisite extensions to the cluster expansion formalism. The reader is referred to earlier reviews on the topic [4–11] or to the first part of this manual [1] for a gentler introduction to the topic.

A *configuration*  $\sigma$  is represented by a vector of occupation variables  $\sigma_i$  indicating which type of atom sits on lattice site  $i$ . In an alloy where site  $i$  can host  $M_i$  components,  $\sigma_i$  could take any value from 0 to  $M_i - 1$ . This type of representation of an alloy is

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**Table 1**

Example of a lattice, based on the Martensite system, written in ATAT's "lattice input file" format.

1	1	1.05	90	90	90	(Tetragonal coordinate system in a b c $\alpha$ $\beta$ $\gamma$ notation)
0.5	0.5	0.5				(Primitive unit cell: one vector per line)
0.5	-0.5	0.5				expressed in multiples of the above coordinate
0.5	0.5	-0.5				system vectors)
0	0	0	Fe,Ni,Cr			(Ternary sublattice)
0	0.5	0.5	C, Vac			(Binary sublattice, where Vac stands for "vacancy",
0.5	0	0.5	C, Vac			with a second symmetrically equivalent site
0.5	0.5	0	C, Vac			and a third inequivalent site due to the tetragonality)

also known as a *lattice gas model*. The CE takes the general form

$$q(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \langle \Gamma_{\alpha}(\sigma) \rangle_{\alpha} \quad (1)$$

where we have used the following definitions:

- $\alpha$  is a *cluster*. In the simple case of a binary alloy, a cluster can be described by a vector of elements  $\alpha_i$  equal to one or zero depending whether site  $i$  belongs to the cluster or not. If site  $i$  can host  $M_i$  components,  $\alpha_i$  can take any values from 0 to  $M_i - 1$ , with 0 indicating that site  $i$  does not belong to cluster  $\alpha$ , while the other positive values reflect various possible functional form dependence of the energy of cluster  $\alpha$  on the occupation  $\sigma_i$  of site  $i$ .
- The sum is over all possible clusters  $\alpha$  that are mutually symmetrically distinct under the space group of the underlying lattice.<sup>1</sup> Note that the determination of the space group of the lattice must account for the fact that sites hosting different sets of atoms are considered symmetrically distinct.
- The average  $\langle \dots \rangle_{\alpha}$  is over all clusters  $\alpha'$  that are equivalent by symmetry to cluster  $\alpha$ .
- $\Gamma_{\alpha}(\sigma)$  are *cluster functions*. They are selected to be of the form

$$\Gamma_{\alpha}(\sigma) = \prod_i \gamma_{\alpha_i, M_i}(\sigma_i) \quad (2)$$

where  $\gamma_{\alpha_i, M_i}(\sigma_i)$  satisfies  $\gamma_{0, M_i}(\sigma_i) = 1$  and the following orthogonality condition

$$\frac{1}{M_i} \sum_{\sigma_i=0}^{M_i-1} \gamma_{\alpha_i, M_i}(\sigma_i) \gamma_{\beta_i, M_i}(\sigma_i) = \begin{cases} 1 & \text{if } \alpha_i = \beta_i \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

(In binary alloys, a common choice is  $\gamma_{0,2}(0) = 1$ ,  $\gamma_{0,2}(1) = 1$ ,  $\gamma_{1,2}(0) = -1$ ,  $\gamma_{1,2}(1) = +1$ .) Although the product (2) is, in principle, over all lattice sites, the choice  $\gamma_{0, M_i}(\sigma_i) = 1$  ensures that it reduces to a product over sites within cluster  $\alpha$  only.

- $m_{\alpha}$  are multiplicities indicating the number of clusters (e.g. per unit cell) equivalent to  $\alpha$  by symmetry.
- $J_{\alpha}$  are expansion coefficients to be determined. They are also called Effective Cluster Interactions (ECI).

It can be shown that when *all* clusters  $\alpha$  are considered in the sum, the cluster expansion is able to represent *any* function  $q(\sigma)$  of configuration  $\sigma$  by an appropriate selection of the values of  $J_{\alpha}$ . The crux of the argument leading to that conclusion lies in establishing that the  $\Gamma_{\alpha}(\sigma)$  form an orthogonal basis for the space of functions of configurations according to a suitably defined inner product. In the general case considered here, the original proof [4] needs to be extended as follows. Given two cluster functions  $\Gamma_{\alpha}$  and  $\Gamma_{\beta}$  associated with two corresponding clusters  $\alpha$  and  $\beta$ , define the inner product:

$$\langle \Gamma_{\alpha}, \Gamma_{\beta} \rangle = \sum_{\sigma} \Gamma_{\alpha}(\sigma) \Gamma_{\beta}(\sigma)$$

where the sum is over all possible configurations  $\sigma$  (i.e., each  $\sigma_i$  ranges from 0 to  $M_i - 1$  in lexicographic order). We can then note that

$$\begin{aligned} \langle \Gamma_{\alpha}, \Gamma_{\beta} \rangle &= \frac{1}{\prod_i M_i} \sum_{\sigma} \left( \prod_i \gamma_{\alpha_i, M_i}(\sigma_i) \right) \left( \prod_i \gamma_{\beta_i, M_i}(\sigma_i) \right) \\ &= \frac{1}{M_1} \sum_{\sigma_1=0}^{M_1-1} \frac{1}{M_2} \sum_{\sigma_2=0}^{M_2-1} \dots \prod_i (\gamma_{\alpha_i, M_i}(\sigma_i) \gamma_{\beta_i, M_i}(\sigma_i)) \\ &= \prod_i \left[ \frac{1}{M_i} \sum_{\sigma_i=0}^{M_i-1} (\gamma_{\alpha_i, M_i}(\sigma_i) \gamma_{\beta_i, M_i}(\sigma_i)) \right] \end{aligned}$$

where the term in bracket is zero for any  $i$  such that  $\alpha_i \neq \beta_i$  by Eq. (3). If no such  $i$  exist, then each term in bracket is equal to 1. It follows that  $\langle \Gamma_{\alpha}, \Gamma_{\beta} \rangle = 0$  if the clusters  $\alpha$  and  $\beta$  differ (even by a single site) and is equal to 1 if they are identical. This establishes that the  $\Gamma_{\alpha}$  are orthogonal. Moreover, there are as many different  $\alpha$  as there are different  $\sigma$  (as  $\alpha_i$  and  $\sigma_i$  both can take on  $M_i$  distinct values), so the "number" of  $\Gamma_{\alpha}$  equals<sup>2</sup> the "dimension" of the configurational space  $\sigma$ . It follows that the  $\Gamma_{\alpha}$  form a complete orthogonal basis. This result is not obvious when lattice sites may host a different number of species (i.e. when  $M_i$  is not constant). In that case, the cluster functions Eq. (2) may involve mixed products between entirely different types of  $\gamma_{\alpha_i, M_i}(\sigma_i)$ .

While, the above discussion is valid for any  $\gamma_{\alpha_i, M_i}(\sigma_i)$  satisfying (3), a specific  $\gamma_{\alpha_i, M_i}(\sigma_i)$  must be selected in practice. By default, the ATAT uses the following choice:

$$\gamma_{\alpha_i, M_i}(\sigma_i) = \begin{cases} 1 & \text{if } \alpha_i = 0 \\ -\cos\left(2\pi \left\lceil \frac{\alpha_i}{2} \right\rceil \frac{\sigma_i}{M}\right) & \text{if } \alpha_i > 0 \text{ and odd} \\ -\sin\left(2\pi \left\lceil \frac{\alpha_i}{2} \right\rceil \frac{\sigma_i}{M}\right) & \text{if } \alpha_i > 0 \text{ and even} \end{cases}$$

where  $\lceil \dots \rceil$  denotes the "round up" operation and where both  $\alpha_i$  and  $\sigma_i$  can range from 0 to  $M_i - 1$ . Note that these functions reduce to the single function  $-(-1)^{\sigma_i}$  in the binary case ( $M_i = 2$ ). User-specified  $\gamma_{\alpha_i, M_i}(\sigma_i)$  can be provided by (i) editing and following the instructions given in the `corrskel.c++` file and by (ii) specifying the `-crf=[keyword]` option on the command line of ATAT commands, where [keyword] is a unique identifier.

Another nonobvious aspect of the above cluster expansion generalization is that the relationship between the point correlations and the composition variables is no longer as trivial as in the well-known single sublattice binary case. In general, there are three different composition-type quantities to consider, each having a specific use.

- (1) The point correlation vector  $\rho$  contains all the expected values of the cluster functions  $\langle \Gamma_{\alpha}(\sigma) \rangle$  associated with a cluster  $\alpha$  such that  $\alpha_i$  is nonzero for a single site  $i$ . They enter the expression of the cluster expansion which is used to predict energies either during the ground state search procedure or in the Monte Carlo simulations.
- (2) The "nonredundant" concentration vector  $c$  are those that remain after all linearly dependent concentrations have been eliminated (of course, there are multiple valid choices of nonredundant concentrations – one convention must be arbitrarily selected). These linear dependencies arise from the constraint that the compositions on each sublattice sum up to one. The nonredundant concentrations are used for the convex hull construction in the ground state search procedure.
- (3) The full vector  $x$  of concentrations has no algorithmic use but provides the most user-friendly output.

<sup>1</sup> Hence, out of each set of equivalent clusters, one representative cluster is kept.

<sup>2</sup> This statement can be made more rigorous by considering a sequence of finite system (with periodic boundary conditions) whose size increases to infinity.

These quantities are linearly related:

$$c = C\rho + c_0 \quad (4)$$

$$x = X\rho + x_0 \quad (5)$$

where  $C$  and  $X$  are constant matrices while  $c_0$  and  $x_0$  are constant vectors. In general, the matrices  $C$  and  $X$  are rectangular and not invertible. (These matrices can be output within ATAT with the `corrump -pcm` command, if the user provides a lattice input file `lat.in`.) Appendix describes how these matrices are calculated.

The matrix  $X$  plays a special role in the conversion of chemical potentials  $\mu$  into shifts of the effective cluster interactions  $J_\alpha$ , as would be needed in a grand canonical Monte Carlo simulation. Note that the chemical potential contribution to any of the grand canonical thermodynamic functions can be written as

$$\begin{aligned} \mu^T x &= \mu^T X\rho + \mu^T x_0 = (X^T \mu)^T \rho + \mu^T x_0 \\ &= \sum_j (X^T \mu)_j \rho_j + \mu^T x_0 \end{aligned}$$

from which it can be inferred that  $\mu^T x_0$  is the shift induced in the empty cluster ECI, while the  $j$ -element of the vector  $X^T \mu$  is the shift induced in the ECI associated with point correlation  $\rho_j$ .

## 2.2. Multicomponent cluster expansion construction

The `mmaps` command is the multicomponent version of the `maps` command (discussed in [1,2]) and works in a similar fashion. It gradually constructs an increasingly more accurate cluster expansion by repeatedly invoking a first-principles code through auxiliary scripts (see Sections 3 and 6 and the documentation of the `pollmach` and `runstruct_xxxx` commands for details). The main difference between the `mmaps` and `maps` codes is that, given the larger number of components allowed in `mmaps`, the input and output files have to contain more information. The main input file (typically called `lat.in`), which describes the lattice, is a natural extension of the `maps` input file, as shown in Table 1.

A second, optional, input file (typically called `crange.in`) provides the ability to specify a region to explore in composition space. This is useful in systems where the provided lattice would be mechanically or thermodynamically unstable beyond certain composition limits. For instance, given the lattice shown in Table 1, one could specify:

```
1*Ni+1*Cr<=0.2
1*C<=0.1
```

where each atom name stands for its overall concentration (it is not the concentration on a sublattice). Only linear constraints are supported (and are implicitly combined with a logical “and”, so that the allowed regions are necessarily convex).

This file not only controls the range of concentration of the structures generated by `mmaps`, but also the composition range where the correct ground states are enforced in the fitting process. Note that, occasionally, structures outside the specified range may be generated in order to ensure that the ground states found within the specified composition range are not masked by ground states outside of it (`mmaps` internally generates structures at all compositions in order to check for this).

Suitable composition limits are not always known in advance. When these limits arise due to mechanical instabilities, one would notice that many of the structures generated by `mmaps` relax to very different types of lattices. A symptom of this is the inability to converge the cluster expansion. A way to check for this problem is to use the `checkrelax` utility, which calculates the mean square of the relaxation strain tensor elements for each of the structures generated by `mmaps`. Note that, by design, this command ignores the isotropic component of the strain. It compares relaxed geometries in the `*/str_relax.out` files to

the corresponding unrelaxed `*/str.out` files. Any value above 0.1 should be regarded as suspect. While having a few isolated overrelaxed structures is not typically a problem, if virtually all structures beyond a certain composition limit are relaxing excessively, then it is advisable to specify a suitable `crange.in` file and restart `mmaps`. It is also recommended to “hide” any overrelaxed structures by issuing the command

```
touch [structure]/error
for each [structure] exhibiting overrelaxation (typically
[structure] is a number referring to one of the subdirectories
generated by mmaps and containing a structure's geometry). This
command creates files called error in the specified directory that
mmaps will perceive as a signal to ignore the structure in question.
```

The relevant composition region is sometimes limited by thermodynamic instabilities. This would be detected, for instance, by doing a separate cluster expansion on a different lattice or by computing the formation energies of known compounds exhibiting a different lattice. In such cases, however, it is not essential to limit the compositions range, since the cluster expansion formalism remains valid for metastable alloys. However, unless the metastable region is of direct interest, a more rapidly converging cluster expansion may be obtained by specifying a suitable `crange.in` file and by excluding non-ground state structures in the metastable region with the `touch` command, as explained above.

It is sometimes tempting to perform a cluster expansion under equality – rather than inequality – composition constraints. This is relevant for ionic systems, where it may be most natural to only keep structures that are “charge balanced” under the assumption that all species keep their nominal charges. This is not implemented in `mmaps`, because it is very risky approach. A cluster expansion providing an excellent fit to charge-balanced structures may inadvertently predict non-charge-balanced ground states. A way to prevent such problems [13] is to restrict compositions to lie in a nonzero-width slice around the charge-balanced hyperplane, as in the following example for the Samarium-doped Ceria system [14]:

```
-2*O+4*Ce+3*Sm<=0.2
-2*O+4*Ce+3*Sm>=-0.2
```

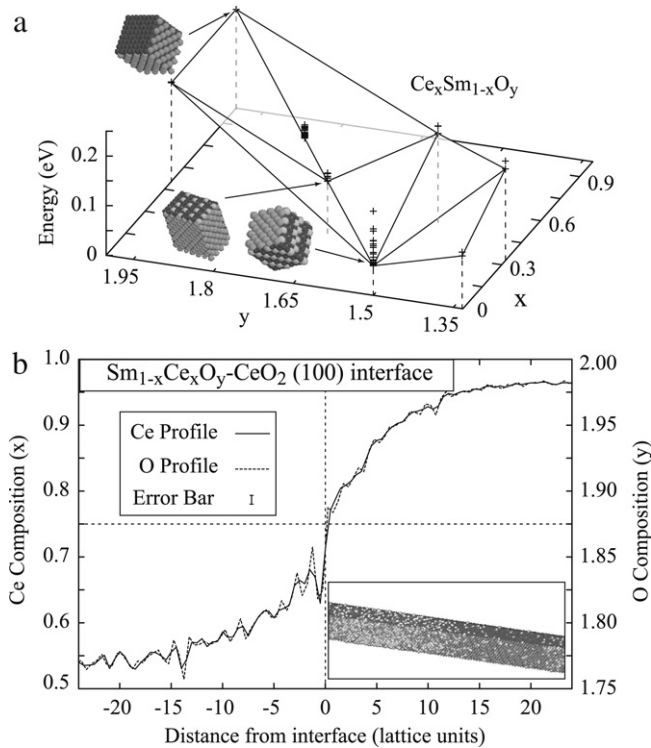
`mmaps` will, if necessary, sample structures outside of the specified range to ensure that no spurious non-charge-balanced ground states exist.

Compared with `maps`, the `mmaps` code has a number of new output files. The `atoms.out` file lists all atomic species given in the input files in the order that will be used to report composition variables in all output files. The `ref_energy.out` file reports the atomic reference energies used to calculate formation energies in all output files (in the same order as in `atoms.out`). These reference energies are the energies of the pure elements, if they are included in the fit. Otherwise, if composition constraints are imposed,<sup>3</sup> the structures with the most extreme compositions<sup>4</sup> are used as reference. These non-standard references are converted into atomic energies before being output in `ref_energy.out`. This default behavior can be overridden by providing user-specified reference energies in a file called `ref_energy.in`.

While the ground state compositions and energies are output in `gs.out`, the file `gs_connect.out` provides the additional information needed, in multicomponent systems, to describe how these ground states are connected by tie lines. Each facet of the ground state convex hull corresponds to a line in the `gs_connect.out` file listing the structure names associated with the vertices of that facet. An example of a convex hull in energy-composition space constructed with ATAT is shown in Fig. 1a).

<sup>3</sup> or if some elements are excluded from some sublattices, thus effectively restricting the composition range.

<sup>4</sup> Specifically, those with the largest sum of squared concentrations.



**Fig. 1.** Computational thermodynamic study of the Samarium-doped Ceria system [14]. (a) Example of ground state search via a convex hull construction in energy-composition space. (b) Equilibrium composition profile across (100) interface obtained through a hybrid canonical/grand-canonical multisublattice multicomponent Monte-Carlo simulation. Inset: Snapshot of the 70,000-atom simulation cell used.

Setting up grand-canonical Monte Carlo simulations (as discussed in the next section) demands the knowledge of the chemical potentials that stabilize various phase equilibria of the system. Since this is not obvious to figure out in a multicomponent system, *mmaps* generates a file *chempot.out* containing:

- (1) The values of the chemical potentials that stabilize each fixed-composition multiphase equilibria of the system at absolute zero (e.g. in a  $n$ -nary system, all the  $n$ -phase equilibria). Each vector of chemical potential correspond to one facet of the ground state convex hull.
- (2) For each ground state, a value of the chemical potentials that stabilize it at absolute zero. This is not a uniquely defined quantity – many possible chemical potentials values are able to stabilize a given ground state. Among the many possible values, *mmaps* calculates one by simply averaging the chemical potentials associated with all facets that intersect a given ground state.

The remaining output files are the same as in *maps*, except that multiple concentration variables are output whenever necessary: *maps.log*, *fit.out*, *predstr.out*, *gs.out*, *gs\_str.out*, *eci.out*, *clusters.out*.

### 2.3. Hybrid multicomponent Monte Carlo simulations

The *memc2* code implements general hybrid canonical/grand-canonical lattice gas Monte Carlo simulations in multicomponent systems. As most of the features are similar to the previous binary version, *emc2*, described in [1,3], we focus here on the differences.

To function, this code requires at least 4 input files: *lat.in* (identical to the one input into *mmaps*), *clusters.out*, *eci.out*, *gs\_str.out*, where the latter three are generated by *mmaps*.

**Table 2**

Example of *control.in* file indicating a scan of the region in  $(T, \mu_1, \mu_2, \mu_3)$ -space defined by  $100 \leq T < 200$  and  $0 \leq \mu_1 < 1.0$  and  $0 \leq \mu_2 < 0.5$  and  $\mu_3 = 0.0$  with a  $10 \times 5 \times 5$  grid.

100	0.0	0.0	0.0
200	0.0	0.0	0.0
100	0.0	0.5	0.0
100	1.0	0.0	0.0

Given the larger number of composition variables, the range of temperatures and chemical potentials scanned in the course of grand-canonical run are no longer specified on the command-line. Instead, the *control.in* input file must be provided in the following format. The first line specify the initial conditions and has the form (for an  $n$ -component system):

$[T] [\mu_1] \dots [\mu_n]$

where  $T$  is temperature and  $\mu_1, \dots, \mu_n$  are the chemical potentials for each chemical species, in the same order as in the *atoms.out* file generated by *mmaps*.<sup>5</sup> Each subsequent line of this file indicates one of the axes along which to scan and has the format:

$[T] [\mu_1] \dots [\mu_n] [s]$

where  $s$  is the number of steps made between the initial conditions and the final conditions given on the line. Table 2 gives an example of such file.

A few important notes:

- (1) Temperatures are given in units of energy unless the  $-k$  or  $-keV$  options are used (the latter indicates temperature in K if energies are in eV).
- (2) By default, the final conditions are excluded from the scan (in the example above the values of the first chemical potential scanned (see the last line) are 0.0 0.2 0.4 0.6 0.8). This behavior can be changed with the  $-il$  option, to give: 0.0 0.25 0.5 0.75 1.0). Alternatively, the  $-hf$  option gives: 0.1 0.3 0.5 0.7 0.9.
- (3) The *mmaps* code generates a file called *chempot.out* which contains special values of the chemical potential that stabilize various types of equilibria. These values are useful guidelines to select relevant regions in  $\mu$ -space to scan.

Canonical or hybrid canonical/grand-canonical simulations can be carried out by specifying, in a file called *conconcs.in*, a set of linear constraints on the composition that must hold throughout the simulation. The code automatically generates a complete list of allowed multi-site Monte Carlo moves. It does so by first considering all possible single-atom identity flips ( $k = 1$ ), then all possible two-atom identity flips ( $k = 2$ ), etc. Any move violating the composition constraints is eliminated. After all  $k$ -atom flips that satisfy the constraints have been considered, the code calculates the linear subspace spanned by the composition changes associated these flips. The process stops if this linear subspace has the same dimension as the space of allowed compositions. The moves generated by this process are guaranteed to satisfy detailed balance because for every move kept, its reverse move is also kept.

The format of the *conconcs.in* file is similar to the *change.in* file of *mmaps*. For instance:

$-2*O+4*Ce+3*Sm=0$

would ensure overall charge balance in the fluorite-type  $Ce_xSm_{1-x}O_yVac_{2-y}$  system. Constraining composition variables is particularly useful to pin down the location of an interface in a multiphase interfacial thermodynamic calculation, because the phase fractions are uniquely determined by the overall composition. An example of this use is illustrated in Fig. 1b).

<sup>5</sup> Alternatively, see the output of *corrump -pcm*.



Any number of constraints can be given up to the point where all concentration variables are fixed, which results in a fully canonical simulation. Note that constant composition simulations do not evade the need to make sure that the cluster expansion does not exhibit spurious ground states away from the specified hyperplane. If such ground states exist, the Monte Carlo code will reveal a phase separation into regions that do not locally satisfy the composition constraint, although the overall simulation cell does. Note that the constant specified on the right-hand side of the `concons.in` file is ignored – this file constrains changes in composition only. The user-supplied initial atomic configuration (via the `-g=[ground state number]` or `-is=[file]` options) implicitly determines the right-hand side constants.

The `memc2` code outputs all of thermodynamic quantities it computes on the standard output and in a log file `mc.out`. Given the large (and variable) number of variables in a multicomponent system, the code writes a `mheader.out` file indicating the content of each column of the main output file. By default all output quantities are grand-canonical in nature (i.e. they contain a “ $-\mu \cdot x$ ” term, where  $x$  is composition and  $\mu$  chemical potential), regardless of the presence of composition constraints. To obtain “canonical” rather than grand-canonical quantities use the `-g2c` option.

In addition to performing Monte Carlo simulations, the `memc2` code reports thermodynamic quantities calculated via the low-temperature expansion (indicated by a `_lte` suffix) or the mean-field approximation<sup>6</sup> (indicated by a `_mf` suffix). A useful feature is the ability to skip Monte Carlo simulations whenever the free energies obtained via mean-field approximation and the low temperature expansion fall within a specified threshold (using the `-mft=[tolerance]` option), as this indicates that either one is sufficiently accurate. These approximations are also used to set initial values of the free energy when performing thermodynamic integrations. By default, if the initial configuration is a ground state (`-gs=[a positive integer]`) the low-temperature expansion provides the starting point while Monte Carlo averages are used to update the free energy as temperature and chemical potentials are varied. If the initial configuration is the fully disordered state (`-gs=-1`) a mean-field approximation (i.e. high-temperature expansion) is used as the starting point instead.

Finally, it is possible to specify temperature-dependent interactions (in a file called `tec1.out`, which, when present, takes precedence over `ec1.out`). This feature can be used to account for nonconfigurational sources of entropy through a coarse-graining scheme [17,18]. Introducing temperature-dependent interactions is not completely trivial, as various averages (such as the internal energy  $E$ ) must correctly account for the temperature dependence of the interactions in order for the following thermodynamic relationship (upon which thermodynamic integration is based) to hold:

$$\frac{\partial (\beta F)}{\partial \beta} = E$$

where  $\beta = (k_B T)^{-1}$  and  $F$  is the Helmholtz free energy. To illustrate this, we express the free energy  $F$  in terms of the partition function and the coarse grained free energy  $F_i$  of each microscopic state  $i$ :

$$\frac{\partial (\beta F)}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln \left( \sum_i e^{-\beta F_i} \right) = \frac{\sum_i [F_i + \beta (\partial F_i / \partial \beta)] e^{-\beta F_i}}{\sum_i e^{-\beta F_i}}.$$

Hence, the quantity to average over the Monte Carlo steps is  $[F_i + \beta (\partial F_i / \partial \beta)]$  instead of just  $F_i$ , as a naive analogy with the constant interaction case would have suggested.

The next section describes how to proceed to obtain suitable temperature-dependent interactions that model vibrational and electronic excitations.

### 3. Nonconfigurational sources of entropy

#### 3.1. Lattice vibrations

The ATAT software offers two techniques to calculate vibrational free energies.

The `fitfc` code constructs a Born–von Kármán spring model by fitting the reaction forces resulting from imposed atomic displacements in a supercell calculation [17,19,20]. This is the preferred method<sup>8</sup> for very accurate calculations, since the range of interactions of the model's effective springs can be increased until the desired accuracy has been reached. However, it is computationally demanding to calculate vibrational free energies for a large number of structures in this fashion (as would be required for cluster expansion construction).

For this reason, ATAT includes an alternative method: the stiffness-vs.-length scheme [17], which is implemented in the `fitsvsl` and `svsl` codes. This approach exploits the fact that the effective springs of a Born–von Kármán model are often transferable from one structure to another (after controlling for simple factors such as bond length [17,27–29], or composition [30]), thus reducing the number of spring constant calculations needed. This method's accuracy is limited by the transferability assumption itself, which typically does not extend beyond nearest neighbor springs. Fortunately, this assumption is verifiable and we shall see how.

##### 3.1.1. The `fitfc` code

Calculations with the `fitfc` code proceed in a series of steps:

- (1) The structure of interest first needs to be fully relaxed. The code expects the relaxed geometry in a file called `str_relax.out`. This file's format is common to all ATAT tools and is described in [1] as well as in the help obtained via `mmaps -h`. The `fitfc` command also expects a `str.out` file containing the **unrelaxed** geometry (which may be the same as the relaxed geometry, if desired). The unrelaxed geometry will be used to determine the neighbor shells and measure distances between atoms. The rationale for allowing for two types of input structure is that it is easier for most users to specify or identify shells of neighbor using “idealized” structures (e.g. hcp with ideal  $c/a$  ratio) rather than using the fully relaxed structures. Moreover, in the context of cluster expansion construction, where phonon calculations on multiple structures are needed, the neighbor shell distances are directly transferable between unrelaxed structures but not between relaxed structures. Typically the user would specify the `str.out` and then obtain the `str_relax.out` file by running an *ab initio* code with a command of such as `runstruct_xxxx`, where `xxxx`

<sup>6</sup> While the `emc2` code also reports the high-temperature limit, this was abandoned in the `memc2` code since it is identical the mean-field values for the pure phases.

<sup>7</sup> In a coarse-graining framework, each microscopic configurational state  $i$  has a free energy that can be expressed in terms of a partition function summing over all vibrational and electronic excitations  $j$  associated with a given configuration  $i$  on the lattice:  $F_i = -\beta^{-1} \ln (\sum_j e^{-\beta E_{ij}})$ .

<sup>8</sup> In principle, linear response calculations [21–26] are even more preferable in the sense that they account for infinite range interactions, which is important in the case of ionic materials. Linear response calculations are to be performed within the *ab initio* code itself and ATAT consequently does not implement them.

stands for the name of the ab initio code used (see Section 6 below for calling ab initio codes within ATAT). Of course, the input files for the xxxx code must indicate that all degrees of freedom need to be relaxed. Alternatively, file `str.out` and `str_relax.out` files could have been automatically generated in a prior `mmaps` execution (in fact, the perhaps odd extension `.out` reflects the fact that these files are typically outputs of the `mmaps` and `runstruct_xxxx` codes.).

- (2) Next, a set of perturbed geometries must be generated. A typical command line is as follows:

```
fitfc -er=11.5 -ns=3 -ms=0.02 -dr=0.1
```

The `-er` option specifies how far apart the periodic images of the displaced atom must be (as measured in the unrelaxed structure `str.out` and in the same units, usually Å). The code uses this information to find the smallest supercell satisfying this constraint. While this is the only required parameter, the user has control over other parameters.

`-dr` specifies the magnitude of the displacement (default: 0.2 Å) of the perturbed atom (in the same units as in the `str.out` file, typically Å)

`-ns` specifies the number of different isotropic strain levels at which phonon calculations will be performed. Specifying `-ns=1` implies a purely harmonic model (the default), while values greater than 1 will invoke a quasiharmonic model. The latter accounts for thermal expansion by allowing the phonon frequencies to be volume-dependent. In subsequent steps, the code will determine the volume as a function of temperature by minimizing the free energy.

`-ms` specifies the maximum level of strain (e.g. 0.02 signifies a 2% elongation along every direction).

The above command writes out a series of subdirectories of the general form `vol_*`, one for each level of strain (\* refers to the usual UNIX wildcard).

If the structure has cubic symmetry and no internal degrees of freedom **or** if one only wishes to use the harmonic approximation, the `fitfc` command should be invoked with the `-nrr` option (do Not ReRelax). In these case, the relaxation step 3 below can be skipped.

- (3) Each `vol_*` subdirectory now contains a `str.out` file which is stretched version of the main `str_relax.out` file provided. (This naming convention is a bit confusing but is dictated by the fact that these `vol_*/str.out` files are the starting point of another relaxation step.) The ab initio code then needs to be invoked to rerelease the geometry at the various levels of imposed strain and obtain the energy as a function of strain. Typically, this is achieved by typing<sup>9</sup>:

```
pollmach -e runstruct_xxxx -w ionrelax.wrap
```

The `pollmach -e ...` prefix causes the command specified next to be run in all subdirectories containing a file called `wait` (a file automatically written by `fitfc` with this purpose in mind) before exiting. Here, the command to be run is `runstruct_xxxx`, which invokes the ab initio code `xxxx`. The option `-w ionrelax.wrap` specifies an alternative user-specified input file for the ab initio code, which must indicate that all degrees of freedom **except volume** must be allowed to relax. This additional relaxation step is needed because stretching may have modified the equilibrium atomic positions. The relaxed (but stretched) structures now reside in the `vol_*/str_relax.out` files while the corresponding energies will be in `vol_*/energy`.

- (4) Now, one needs to invoke `fitfc` again to generate perturbations of the atomic position for each level of strain, e.g.:

```
fitfc -er=11.5 -ns=3 -ms=0.02 -dr=0.1
```

This is exactly the same command as before but the code notices the presence on the new files and proceeds further.

At this point the files generated are arranged as follows. At the top level, there is one subdirectory per level of strain (`vol_*`, where \* is the strain in percent), and in each subdirectory, there is a number of subsubdirectories, each containing a different perturbation. The perturbation names have the form

```
p[+/-][dr]_[er]_[index],
```

where `[pertmag]` is the number given by the `-dr` option, `[er]` the number given by the `-er` option and `[index]` is a number used to distinguish between different perturbations. Two perturbations that differ only by their signs are sometimes generated and are distinguished by a + or - prefix. (These opposite-sign perturbations ensure that the effect of third-order force constants cancel out exactly in the fit. Note that whenever the third-order terms cancel out by symmetry, the code will recognize this and only generate the “positive” perturbation. If one is not concerned with errors introduced by third-order force constants and wishes to save time, “negative” perturbations can be ignored at this point by deleting the `vol_*/p-*/wait` files.) Each subdirectory of the form `vol_*/p*` contains (i) the ideal unrelaxed supercell in a `str_ideal.out` file, (ii) the relaxed but unperturbed supercell in a `str_unpert.out` file and (iii) the actual geometry of perturbed supercell calculation in a `str.out` file.

- (5) The ab initio code must be invoked again, this time to calculate reaction forces for each perturbation. This will typically be accomplished by typing the now familiar construct:

```
pollmach -e runstruct_xxxx -w force.wrap
```

where the `force.wrap` must now indicate that **no** degrees of freedom are allowed to relax.<sup>10</sup> Each subdirectory of the form `vol_*/p*` will now contain a `force.out` file (and a number of other ab initio code-specific files not read by `fitfc`). A `str_relax.out` is also generated, although it contains the same geometry as the `str.out` file since no relaxation took place.<sup>11</sup> This concludes the “generation” phase of the process.

- (6) Next, the code must fit the force constants and perform the actual phonon calculations. This mode is invoked via the `-f` option:

```
fitfc -f -fr=...
```

In addition, the range of the springs to be included in the fit is specified using the mandatory parameter `-fr=...`. Usually, the range specified with `-fr` should be no more than half the distance specified with the `-er` option earlier. Distances are measured according to the atomic positions given in `str.out` and in the same units (typically Å). It is a good idea to try different values of `-fr` (starting with the nearest neighbor bond length) and check that the vibrational properties converge as `-fr` is increased. The output files will be described below.

<sup>9</sup> The `pollmach` command looks for files called `wait` in all subdirectories as a signal that the specified command must be run in the directory containing that file. Hence it is prudent to double check that there are no leftover `wait` files from earlier calculations: `find. -name wait`.

<sup>10</sup> A special note to VASP users: Smearing methods must be used for Brillouin zone integration in force calculations, unless the system is insulating. Do not use the `DOSTATIC` option in the `force.wrap` file (this is not VASP keyword per se but it is interpreted by the `runstruct_vasp` command).

<sup>11</sup> For some ab initio codes, the ordering of the atoms in `str.out` and `str_relax.out` may differ, but `fitfc` is able to figure out how to assign each force to the correct atom, provided the atoms in `str_relax.out` and in `force.out` are in the same order. All the `runstruct_xxxx` commands provided with ATAT ensure that this is the case.

- (7) Sometimes, the message 'Unstable modes found. Aborting.' is printed. This indicates that the structure considered **may** be mechanically unstable. If, in addition, you see the warning 'Warning: p... is an unstable mode.', then the structure is certainly mechanically unstable. Otherwise, it may be an artifact of the fitting procedure. To find out, the code can generate perturbations along the unstable directions and let the ab initio code calculate the reaction forces which can then be included in the fit to settle this issue. First, to view the unstable modes, use the `-fu` option. The output will be in `vol_*/unstable.out` and has the form:

```
u [index] [nb_atom] [kpoint] [branch]
[frequency] [displacements...]
```

where `[index]` is a reference number, `[nb_atom]` is the size of the supercell needed to represent this mode and `[displacements]` is a vector of  $3n$  elements defining the displacement mode, where  $n$  is the number of atoms in the unit cell. The other entries are self-explanatory. (If this file contains only entries with `nb_atom=too_large`, one needs to increase the `-mau` option beyond its default of 64.) One of these modes can be selected to be written out to disk with the option `-gu=[index]` where `[index]` is the one reported in the `unstable.out` file. This new feature aimed at the elimination of fictitious unstable modes was first used in [31,32].

- (8) The ab initio code should then be run in the subdirectory generated (named `vol_*/p_uns_[dr]_[kmesh]_[number]`) and rerun, from the top-level directory, `fitfc -f -fr=...`. If the message "Warning: p... is an unstable mode" appears, then a true instability has been found. If only "Unstable modes found. Aborting" is printed, one may repeat the process until the message disappears or a truly unstable mode is found.

Note: The `-fn` option can be used if one wishes to generate a phonon DOS even if there are unstable modes. The unstable modes will be shown as negative frequencies. The `-fn` option eliminates the printed error message but not the underlying problem.

The output files are as follows:

- (1) `fitfc.log`: A general log file.
- (2) `vol_*/vdos.out`: the phonon density of states for each volume considered
- (3) `vol_*/fc.out`: The force constants. For each force constant a summary line, prefixed with "svsl" gives: (i) the atomic species involved, (ii) the 'bond length', (iii) the stretching and bending terms. This can be useful to check the validity of the length-dependent transferable force constant approximation. Then, each separate component of the force constant is given and, finally, their sum.
- (4) `vol_*/svib_ht`: gives the high-temperature limit of the vibrational entropy (in units of Boltzman constant per atom) in the harmonic approximation, excluding the configuration-independent contribution at each unit cell volume considered (so, this just  $-3$  times the average log phonon frequency).
- (5) `fitfc.out`: gives along each row, the temperature, the free energy, and the linear thermal expansion (e.g. 0.01 means that the lattice has expansion by 1% at that temperature).
- (6) `fvib`: gives only the free energy (this is the output file that may be subsequently use to construct a cluster expansion)
- (7) `svib`: gives only the entropy (in energy/temperature, by default, eV/K)
- (8) `eos0.out`: equation of state at 0 K (each line reports one level of strain and its associated energy)
- (9) `eos0.gnu`: gnuplot script to plot the equation of state polynomial and data.

The files within the subdirectories `vol_*` are based on the harmonic approximation for a given fixed volume while the files in the main directory give the output of the quasiharmonic approximation if `ns > 1` and the harmonic approximation if `ns = 1`.

Examples studies employing this code can be found in [31–34], among others.

### 3.1.2. The *fitsvsl* and *svsl* codes

The *fitsvsl* code determines bond stiffness vs bond length relationship for the purpose of calculating vibrational properties (with the *svsl* code, described subsequently). Using this pair of codes pays off only if vibrational properties of large number of similar structures are needed, because the so-called transferable length-dependent force constants can be determined from a small set of structures with the *fitsvsl* code, while vibrational properties can then be quickly predicted for a much larger set of structures with the *svsl* code.

*fitsvsl* requires the following files as an input.

- (1) A lattice file (`lat.in`) which allows the code to determine what chemical bonds are expected to be present in the system. The format is as described in the *mmaps* documentation (see *mmaps -h*).
- (2) A file called `strname.in` containing a white space<sup>12</sup> – separated list of directories containing structures that will be used to calculate force constants. Typically these would numbered directories previously generated by *mmaps*, although user-specified directories can be included. This set of structures must be diverse enough so that it contains at least one chemical bond of each type that will be encountered with the *svsl* code. For a binary A-B alloy this typically involves the need for a "pure A" and a "pure B" structure, in addition to one with an intermediate composition. Each of the directories listed in `strname.in` must contain:
  - (a) a `str.out` file containing an ideal unrelaxed structure that will be used to automatically determine the nearest neighbor shell,
  - (b) a `str_relax.out` file containing the relaxed structure that will be used to calculate bond lengths and that the code will perturb in various ways to determine the force constants.

Like the *fitfc* code, the *fitsvsl* code can operate in two modes: a structure generation mode and a fitting mode (indicated by the `-f` option). In structure generation mode, all the above input files are needed and the option `-er` must be specified in order to indicate the size of the supercells generated. The `-er` option specifies the minimum required distance between a displaced atom's periodic images. The code will automatically infer the smallest supercell satisfying this constraint. Typically, `-er` should be 3 or 4 times the nearest neighbor distance. All of these distances are measured using the ideal structures (`str.out`).

Various optional parameters (which have reasonable default values) can be specified: the `-dr`, `-ms` and `-ns` options have the same meaning as for the *fitfc* code. Unlike the *fitfc* code, the default number of different isotropic strain levels considered is 2 because this is the minimum needed to be able to determine the length-dependence of bond stiffness. More than one level of strain is necessary even if only the harmonic approximation is desired. Another difference is that the *fitsvsl* code is typically run from a "top level" directory containing multiple structure subdirectories (e.g. as generated by *mmaps*), because it handles properties that are transferable across structures. The *fitfc* code is to be run within a structure directory because it applies to one structure at the time.

<sup>12</sup> A "white space" is a space, tab or newline.



After the structure generation step, each of the directory specified in `strname.in` will contain a hierarchy of subdirectories with various perturbed structures with a layout identical to the one described in step 4 of Section 3.1.1. The appropriate first-principles calculations are then carried out as in step 5 of that same section.

After completion of the first-principles calculations, `fitsvsl` must be invoked in fitting mode (with the `-f` option). The lattice file (e.g. `lat.in`) must be present and the code will look for data to fit in all files of the form `*/force.out`, `*/*/force.out` and the corresponding files `*/str.out`, `*/str_relax.out`, `*/*/str.out`, `*/*/str_relax.out`.

The code will then use that information to create the length-dependent force constants (this may take a few minutes) and outputs them in `slspring.out`. Here is an example of the format of this file:

```
A1 A1 (gives the type of bond)
2      (2 parameters: linear fit is used)
      (polynomial coefficients of the stiffness vs length
      relationship for stretching term:)
50.29 (constant, typically in eV/Å2)
7.89  (slope coefficient, typically in eV/Å3)
2      (idem for bending term, 2 parameters for a linear fit)
6.13  etc.
-1.02
A1 Ti (repeat for each type of chemical bond)
...
```

Whenever there is not enough data to fit a given parameter, it will appear as 0 in the above output file, so the user must carefully inspect this file. This may happen if there are not enough structures in the `strname.in` file or if there are too few levels of strain applied (`-ns` option) or if some ab initio calculations aborted without producing a `force.out` file.

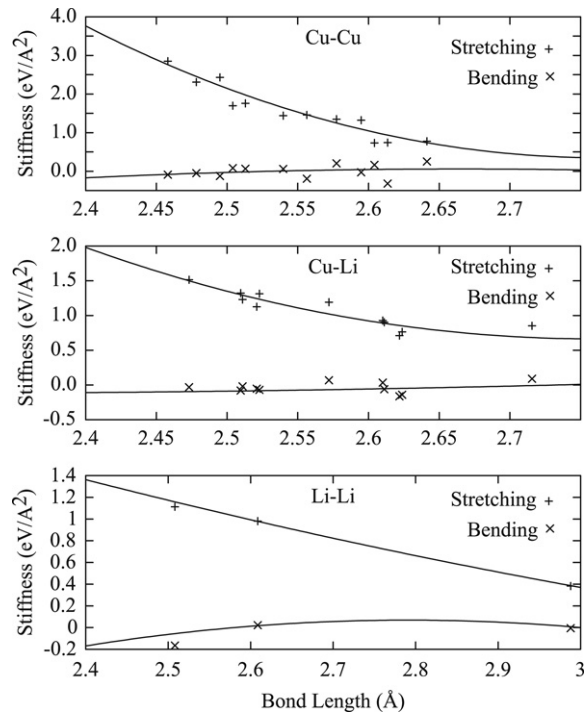
A few options are available to control the fitting process. The `-op` option specifies the order of the polynomial used to fit the stiffness vs length relationship (the default is `-op=1` for a linear relationship). More sophisticated models<sup>13</sup> are also available, such as direction-dependent force constants (`-dd` option) or composition-dependent force constants [30] (the `-pc` option specified the order of the polynomial representing the composition-dependence).

Diagnostic files are also output: the `fitsvsl.log` file contains all the matrices generated in the fitting process, including the actual forces, compared with the ones predicted by the spring model. A plot of the stiffness vs. length relationship is available in the files `fitsvsl.gnu` (a gnuplot script) and `f_*.dat` the raw stiffness data to be plotted. This is helpful for assessing the validity of the transferability assumption, as illustrated in Fig. 2.

Note that the `fitfc` and `fitsvsl` codes are mutually compatible: the perturbations generated with one code can be used in a fit carried out with the other. This is useful if one realizes midway through the process that one approach is too slow or the other too inaccurate.

Once the `slspring.out` file has been generated with `fitsvsl`, the `svsl` code can exploit it to rapidly predict vibrational properties of numerous similar structures. Like `fitfc`, `svsl` is structure-specific and must be run within a structural directory containing the following files (three of which should now be familiar):

- (1) a “relaxed” structure file (`str_relax.out`) and
- (2) an “unrelaxed” structure file (`str.out`). The latter provides the ideal atomic positions that are used to automatically



**Fig. 2.** Bond stiffness versus bond length relationship in the fcc Cu-Li system. The proximity of the crosses to the solid lines is a strong indication of the model's predictive power in this system.

determine which atoms lie in the nearest neighbor shell. This file can be the same as the relaxed structure but then the determination of the nearest neighbor shell may be less reliable.

- (3) In addition, `svsl` requires a transferable force constant file `slspring.out`. It looks for this file in the current directory and, if not found, it also looks one directory up, where it would typically have been placed by an earlier `fitsvsl` command.
- (4) An optional input file defining the atomic masses can be provided. By default, the code looks in the `~/ .atat.rc` file to determine the directory where ATAT is installed and then loads the file `data/masses.in`. This behavior can be overridden with the `-m` option.
- (5) By default, the bulk modulus is calculated from the force constants (which is quick but potentially inaccurate) but it can also be read from a file (whose name is specified with the `-bf` option) or specified on the command line with the `-b` option.

A few parameters govern the accuracy of the calculations. (The default values are all reasonable starting points.)

- (1) By default the code uses the harmonic approximation, but thermal expansion can be accounted for by specifying the `-ns` option with a value `ns` greater than 1. In that event, `svsl` calculates the vibrational free for `ns` different lattice parameters ranging from its equilibrium 0 K value to a value  $(1 + ms)$  times larger, where `ms` is specified via the `-ms` option (the default is 0.05). Typically `-ns=5` is sufficient, but the computational cost of using higher values is minimal.

The code calculates the vibrational free energy for temperatures ranging from  $T_0$  to  $T_1$  in steps of  $dT$ , where these three values are determined as follows.

- (a) The defaults are  $T_0 = 0$ ,  $T_1 = 2000$ ,  $dT = 100$ .
- (b) If a `Trange.in` file exists in the next upper directory, it is used to set  $T_0$ ,  $T_1$ ,  $dT$ : It must contain two numbers on one line separated by a space:  $T_1 (T_1/dT + 1)$ . Note that  $T_0 = 0$  always. For phase diagram calculations, this

<sup>13</sup> A more general format for the `slspring.out` file then used – contact the author for more information.



method must be used to specify the temperature range because it ensures that all calls to `svsl` (and to other codes described subsequently) use the same temperature range.

(c) The above values can be overridden by the `-T0 = T0`, `-T1 = T1` and `-dT = dT` options.

- (2) The  $k$ -point sampling grid is specified with the `-kp = kp` option. The actual number of  $k$ -points used is at least  $k_p$  divided by the number of atoms in the cell. An internal algorithm builds a  $k$ -point grid that equalizes as much as possible the  $k$ -point density along all directions in space

The output files are as follows:

- (1) `svsl.log`: a log file giving some of the intermediate steps of the calculations in particular, the predicted bulk modulus which should be checked for accuracy.
- (2) `vdos.out`: the phonon density of states for each lattice parameter considered (unstable modes appear as negative frequencies).
- (3) `svsl.out`: gives along each row, the temperature, the free energy, and the linear thermal expansion (e.g. 0.01 means that the lattice has expansion by 1% at that temperature).
- (4) `fvib`: similar to `svsl.out` but gives only the free energy.

Examples of studies employing this code can be found in [34–36]

### 3.2. Electronic excitations

The `felec` code calculates the electronic free energy within the one-electron and temperature-independent bands approximations. It expects a `dos.out` input file containing an electronic density of states and the number of electrons to populate it. This file is typically generated by the `ab initio` call up utilities `runstuct_xxxx` (see Section 6). It is rarely needed to use anything but the default option:

```
felec -d
```

The output files are:

- (1) `felec.log`, containing the temperature and corresponding free energy (per unit cell) on each line.
- (2) `felec` is similar to `felec.log` but only contains the free energies.
- (3) `plotdos.out` contains the `dos` in a format suitable to be plotted, with the energy normalized so that the Fermi level is at 0.

It should be noted that the above approximation are not always satisfactory, notably in magnetic systems. There are two (currently experimental) magnetic free energy calculators included in ATAT:

- (1) `fmag`, which relies on a simple quantum mechanical mean field model and
- (2) `fempmag`, which implements the widely used semi-empirical method introduced in [37].

### 3.3. Cluster expansions of nonconfigurational free energies

The `fitfc`, `svsl` and `felec` codes enables the calculation of free energies of individual configuration on a lattice. However, to properly calculate the free energy of system exhibiting both configurational and nonconfigurational disorder, a cluster expansion needs to be constructed to be able to predict the nonconfigurational free energy of any given configuration. This cluster expansion can then be provided as an input to the Monte Carlo code `memc2` which will now be able to properly account for both configurational and nonconfigurational contributions to the free energy. Here is how to proceed.

- (1) First create a `Trange.in` file indicating the temperature range to be sampled. For instance, if one wishes to sample from 0 K to 2000 K in intervals of 100 K, type

```
echo 2000 21 >Trange.in
```

(The lowest temperature is always 0 K and note that  $2000/(21 - 1) = 100$ .)

This ensures that all calls to `fitfc`, `svsl` and `felec` will use the same temperature range.

- (2) ATAT provides the `foreachfile` utility to repeat the same command in all subdirectories containing a specified file. For instance, to calculate the vibrational free energy using `svsl` in all structure subdirectories, one could type

```
foreachfile -e str_relax.out svsl -d
```

This executes the `svsl` code with the default options (`-d`) in each subdirectory containing a `str_relax.out` file while skipping directories with an error file (`-e`). If desired, a similar process can be used for the electronic free energies:

```
foreachfile -e dos.out felec -d
```

- (3) Next, construct a cluster expansion of the vibrational free energy data contained in the `*/fvib` files:

```
clusterexpand fvib
```

Note that the files `*/fvib` actually contain a column of numbers (one for each temperature) – `clusterexpand` simply produce a separate cluster expansion for each scalar element in `*/fvib`. By default, this commands reads in the clusters from the `clusters.out` file, as they were generated earlier by `mmaps`.<sup>14</sup> The user has some control over which clusters to include (1) or exclude (0) via the `-s=[comma-separated string of 0s and 1s]` option. The user can also check if the crossvalidation score, reported with `-cv` option, can be improved by changing the cluster selection. A similar expansion can be done for electronic contributions:

```
clusterexpand felec
```

- (4) Finally, combine the energy cluster expansion from `eci.out` (generated by `mmaps`) with the vibrational (`fvib.eci`) and electronic (`felec.eci`) cluster expansions created in the previous step into a single “master” cluster expansion file (`teci.out`) that will be read by the Monte Carlo code:

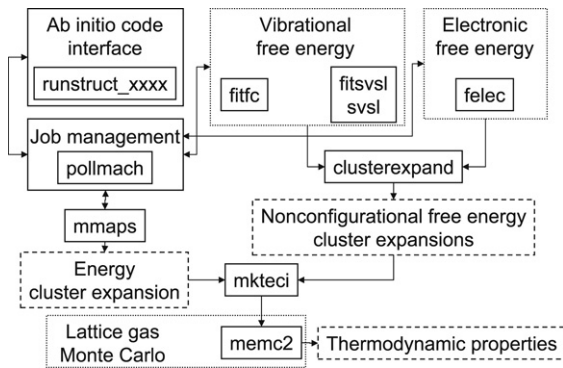
```
mkteci fvib.eci felec.eci
```

For this step to succeed it is essential that all `clusterexpand` commands were run with the same `mmaps`-generated `clusters.out` file (although different clusters can be included or excluded with the `-s` option of `clusterexpand` without any problem).

- (5) Run `memc2`. It is often instructive to try and compare simulations that include or exclude some components of the nonconfigurational free energy. To this effect, one can simply rerun `mkteci` with the list of contributions to include before rerunning `memc2`.

Example of the use of this methodology can be found in [34–36]. For easy reference, Fig. 3 shows a flowchart of the entire procedure while Fig. 4 showcases a practical example of this methodology.

<sup>14</sup> If the user wishes to use `clusterexpand` without first running `mmaps`, a suitable `clusters.out` file can be generated with a command of the form `corrump -clus -2=[max pair radius] -3=[max triplet radius]` etc. A `lat.in` file still needs to be supplied.



**Fig. 3.** Flowchart of ATAT's approach to the integration of configurational and nonconfigurational contributions to the thermodynamics of alloys.

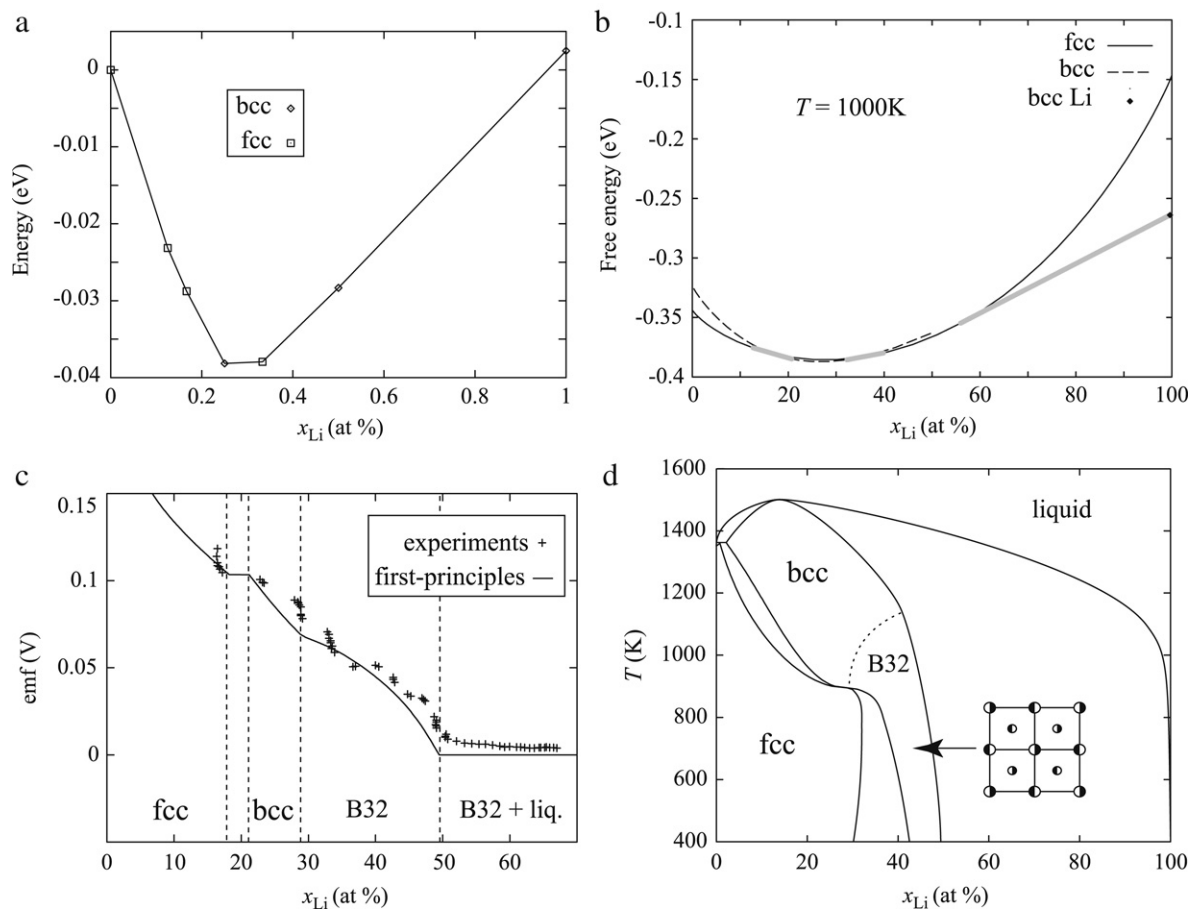
#### 4. Special Quasirandom Structure generation

The use of the cluster expansion is essential to properly model nondilute alloys exhibiting configurational disorder with potential short-range order [39]. However, at sufficiently high temperatures, the limiting case of a fully random alloy provides a useful approximation. Although this limit can be calculated with a cluster expansion, it is sometimes convenient to directly determine

high-temperature limiting quantities with a small number of supercell ab initio calculations without first constructing a cluster expansion. The concept of Special Quasirandom Structures (SQS) [40] provides an efficient way to take this route. An SQS represents the best periodic supercell approximation to the true disordered state for a given number of atoms per supercell. The quality of an SQS is measured in terms of the number of correlations of the fully disordered state it is able to match exactly. Typically, one attempts to preferably match shorter-range correlations while gradually enlarging the supercell to extend the range of matching correlations until convergence of the properties of interest. Traditionally, SQS are built based on matching the pair correlations, although for best performances, multibody correlations should be considered as well. The SQS generation utility included in ATAT (*gensqs*) can account for any user-specified set of correlations.

The SQS generation process in ATAT (as used, for instance, in [16,39,41]) is as follows:

- (1) Prepare a *lat.in* file (just like the one used for the *mmaps* and *memc2* codes).
- (2) Prepare a file (say, *conc.in*) specifying a structure having the same overall composition as the disordered state of interest. The exact geometry of this structure is irrelevant – it only needs to have the correct overall composition and be a proper



**Fig. 4.** Ab initio thermodynamics of the Cu–Li system [34]. (a) Ground state convex hull (merging bcc and fcc superstructures). (b) Calculated free energy as a function of composition including both configurational, vibrational and electronic contributions. Nonconfigurational contributions are essential to accurately predict the numerous phase transitions between bcc- and fcc-based phases. Two-phase equilibria are marked by thick gray tie-lines. (c) Calculated electromotive force (emf) inferred from the calculated free energy in (b) and compared with experimental data. (The solid–liquid Li free energy difference was left as a parameter adjusted to provide the best agreement.) (d) Calculated phase diagram obtained via tangent constructions as in (b) over a range of temperatures. The liquid phase excess free energy is taken from the COST database [38]. Note that most of the ground states from (a) disorder at low temperature and are not visible in the phase diagram. Interestingly, neither the magnitude of each ground state's formation energy nor the sharpness of the vertex where a ground state touches the hull bear any correlation with a ground state's disordering temperature. The B32 ground state at 50% (shown in inset) does not have the most negative formation energy and barely breaks the hull. Yet it exhibits tremendous stability due to entropy-driven stabilization. The dashed line marks the location of a second-order transition, determined by locating a peak in the heat capacity.

superstructure of `lat.in`. Each site must be occupied by one and only one atom. For instance, given the lattice of Table 1, a valid `conc.in` file could be:

```
1 1 1.05 90 90 90
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
0 0 0 Fe
0 0.5 0.5 C
0.5 0 0.5 C
0.5 0.5 0 Vac
0.5 0.5 0.5 Ni
0.5 1.0 1.0 Vac
1.0 0.5 1.0 Vac
1.0 1.0 0.5 Vac
```

This way of specifying composition was selected because it allows the user to individually control the composition on each sublattice.

- (3) Select a small number of correlations to match exactly and compute their value in the disordered state:

```
corrump -noe -rnd -s=conc.in -2=[pair max radius] --3=[triplet max radius] >tcrr.out
```

This command writes the nonempty (`-noe`) correlations of the disordered state (`-rnd`) having the same composition as the structure `conc.in` into the file `tcrr.out`. Pair correlations up to distance `[pair max radius]` and triplet correlations up to `[pair triplet radius]` are considered (larger clusters can also be specified with `-4=...`, etc.). This command also writes a cluster file `clusters.out` that will be read in the step.

- (4) The SQS generation step is initiated with, for instance,

```
gensqs -n=16 >sqs16.out
```

which generates 16-atom SQS and puts them into the `sqs16.out` file. If this file is empty, the range of correlations to be matched exactly needs to be reduced in step 3. A word of caution: `gensqs` only generates structures containing exactly the number of atoms per unit cell specified by the `-n` option (i.e., if an SQS with a smaller unit cell exists, it will not be listed).

- (5) The output file `sqs16.out` may contain a large number of candidate SQS. While these match the specified criteria, they may differ in quality in terms of the correlations not included in the screening process. Further screening can be performed with the command

```
corrump -2=[another radius] -3=[another radius] -4=[another radius] -noe -s=sqs16.out
```

which will output the correlations of all SQS in `sqs16.out`. Clearly, the radii specified should be larger than in step 3 in order to distinguish and rank these SQS.

While there are no formal rules to decide whether it is preferable to match more pairs or more multi-body correlations, general guidelines can be given. In general, it would be unusual to match longer range  $n$ -body correlations than  $m$ -body interactions if  $n > m$ . In systems exhibiting large relaxations (due to large atomic size mismatches), multi-body correlations are expected to be important, while in ionic systems, pair interactions are expected to dominate.

SQS generation via exhaustive enumeration is time-consuming. This can be alleviated by exploiting parallelism. Multiple independent copies of `gensqs` can be run on separate processors if one specifies the `-ip=[index]` and `-tp=[number of processes]` options. The `[index]` runs from 0 to `[number of processes-1]` and is used to tell each copy of `gensqs` which portion of the space to scan. For maximum efficiency, `[number of processes]` should be a factor of the total number of possible supercells, which can be determined, e.g., with the `gensqs -n=16 -pc` command.

Another way to improve SQS generation speed is via stochastic sampling [42]. Such an approach seeks to quickly find close-to-optimal solutions rather than slowly finding an exact solution. Another approach is to scan through configurations in such a way that only the desired composition is sampled, using atom permutations rather than atom “transmutations”. This scheme becomes increasingly advantageous as one moves away from equiatomic compositions. Yi Wang contributed a useful code implementing these two algorithms (that were used in [16]), which will be included in the ATAT distribution shortly.

Finally, we note that SQS prove useful in the construction of a cluster expansion as well. Any generated SQS can be included into the set structures used to fit a cluster expansion as a way to ensure that the properties of the disordered state are properly reproduced. In practice, one can merely place the desired SQS into a `str.out` file within a subdirectory and run an *ab initio* code on it with `runstruct_xxxx`. The `mmaps` code will readily read in any user-specified structure placed in its directory hierarchy (provided the `lat.in` files used in `mmaps` and `gensqs` are identical).

## 5. The tensorial cluster expansion

While the formalism enabling the cluster expansion of tensors has been derived in [43], we provide here a brief explanation of how to use this feature. In Section 3.3, it was shown how to cluster expand a scalar – the process is similar for tensors.

- (1) Create a `lat.in` providing the lattice and a `gctensor.in` file describing the type of tensor in the form:

```
[rank]
[list of pairs of indices indicating which
 simultaneous index permutations leave the
 tensor invariant]
[next list, etc...]
```

To fix the ideas, here are a few examples. For strain or stress the `gctensor.in` should be:

```
2
0 1 (indicating that such tensor is symmetric, i.e.,  $\varepsilon_{ij} = \varepsilon_{ji}$ )
while for elastic constants, it should be:
4
0 1 (indicating  $c_{ijkl} = c_{jikl}$ )
2 3 (indicating  $c_{ijkl} = c_{ijlk}$ )
0 2 1 3 (indicating  $c_{ijkl} = c_{klij}$ ).
```

- (2) Generate a list of clusters with the command `gce -clus -2=[max pair radius] -3=[max triplet radius]` etc. Note that `gce` (which stands for Generalized Cluster Expansion) admits essentially the same syntax as `corrump` in the scalar case.

- (3) Calculate the property tensor associated with each structure.<sup>15</sup> This is highly application-dependent. For instance, to calculate the static lattice strain, one could use (assuming *ab initio* calculations have been run in each subdirectory):

```
foreachfile -e str_relax.out analrelax -d
">" strain
```

To calculate the elastic constants one could use:

```
foreachfile -e str_relax.out calcelas -d (this
 generates perturbations)
pollmach -e runstruct_xxxx -w force.wrap (this
 calculates the induced reaction stresses)
foreachfile -e str_relax.out calcelas -f
">" elas
```

(this fits the elastic tensor and writes it in the file `elas`.)

<sup>15</sup> This list of structures could come from a previous `mmaps` run, for instance, or it could be generated manually using the `genstr` command.

(4) Finally, do the cluster expansion itself with:

```
clusterexpand -pa -g strain
```

```
clusterexpand -pa -g elas
```

the `-g` invokes the generalized cluster expansion option while the `-pa` indicates that the quantities to be expanded are intensive (i.e. per atom).

## 6. Interfaces with ab initio codes

All interfaces have the general name `runstruct_xxxx`. Currently, the following are supported: `runstruct_vasp` (for the VASP code [44,45]) `runstruct_abinit` (for the abinit [46,47] code), `runstruct_gulp` (for the GULP code [48,49]). In addition, Monodeep Chakraborty, Jürgen Spitaler, Peter Puschnig and Claudia Ambrosch-Draxl have written an interface with WIEN2k [50], which will be publicly available shortly. Finally, `runstruct_pwscf` (for the PWscf code [51]) is under development.

Each interface has the following characteristics in common:

- (1) It reads the geometry of a structure from the `str.out` file in current directory, written in the ATAT format. If a `str_hint.out` file exists, it takes precedence over the `str.out` file. This is useful to provide educated guesses of the relaxed geometry via external user-supplied codes.
- (2) It reads some code-specific parameters from a file called `xxxx.wrap` (or specified with `-w [file]`) located in the current directory or up to two levels above. This separation between the geometry and calculation parameter input files is essential to ensure that all the pieces of ATAT are fully interoperable.
- (3) It runs the appropriate ab initio or atomistic code. If an argument is given to the `runstruct_xxxx` this string is used as prefix to the ab initio command. This feature is used to run the appropriate code remotely without having to install ATAT on the compute nodes.
- (4) It writes the structure's energy in the file `energy` and the structure's relaxed geometry in `str_relax.out`. (If no relaxations are allowed, then the unrelaxed geometry is written in `str_relax.out`.)
- (5) It writes the forces acting on all atoms in `forces.out`, the stress acting on the cell in `stress.out` and the electronic density of states in `dos.out` (although these are not yet implemented in all `runstruct_xxxx` commands).
- (6) If anything goes wrong with the calculations, a file called `error` is written.

Typically the ab initio codes are not called one run at the time but rather as a batch of many jobs. The `pollmach` command manages such pools of jobs. The basic principle is simple: if a file called `wait` exists in a subdirectory, `pollmach` will find it and run the command specified on the command line within that directory. For instance,

```
pollmach runstruct_xxxx
```

will repeatedly wait for a `wait` file to be found, delete it, and then run `runstruct_xxxx` with the corresponding directory. In a multiprocessor environment, `pollmach` can simultaneously dispatch different jobs to different processors. This simple mechanism allows most of the ATAT codes to be completely platform-independent, with `pollmach` being the only platform-dependent piece.

The first time `pollmach` is run, default configurational files are set up and the user will be asked to tailor them to the local computing environment. The ATAT distribution includes many examples of setups, including the increasingly common case of a large pool of processors to be divided up into subgroup that each run a separate parallel version of an ab initio code.

## 7. Utilities

We now briefly mention some utilities to give users direct access to some of the inner algorithms of ATAT.

- (1) `corrump` finds symmetry operations, enumerates clusters, calculates correlations (including of the disordered state), etc.
- (2) `genstr` enumerates superstructures of a given lattice.
- (3) `pdef` generates substitutional point defect supercells.
- (4) `cellcvrt` manipulates ATAT-formatted structure files, changing coordinate systems, converting fractional to cartesian coordinates, finding supercells and subcells, etc.
- (5) `lsfit` implements least-squares fitting.
- (6) `nnshell` finds nearest-neighbor shells.
- (7) A number of text parsing utilities: `getvalue`, `getline`, `sspp`.

More information regarding these utilities can be found in their respective help files (accessed by specifying the `-h` option).

## 8. Conclusion

This completes this overview of the various new features added to ATAT in recent years. What's next? Probably:

- (1) A tighter integration between the output of the Monte Carlo code and thermodynamic databases for use with softwares such as Thermocalc and Pandat;
- (2) Material property optimization modules exploiting the tensorial cluster expansion;
- (3) More automated ways to include nonconfigurational free energy;
- (4) Better electronic free energy calculators.

However, in large part, what will be next will depend on what users express interest in and what the author can get funding for....

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## Appendix. Correlation to concentration conversions

ATAT calculates the matrices  $C$  and  $X$  and vectors  $c_0$  and  $x_0$  in Eqs. (4) and (5) as follows.

- (1) Start enumerating all structures (in order of increasing unit cell size) while computing the point correlation vector  $\rho$  for each of them. Let  $\bar{\rho}$  denote the corresponding point correlation vector with a constant element appended to it. Skip any structures whose  $\bar{\rho}$  is colinear with the  $\bar{\rho}$  of earlier structures. Terminate this step when the number of structures kept is equal to the dimension of  $\bar{\rho}$ .
- (2) For each of the kept structures, calculate its full concentration vector  $x$ . Create a matrix  $A$  by pasting the column vectors  $x$  just obtained side by side. Similar, create a matrix  $B$  by pasting the column vectors  $\bar{\rho}$  previously obtained. Note that  $B$  is square and invertible by construction and calculate  $\bar{X} = AB^{-1}$ .
- (3) All columns of  $\bar{X}$  but the last provide  $X$  while the last column of  $\bar{X}$  gives  $x_0$ .
- (4) Eliminating all colinear rows from  $X$  gives  $C$  while eliminating the corresponding elements of  $x_0$  gives  $c_0$ . (Note: in ATAT,  $c_0$  is just set to zero since this makes no difference for convex hull construction. But  $x_0$  is fully calculated.)

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