



# On the use of the symmetry-adapted Monte Carlo for an effective sampling of large configuration spaces. The test cases of calcite structured carbonates and melilites



Valentina Lacivita<sup>a,b,\*</sup>, Philippe D'Arco<sup>c</sup>, Sami Mustapha<sup>d</sup>, Daniel Faria Bernardes<sup>e</sup>

<sup>a</sup>UPMC Paris 06, Sorbonne Universités, Institut du Calcul et de la Simulation & Institut des Sciences de la Terre de Paris, Paris, France

<sup>b</sup>Università degli Studi di Torino, Dipartimento di Chimica, Torino, Italy

<sup>c</sup>UPMC Paris 06, Sorbonne Universités, Institut des Sciences de la Terre Paris, Paris, France

<sup>d</sup>UPMC Paris 06, Sorbonne Universités, Institut de Mathématiques de Jussieu, Paris, France

<sup>e</sup>Univ. Paris 13, Sorbonne Paris Cité, Laboratoire de Traitement et Transport de l'Information, Villetaneuse, France

## ARTICLE INFO

### Article history:

Received 4 July 2016

Received in revised form 18 September 2016

Accepted 25 September 2016

### Keywords:

Symmetry-adapted Monte Carlo

Symmetry

Calcite structure

Carbonate

Soda-melilite

Solid solution

Disorder

*Ab initio*

Crystal

## ABSTRACT

The symmetry-adapted Monte Carlo sampling scheme is applied for the *ab initio* study of two mineral systems, namely the calcite structured compound  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$  and soda-melilite  $(\text{Na,Ca})\text{AlSi}_2\text{O}_7$ . It is shown how an extensive use of symmetry, from the sampling of atomic configurations up to the quantum-mechanical calculation, makes feasible the investigation of large configuration spaces. As for the sampling, we describe an effective procedure to specifically target low-energy configurations on the potential energy surface of supercells of virtually any size. It is based on the suggestion that a correlation between symmetry and energy of the configurations exists according to which atomic distributions of minimum and maximum energy are likely to have some spatial symmetry. This hypothesis is verified empirically and leads to a significant alleviation of the original problem by virtue of the possibility of tailoring the symmetry-adapted Monte Carlo to select only symmetric configurations. The latter are also found to display a probability distribution similar to that of the entire set of configurations, thus providing, eventually, a suitable *ab initio* reference for the parameterization of model Hamiltonians. The most stable configuration so identified is used as pivot for the selection of new configurations having the same atomic distribution but for the exchange of a couple of atoms. These are called “neighbors” to highlight both their structural and energetic proximity to the pivot. We illustrate how, by collecting neighbors of configurations of increasing energy, the description of the system can be progressively and deterministically improved up to convergence of the calculated average properties, whatever the temperature. The same scheme works when moving to a supercell larger than the initial one (but of equivalent symmetry) since it is shown that stable structures remain so at any volume.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Much of today's advanced technology is based on crystals. Several crystal properties are tuned by controlling the composition of solid solutions or the disorder at a given composition. In this context, modeling and simulation are important to allow for efficient design and testing. However, practical difficulties and methodological shortcomings have seriously hindered theoretical approaches to this kind of system so far. Both solid solutions and disordered materials are characterized by fractional occupations of some sites.

Natural examples are extremely common (mineral solid-solutions, non-stoichiometric compounds). Simulating fractional site occupations implies dealing with large low-symmetry supercells where different atomic distributions correspond to multitudes of structure configurations: their number increases as  $R^D$ , with  $R$  and  $D$  the species and sites, respectively. The result is an enormous computational effort that often forces to compromise on accuracy. A typical example is that of the cluster expansion (CE), where the truncation of the series of multi-body interaction terms (high-order terms are computationally prohibitive) prevents from guaranteeing convergence, and no structural relaxation is usually allowed.

Attempts to overcome these drawbacks were made by calculating the relative stability of configurations either randomly sampled

\* Corresponding author currently at: Materials Science Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720, USA.

E-mail address: [vlacivita@lbl.gov](mailto:vlacivita@lbl.gov) (V. Lacivita).

via a direct Monte Carlo (MC) or selected with the MC Metropolis algorithm [1]. However, some critical issues remain concerning the convergence of the Metropolis Markov chain [2] and the inefficiency of exploring the whole configuration space (CS) [3,4]. In fact, as was first suggested by Grau-Crespo et al. [4], the number of atomic configurations to be calculated can be drastically reduced by exploiting symmetry equivalences. The space group  $\mathcal{G}$  of the end-member structure - also called “aristotype”, i.e., the structure with the highest possible symmetry for the chosen system - partitions the configurations into symmetry-independent classes (SICs). Note that here by  $\mathcal{G}$  we mean a finite group factorized by the subgroup of lattice translations. The number of SICs is given by Pólya's theorem [5,6]. Configurations within a SIC are degenerate and share equivalent properties. Thus, sampling the SICs space is equivalent to sampling the CS, but indeed much more efficient because a single SIC covers a number of configurations equal to the multiplicity of the class itself. The multiplicity of a SIC  $i$  is easily calculated as  $\mathcal{M}_i = |\mathcal{G}|/|\mathcal{G}_i|$ , where  $|\mathcal{G}|$  is the cardinal of  $\mathcal{G}$  and  $|\mathcal{G}_i|$  is the number of symmetry operators retained by configurations within the  $i$ -th SIC.

Average properties can be computed considering either the full set of SICs (when not too large) or a subset of SICs randomly chosen. In the latter case, a bias issue emerges with standard MC samplings. In fact, given that multiplicity and number of symmetry operators of the SICs are inversely proportional, a random search performed directly on the CS naturally enhances the visibility of low-symmetry SICs, while high-symmetry classes are under-represented. This is particularly problematic because a conjectured energy-symmetry relationship suggests that the critical points on the potential energy surface (PES) correspond precisely to symmetric structures [7–9]. A well-documented example is that of binary calcite-structured carbonates [10–12]. To overcome this flaw, a novel symmetry-adapted Monte Carlo (SA-MC) sampling method has recently been developed [6,13] exploiting the fact that a uniform distribution on the SICs exists in Bayesian connection with the probability distribution of the conjugacy classes of the aristotype space group [14]. In this scheme, high- and low-symmetry SICs have the same draw probability and the sampling can even be tuned to favor symmetric classes, namely SICs that exhibit spatial symmetry elements other than the sole identity.

In the present work, we aim to explore the potential of the SA-MC sampling scheme via application to the case study of a solid solution of Ca-Mg carbonate,  $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$ . We will refer to a  $2 \times 2 \times 1$  hexagonal supercell of calcite (120 atoms, 144 symmetry operators, 24 cation sites available for substitution) of composition  $x = 0.25$ . This spans a CS of 134,596 possible cation distributions partitioned into 1033 SICs. The reason for this choice is that this is a fairly large number of SICs, such as to enable a meaningful test of the method without being prohibitive with respect to the computational resources at our disposal. Also, despite it is known that the solid solution  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$  is unstable at low temperatures [15], various experimental works have associated this composition to domains with ordered superstructures observed in magnesian calcites [16,17] and calcian dolomites [18,19]. Results obtained for other mineral systems (e.g., garnets, spinels, melilites) will also be reported to support outcomes of general character which will be highlighted along the way. As for our reference system, the space of the SICs has been analyzed entirely, by computing from first-principles one fully-relaxed structure for each class. Calculations were performed at the B3LYP hybrid level of theory using the CRYSTAL14 [20] software package, which features various options to generate SICs for a chosen composition and to carry out the ensuing geometry optimizations in a massively parallel computing framework.

To the authors' knowledge, this is the first fully *ab initio* study of a complete (so large) CS in a calcite-type carbonate solid solution.

Previously, Burton and Van de Walle [10] used a combination of quantum-mechanical and cluster expansion Hamiltonians as a powerful and computationally less expensive approach to construct complete phase diagrams by sampling large CS at different compositions. This is not the case here since we considered only one composition. Our goal in the present work is to outline strategies to tackle multiconfigurational simulations just from first-principles. We believe it is worth attempting this route in order to enable access to accurate local geometries, electronic structures, vibrational properties, etc. This might give new insight for theoretical understanding of crystal physics.

Relying on a comprehensive and accurate knowledge of the CS of the  $2 \times 2 \times 1$  supercell of solid solution  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$ , we verify the alleged connection between space group symmetry of the SICs and critical points of the PES. This turns out to be appealing in the prospect of tuning the SA-MC sampling to favor symmetric SICs because they are far less numerous than the asymmetric ones. From this observation stems the operative protocol we propose here for an effective *ab initio* computational approach to solid solutions and disordered crystalline systems via the SA-MC method. Essentially, the path is targeted to the identification of local energy minima on the PES and to the subsequent exploration of their surroundings. The first step consists in computing minimum energy structures for the subset of symmetric SICs which are likely to span the whole energy range. Once selected the most stable SIC among these, configurations nearby are generated by swapping two atoms involved in the disorder at a time. Those “neighbors” (so we will call them in the following) not equivalent to the parent structure (which will also be called pivot as a shortcut), nor to the other SICs already attained, are then structurally optimized and add up to the whole analyzed sample. Afterwards, the same procedure is repeated for the second most stable SIC and so forth. We will show that such approach allows tracing a systematic route to the convergence of the calculated properties while the number of calculations is minimized avoiding repetitions.

The described procedure relies on the simple assumption that two structures with almost equal atomic distributions should be very close in energy. Obviously, if one assimilates the exchange of atoms to the introduction of a defect in the mother structure, it is to be expected that the energy difference between the pivot and its neighbors depends on the size of the supercell which determines the interaction distance between the defects. The wider the supercell, the more the defects are spaced out, so that their interactions are damped and the difference in energy is reduced.

The question as to what is a proper size for the adopted structural model is of major concern in the simulation of solid solutions and disordered crystalline systems. In general, the larger the supercell the closer the comparison with the real system, but the magnitude of the SICs space quickly blows up. It is necessary to find a balance between accuracy and computational feasibility through careful consideration of the type of system under study and the properties of interest. For example, relating with thermodynamic properties, it is well-known that Gibbs free energy and configuration entropy converge much more slowly than the enthalpy with the size of the supercell [1]. Below we will show the case for our reference system.

When the number of SICs becomes unworkable, as it easily happens in presence of comparable concentrations of exchangeable species, some strategy must be conceived. One way around the problem was attempted by Vinograd et al. [11] who cluster expanded a large set of force-field relaxed static structure energies after testing the adequacy of the empirical interatomic potentials against previous *ab initio* calculations. The strategy we propose here leans on the preliminary analysis of a cell small enough to allow for a full investigation of its SICs space. Assuming that stable and unstable SICs remain such or close to being so in a larger

Download English Version:

<https://daneshyari.com/en/article/5453554>

Download Persian Version:

<https://daneshyari.com/article/5453554>

[Daneshyari.com](https://daneshyari.com)