Direct coupling of first-principles calculations with replica exchange Monte Carlo sampling of ion disorder in solids

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Abstract

We demonstrate the feasibility of performing sufficient configurational sampling of disordered oxides directly from first-principles without resorting to the use of fitted models such as cluster expansion. This is achieved by harnessing the power of modern-day cluster supercomputers using the replica exchange Monte Carlo method coupled directly with structural relaxation and energy calculation performed by density functional codes. The idea is applied successfully to the calculation of the temperature-dependence of the degree of inversion in the cation sublattice of MgAl$_2$O$_4$ spinel oxide. The possibility of bypassing fitting models will lead to investigation of disordered systems where cluster expansion is known to perform badly, for example, systems with large lattice deformation due to defects, or systems where long-range interactions dominate such as electrochemical interfaces.

Keywords: replica exchange, first-principles simulation, configurational sampling, spinel

(Some figures may appear in colour only in the online journal)
with low calculation cost can be quite challenging for systems with complex long-range (e.g. Coulombic or dispersion) interactions [12]. Lattice relaxation effects, which are rather pronounced in oxides with defects, are also known to decrease the accuracy of derived cluster expansion Hamiltonians [13]. And such interactions are especially important for multivalent ion oxides and various heterointerfaces that are central to many applications of functional materials.

We note that when a moderately accurate but inexpensive potential is available for the system under study, MC simulation with such a potential can be ‘nested’ between MC steps taken with DFT energies to speed up the sampling. The efficiency of this ‘nested Monte Carlo’ method [14, 15] depends on the quality of the potential, and thus the method does not allow the user to fully escape from the difficulties mentioned above.

In view of such difficulties, we decided to reexamine the feasibility of bypassing fitting models and performing direct thermodynamic sampling on DFT energies. While such an undertaking may have been viewed as out of the question a decade ago in all but the simplest systems, the steady increase in computational power available to researchers has changed the situation. Algorithms in computational statistical mechanics have evolved to take advantage of massively parallel supercomputers now available such as the replica exchange (RX) [16–19] and population annealing [20, 21] methods, as well as parallel multicanonical [22, 23] or Wang–Landau methods [24]. Machine learning techniques and ‘materials informatics’ have also emerged as possible game-changers due to the ability to generate huge amounts of data.

In this work, we present an implementation of a Python framework for replica exchange Monte Carlo (RXMC) sampling coupled directly with local structural relaxation and energy calculation using DFT codes. The RXMC technique was first applied to spin glasses [17], and later combined with classical MD to examine protein folding [18], although we could not find any literature on its application to realistic solid state systems. Here, we benchmark the feasibility of bypassing fitting models and performing direct thermodynamic sampling on DFT energies. While such a potential is available for the system under study, MC simulation coupled with energy calculation using DFT codes can be represented by a list of site occupations. The Metropolis MC algorithm [25] proceeds as follows:

(i) Start with an initial crystal structure \( \mathbf{X} \) with energy \( E(\mathbf{X}) \).
(ii) Generate a trial structure \( \mathbf{X}' \) by perturbing a part of the previous structure and calculate the energy \( E(\mathbf{X}') \).
(iii) Accept the trial structure as the next structure (set \( \mathbf{X} \leftarrow \mathbf{X}' \)) according to the following probability

\[
P = \min\{1, \exp[-\beta (E(\mathbf{X}') - E(\mathbf{X}))]\}
\]

where \( \beta = (k_B T)^{-1} \) is the inverse temperature.
(iv) Repeat from (ii).

We note that how the trial structure is generated (step ii) has a profound effect on the efficiency of the algorithm. In the original Metropolis paper for rigid discs [25] and in molecular simulations today, the trial step consists of choosing a particle and displacing it by a random amount. This does not work well for solid state systems because they are more or less close-packed, and such trial steps tend to result in a large increase in energy and thus very small acceptance ratios. Instead, our scheme consists of picking two distinct atoms or vacancies and exchanging them. Basically, crystalline systems have well-defined ion sites, so the configuration \( \mathbf{X} \) can be represented by a list of site occupations. The Metropolis trial step then consists of picking two sites with different ions, exchanging them to generate the trial structure, and also considering the energy from the DFT output. The DFT calculation can include local optimization of the structure to account for relaxation effects. In this case, the simulation can be considered to be an implementation of basin-hopping MC method [26]. The kinetic energy can, in theory, also be included by calculating the phonon density of states \( D(\omega) \) at each step and integrating with the Bose–Einstein distribution as

\[
U_{\text{kin}} = \int_0^\infty \frac{D(\omega) \hbar \omega}{\exp(\hbar \omega / k_B T) - 1} \, d\omega.
\]
In this work, we assume that the contribution from $U_{\text{kin}}$ is small enough so that we can neglect it. Rationale is given in section 3.1.

### 2.2. Replica exchange

Even with carefully chosen structure update schemes, the Metropolis algorithm tends to get stuck in local minima, especially when the temperature is low. The RX algorithm, also known as parallel tempering, provides a method to overcome this limitation. The basic idea is to simulate $N_{\text{rep}}$ copies, or replicas, of the system under study, usually at different temperatures. The simulation on each replica can be performed using MC or MD methods. At certain intervals in the simulations, the temperatures are swapped between replicas (or replicas are swapped between temperatures) based on a Metropolis criterion:

$$P = \min \{1, \exp[\beta_i - \beta_j](E(X_i) - E(X_j))\}. \quad (3)$$

This allows each replica to travel between low and high temperatures, making it possible to overcome high energy barriers between local minima and provide sampling over a representative set of low-temperature regions in the global configuration space. Since each replica simulation can run independently between exchange attempts, the RX algorithm is well-suited for use on massively parallel cluster supercomputers. Temperature-dependent quantities can be calculated by sampling from the replica with the specified temperature at each MC step.

### 2.3. Parallel implementation

Our implementation scheme is shown schematically in figure 1. The RXMC part is implemented using Python with mpi4py [27–29] for distributed parallel processing using the message passing interface (MPI). The program is started with $N_{\text{rep}}$ processes, each of which takes care of MC sampling of each replica. At every trial step, each of the $N_{\text{rep}}$ processes prepares the DFT input files including the trial structure, spawns $N_{\text{DFT}}$ parallel MPI processes for running a DFT package, collects the results, and accepts or rejects the trial structure based on the Metropolis criteria mentioned above. At preset intervals, temperature exchange is attempted between replicas with adjacent temperatures. More concretely, the first exchange attempt is made between $T_0$ and $T_1$, $T_2$ and $T_3$, and so on. This allows each temperature to travel between all replicas.

### 3. Benchmark calculation on MgAl$_2$O$_4$

As mentioned in the introduction, we choose to calculate the degree of inversion in the cation sublattice of MgAl$_2$O$_4$ spinel oxide as a benchmark for the feasibility of the present approach. The results can be compared directly with a previous MC simulation using a cluster expansion + screened-point charge (CE + SPC) Hamiltonian that was fitted to first-principles results [12]. If the results turn out to be similar, then we can conclude that it is feasible to bypass fitting models and directly sample from first-principles results to obtain reliable thermodynamic quantities in disordered solids.

#### 3.1. Computational parameters

The DFT calculation part is performed using Vienna $ab$ initio simulation package [33]. The calculation supercell contains 16 Mg, 32 Al, and 64 O atoms. The GGA-PBE functional is used to approximate the exchange-correlation energy, and the projector augmented wave method [34] is used to describe electron–ion interactions. A plane wave basis set with a cutoff energy of 300 eV is used to express the valence wave functions. We only sample the $\Gamma$ point in the Brillouin zone. Structural relaxation is performed at each MC step until the forces are below 0.04 eV Å$^{-1}$. The above parameters are set not very much for accuracy but rather for speed. We will see if the accuracy is high enough and we can get away with such a setup. It is noted that about ten ionic steps, which take less than one minute using two Intel Xeon Gold 6148 processors, turn out to be enough to optimize the structure using this setup at each MC step. This means that we can sample more than 20000 configurations in one day when using only 16 compute nodes with two processors each.
We note that the internal and lattice parameters are simultaneously relaxed in this simulation. The relaxation is performed with a constant basis set that is determined for the initial structure based on the plane wave cutoff energy. This means that if the lattice parameters change significantly in the course of the relaxation, the basis set would correspond to a different cutoff energy for the final structure. To alleviate this problem, we restart the relaxation several times with constant energy cutoff, so that the final structures and energies consistently correspond to the preset cutoff energy of 300 eV.

As for the replica exchange parameters, we use 16 replicas spaced evenly between 600 K and 1500 K. Temperature exchange is attempted at every MC step. It is noted that disorder is considered only in the cation sublattice, and the O sublattice stays completely ordered throughout the simulation. The numbers of each of the ion species are also constant throughout the simulation; that is, we are sampling from the canonical ensemble with a total of \(48C_{16} = 2254,848,913,647\) possible configurations (we do not consider any symmetry for reducing the number of independent configurations). Furthermore, since we are working with a constant number of ions, and since we are sampling within the space of the spinel structure, we assume that the phonon energies among different configurations are very similar and neglect \(U_{\text{kin}}\). This has implicitly been assumed in previous works using cluster expansion mentioned above, although its correctness will need to be tested when more computer resources become available to researchers.

We compared two simulations starting from randomly initialized configurations and ordered spinel configurations to examine the possibility of sampling bias due to the choice of the initial configurations. The randomly initialized simulation was carried out for 16,750 steps, while the simulation starting from the ordered structure was carried out for 13,000 steps.

### 3.2. Results

To assess the efficiency of the algorithm, we first examine the temperature, energy, and degree of inversion (DOI) histories of one of the replicas in the randomly initialized simulation (figure 2). The DOI is defined as the ratio of Mg sites that are occupied by Al ions. It is noted that the DOI is 0 for the perfectly ordered spinel structure and \(2/3\) when the cation sublattice is completely disordered. Perhaps trivially, low energy corresponds to low DOI and low temperature. The lowest energy corresponds to the ordered spinel structure with DOI of zero, and we find that when a replica finds this structure, it tends to get stuck there for thousands of steps. The replica shown in figure 2 exhibited a configuration trial acceptance ratio of \(\sim 14\%\) for the first 4000 steps, after which it was stuck in the ordered configuration for nearly 4000 steps with zero acceptance ratio. This is because of an ‘energy gap’ of about 0.4 eV versus the second lowest energy structure, which can only rarely be overcome. Temperature exchange according to equation (3) does not help much, since the replica with the lower energy is unlikely to travel to higher temperatures (see steps 4000–8000 in figure 2 bottom). This results in a rather acute degradation of the sampling efficiency, and is a known deficiency of RXMC method for first-order phase transitions [21]. Multicanonical techniques [35, 36] are known to perform better in this regard. The application of such alternate sampling techniques for direct first-principles sampling is an important direction for future works.

Nevertheless, having 16 replicas seems to alleviate this problem somewhat, and the acceptance ratio of \(\sim 14\%\) when the replicas are not stuck turn out to be good enough for this system. We plot the degree of inversion of the replica with temperatures of 600 K, 1020 K, and 1440 K at each MC step in figure 3. We find that the 600 K series finds the lowest-energy...
ordered spinel structure within 300 steps, showing that the method is working rather well not only as a sampler but also as an optimizer considering that it found the single most stable structure out of 2254 848 913 647 possible configurations. The higher-temperature series seem to be well equilibrated after \( \sim 1500 \) steps. To be on the safer side, we threw out the first 3000 steps and performed averages over the remaining steps to obtain the temperature-dependent expectation value of the DOI as shown in figure 4. Calculated DOI from the two simulations starting from randomly initialized configurations and that starting from the ordered spinel structure coincide within the size of the symbols in the figure. This suggests that enough MC steps were performed to obtain results that do not spuriously depend on the initial configurations. Most importantly, our results are virtually identical to the results from the CE + SPC model, strongly suggesting that indeed, we can perform sufficient sampling directly from first-principles. The slight but systematic difference (our results predict a slightly smaller DOI) may be due to the smaller unit cell in our calculation, or due to the less accurate DFT calculation parameters that were chosen in favor of calculation speed.

4. Conclusion

In this work, we presented a scheme for performing thermodynamic sampling of disorder in materials by combining the replica exchange MC method directly with structural relaxation and energy calculation using DFT. The multilevel parallelism in the scheme allows for efficient execution on today’s massively-parallel supercomputers. We successfully calculated the temperature-dependent disorder in spinel oxide using this scheme and demonstrated that such direct sampling of DFT results is indeed feasible. Hence, the present scheme provides a way to sample materials disorder in systems where reliable model fitting has been very difficult, if not impossible. In addition, the approach was shown to work rather well as a global optimization method in configuration space of the disordered lattice. Performance comparisons versus other global optimization methods such as simulated annealing, genetic algorithms [37], or particle swarm optimization [38] are beyond the scope of this work, but we stress that unlike those approaches, the RXMC scheme allows for simultaneous sampling of finite-temperature properties while searching for the global optimum. We also note that the current scheme should work just as well for surface/interface systems as long as the configuration \( X \) can be represented by site occupations as mentioned in section 2.1. This admittedly brute-force approach will allow us to tackle problems in technologically relevant systems such as disordered oxides and electrochemical interfaces that were previously impossible to handle due to the number of first-principles calculations necessary for sufficient sampling.

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