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Supercell design for first-principles simulations of solids and application to diamond, silica, and superionic water

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ABSTRACT

For efficient first-principles computation of crystalline materials at high density and temperature, an optimal choice of the supercell is important to minimize finite size errors. An algorithm is presented to construct compact supercells for arbitrary crystal structures. Rather than constructing standard supercells by replicating the conventional unit cell, we employ the full flexibility that we gain by using arbitrary combinations of the primitive cell vectors in order to construct a series of cubic and nearly cubic supercells. In cases where different polymorphs of a material needed to be compared, we are able construct supercells of consistent size. Our approach also allows us to efficiently study the finite size effects in systems like superionic water where they would otherwise difficult to obtain because a standard replication of the unit cells leads to supercells that are too expensive to be used for first-principles simulations. We apply our method to simple, body-centered, and face-centered cubic as well as hexagonal close packed cells. We present simulation results for diamond, silica in the pyrite structure, and superionic water with an face-centered cubic oxygen sub-lattice. The effects of the finite simulation cell size and Brillouin zone sampling on the computed pressure and internal energy are analyzed.

1. Introduction

First-principles computer simulations contribute to our understanding of a wide range of phenomena in physics [1], chemistry [2], geophysics [3–5], and to some extend also in molecular biology [6]. While ground-state calculations of crystalline materials can often be performed in primitive crystallographic cells with a small number of atoms, simulations at finite temperature require cells with a much larger number of atoms. To simulate liquids, one typically chooses cubic cells [7] and increases the number of atoms until the artificial correlation, that is introduced by the periodic boundary conditions, has a negligible impact on the computed properties [8]. Simulations of crystalline materials often require the consideration of a comparable number of atoms. Therefore, one constructs supercells by replicating the primitive cell in all spatial directions. Such supercells allow one to perform density functional molecular dynamics simulations (DFT-MD) to determine the thermodynamic properties of solids [9–11] at elevated temperatures where the quasi-harmonic approximation is no longer applicable [12]. Quasi-harmonic calculations typically use primitive cells and perturbation theory [13] but, occasionally, supercells are still in use [14]. Supercells are also employed to study the effects of disorder in different types of alloys and solid solutions [15–18]. Computational studies of defects in solids also require supercells to reduce the interaction between defect images [19–27]. For simulations of materials with incommensurate crystal structures, one also constructs periodic supercells that approximate incommensurate spatial periodicities as close as possible [28,29]. The determination of the magnetic state of a structure with multiple transition metal atoms may also require supercells [30–32]. The computation of x-ray absorption near edge structures (XANES) is performed in supercells [33]. Direct melting simulations and the two-phase methods [34,35] also rely on supercells. Variable cell dynamics simulations [3] as well as the study of amorphization [36] and other structural changes in solids [37] employ supercells as well. Quantum Monte Carlo (QMC) calculations employ supercells to better capture the interaction effect between all electrons [4,38,39]. Since QMC calculations are significantly more expensive than density functional simulations, one is even more constrained when choosing the supercell.

Despite all these applications, no general algorithm exists to construct appropriate supercells molecular dynamics or Monte Carlo simulation where one wants to minimize the artificial interaction between period images. For cubic cells, one typically replicates the unit cell uniformly in all spatial directions, $n \times n \times n$. This may, however, lead rather rapidly to cells that are prohibitively expensive. In the case of superionic water in a face-centered cubic (fcc) structure, the cubic unit cell has four water molecules. Thus, in Ref. [40], most simulations were performed in a $2 \times 2 \times 2$ with supercell with 32 molecules and only one, rather demanding finite-size test with 108

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molecules was conducted. In an earlier study of body-centered cubic (bcc) superionic water [41], results for $2\times2\times2$ and $3\times3\times3$ supercells with 56 and 128 molecules, respectively, were reported. No other cells were considered while, as we demonstrate in the article, a number of intermediate nearly cubic cells could have been chosen to facilitate a more efficient finite-size analysis.

Supercells of different shapes have constructed to study solid solutions where, e.g., atoms of type A or B can occupy the sites in an fcc or bcc lattice [42]. Algorithms have been advanced to generate *all possible* configurations for a given supercell size [43] and efficient methods exit to remove symmetry-equivalent configurations [44]. The goal of our algorithm is different, however. We do not deal with atomic disorder and, rather than generating all possible supercells, we want to construct the best possible supercell for a given size in order to minimize finite-size effects in many-body simulations.

The question of choosing the appropriate supercell becomes even more difficult when one deals with non-cubic primitive cells. For orthorhombic structures, one may construct $n_1\times n_2\times n_3$ supercells that are nearly cubic while preserving the orthorhombic character. For arbitrary triclinic cells, it is less obvious how to proceed. For water ice at megabar pressures [45], a monoclinic structure with $P2_1$ symmetry, an orthorhombic structure with *Pcca*, and a hexagonal structure with $P3_121$ symmetry have recently been predicted to form at zero temperature [46]. To determine whether these groundstate structures lead to superionic systems that are thermodynamically more stable than the recently predicted fcc structure, one needs to construct supercells, heat the structure up in with DFT-MD simulations and compare their Gibbs free energies that may be obtained via thermodynamic integration (TDI) [40]. For the monoclinic, orthorhombic, hexagonal structures, one would want to construct supercells that are again nearly cubic. Ideally one would choose a cell of comparable size as in the bcc and fcc calculations but there is no straightforward method available to construct such cells.

The question how to construct supercells of comparable size for different structures will always be relevant when a material has different polymorphs that need to be compared. Silica, SiO_2 is a archetypal example with more than ten crystal structures [4,5]. Its pyrite-type polymorph has a cubic unit cell with 12 atoms. We will demonstrate that various reasonable supercell choices exist in additiona to a simple $n\times n\times n$ replication.

Recently, significant progress has been made in predicting groundstate crystal structures with evolutionary algorithms [47], random search techniques [46,48], and others methods [49], and number of theoretical predictions have later been confirmed experimentally [50]. Crystal structure prediction at higher temperature outside of the quasi-harmonic regime is more difficult and requires the comparison of the Gibbs free energy of thousands of structures. Supercells need to be constructed in order to facilitate DFT-MD simulations and TDI calculations [51–55]. Rather than relying on human intervention, we would want to use a computer algorithm that constructs reasonable supercells automatically for any cell shape, which is the goal of this article.

2. Methods

Rather than constructing standard $n\times n\times n$ supercells by replicating the conventional unit cell, we employ the full flexibility that we gain by using an arbitrary combination of the primitive cell vectors, $\vec{a}$, $\vec{b}$, and $\vec{c}$. We construct vectors of the supercell from a linear combination of the primitive cell vectors [56],

$$\begin{aligned}\vec{a}_{\rm SS} &= i_a\vec{a}+j_a\vec{b}+k_a\vec{c},\\ \vec{b}_{\rm SS} &= i_b\vec{a}+j_b\vec{b}+k_b\vec{c},\\ \vec{c}_{\rm SS} &= i_c\vec{a}+j_c\vec{b}+k_c\vec{c}\,.\end{aligned}\tag{1}$$

For each supercell vector, the coefficients i, j, and k are arbitrary integers that we restrict to take values from $-$n to n. We typically set n between 5 and 10. j_a, k_a, and k_b can be set zero for bcc and fcc lattices [44]. In general, however, the construction of a supercell turns into a 9-dimensional optimization problem but symmetry arguments can be used to reduce the search space significantly,

$$\left[\vec{a}_{\rm SS},\vec{b}_{\rm SS},\vec{c}_{\rm SS}\right](V_{\rm SS})=\max_{i_a=1}^{n}\max_{j_a=-{\rm n}}^{n}\max_{k_a=-{\rm n}}^{n}\max_{i_b=-{\rm i_a}}^{i_a}\max_{j_b=-{\rm n}}^{n}\max_{k_b=-{\rm n}}^{n}\Big[\ \ldots\ \underset{|\vec{a}_{\rm SS}|>0}{}\ \underset{|\vec{b}_{\rm SS}|>0}{}$$
$$\ldots\max_{i_c=-|i_b|}^{|i_b|}\max_{j_c=-|j_b|}^{|j_b|}\max_{k_c=-{\rm n}}^{n}\ \underset{(\vec{a}_{\rm SS}\times\vec{b}_{\rm SS})\cdot\vec{c}_{\rm SS}=V_{\rm SS}}{}\ \mathcal{O}(\vec{a}_{\rm SS},\vec{b}_{\rm SS},\vec{c}_{\rm SS})\ \Big].\tag{2}$$

The volume of the supercell can only be a multiple of primitive cell volume, $V_{\rm SS}=mV_{\rm P}$. For a given volume ratio, m, one needs to decide what optimization criteria, $\mathcal{O}$, to employ. There are two obvious choices.

(a) First one can maximize the distance to the nearest periodic image, $d_{\rm min}$. In the limit of large m, this will not lead to formation of cubic cells. Rather hexagonal cells with $|\vec{a}_{\rm SS}|=|\vec{b}_{\rm SS}|=|\vec{c}_{\rm SS}|$, $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$ will be favored[1]. While this may be a valid criteria for some problems, for fcc systems, it means that the conventional cubic supercells would not be reproduced.

(b) Alternatively one can design compact cells by minimizing the radius of a sphere that is needed to enclose the supercell. For a given cell, this radius is given by the maximum distance that any cell corner is separated from the cell center,

$$R_{\rm max}=\max_{\substack{i=\{-1,+1\}\\ j=\{-1,+1\}\\ k=\{-1,+1\}}}\frac{1}{2}\left|i\vec{a}_{\rm SS}+j\vec{b}_{\rm SS}+k\vec{c}_{\rm SS}\right|.\tag{3}$$

This criteria allows us to pick cubic and nearly cubic cells. For the remainder of this article, we employ the following optimization strategy. We use (b) as our primary criteria. If the $R_{\rm max}$ values of two cells are identical, we select the cell with the larger minimum image distance, $d_{\rm min}$. In rare cases where both of those values are identical also, we prefer the cell where the angles deviate the least from 90° and where the cell vectors deviate the least from each other in length.

The minimum image distance is defined as,

$$d_{\rm min}=\lim_{n=1}^{\infty}\min_{(i,j,k)=-{\rm n}}^{n}\left|i\vec{a}_{\rm SS}+j\vec{b}_{\rm SS}+k\vec{c}_{\rm SS}\right|,\qquad i^2+j^2+k^2>0\tag{4}$$

but one needs a more efficient method for its determination that is applicable to arbitrary cell shapes. We use the following approach where the lattice vectors are re-assigned to point to closer images. We start with the assignment, $\vec{a}'_{\rm SS}=\vec{a}_{\rm SS}$, $\vec{b}'_{\rm SS}=\vec{b}_{\rm SS}$, and $\vec{c}'_{\rm SS}=\vec{c}_{\rm SS}$ and order the vectors by magnitude such that, $|\vec{a}'_{\rm SS}|\le|\vec{b}'_{\rm SS}|\le|\vec{c}'_{\rm SS}|$. Then we successively derive new vectors that point to closer and closer images using the following re-assignments,

$$\vec{b}'_{\rm SS}\ \rightarrow\ \vec{b}'_{\rm SS}-\vec{a}'_{\rm SS}\,{\rm round}\,[\vec{b}'_{\rm SS}\cdot\vec{a}'_{\rm SS}/\vec{a}'^2_{\rm SS}],\tag{5}$$

$$\vec{c}'_{\rm SS}\ \rightarrow\ \vec{c}'_{\rm SS}-\vec{a}'_{\rm SS}\,{\rm round}\,[\vec{c}'_{\rm SS}\cdot\vec{a}'_{\rm SS}/\vec{a}'^2_{\rm SS}],\tag{6}$$

$$\vec{c}'_{\rm SS}\ \rightarrow\ \vec{c}'_{\rm SS}-\vec{b}'_{\rm SS}\,{\rm round}\,[\vec{c}'_{\rm SS}\cdot\vec{b}'_{\rm SS}/\vec{b}'^2_{\rm SS}].\tag{7}$$

We keep re-assigning and re-ordering these vectors until no more changes occur. Then we can derive $d_{\rm min}$ from $\vec{a}'_{\rm SS}$, $\vec{b}'_{\rm SS}$, and $\vec{c}'_{\rm SS}$ by setting $n=1$ in Eq. (4).

[1] We derived this result using a simulated annealing technique that optimized minimum image distance by varying all cell parameters at constant volume.