

UC Berkeley

UC Berkeley Previously Published Works

Title

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

Permalink

<https://escholarship.org/uc/item/71s2s5fh>

Author

Militzer, B

Publication Date

2016-12-01

DOI

10.1016/j.hedp.2016.09.003

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Supercell Design for First-Principles Simulations of Solids and Application to Diamond, Silica, and Superionic Water

Burkhard Militzer

Department of Earth and Planetary Science, Department of Astronomy, University of California, Berkeley, CA 94720, USA

E-mail: militzer@berkeley.edu

December 9, 2015

Abstract. An algorithm is presented to construct compact supercells for first-principles computer simulations of crystalline materials. 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 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 with same size. Our approach also allows us to study the finite size effects efficiently in systems like superionic water where they would otherwise difficult to obtain because a standard $n \times n \times n$ -fold replication of the unit cells leads to supercells that are disproportionately 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, SiO_2 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.

PACS numbers: 71.15.-m, 63.20.dk, 64.10.+h, 71.15.Pd

Keywords: first-principles computer simulations, Submitted to: *J. Phys. A: Math. Gen.*

1. Introduction

First-principles computer simulations contribute to our understanding of a wide range of phenomena in physics [1], chemistry [2], geophysics [3, 4, 5], and to some extent 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, 10, 11] at elevated temperatures where the quasi-harmonic approximation is no longer applicable. Quasi-harmonic calculations typically use primitive cells and perturbation theory [12] but, occasionally, supercells are still in use [13]. Supercells are also employed to study the effects of disorder in different types of alloys and solid solutions [14, 15, 16, 17]. Computational studies of defects in solids also require supercells to reduce the interaction between defect images [18, 19, 20, 21, 22, 23, 24, 25, 26]. For simulations of materials with incommensurate crystal structures, one also constructs periodic supercells that approximate incommensurate spacial periodicities as close as possible [27, 28]. The determination of the magnetic state of a structure with multiple transition metal atoms may also require supercells [29, 30, 31]. The computation of x-ray absorption near edge structures (XANES) is performed in supercells [32]. Direct melting simulations and the two-phase methods [33, 34] also rely on supercells. Variable cell dynamics simulations [3] as well as the study of amorphization [35] and other structural changes in solids [36] employ supercells as well. Quantum Monte Carlo (QMC) calculations employ supercells to better capture the interaction effect between all electrons [37, 4, 38]. 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 want to minimize the unwanted interaction between period images. For cubic cells, one typically replicates the unit cell, $n \times n \times n$. 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. [39], 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 molecules was conducted. In an earlier study of body-centered cubic (bcc) superionic water [40], results for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ 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 been constructed to study solid solutions where, e.g., atoms of type A or B can occupy the sites on an fcc or bcc lattice [41]. Algorithms have been advanced to generate *all possible* configurations for a given supercell size [42] and efficient methods exist to remove symmetry-equivalent configurations [43]. 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 predict the best possible supercell for given size that 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 [44], 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 [45]. 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) [39]. 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 other reasonable supercell choices exist than just a simple $n \times n \times n$ replication.

Recently, significant progress has been made in predicting groundstate crystal structures with evolutionary algorithms [46], random search techniques [47, 45], and other methods [48], and number of theoretical predictions have later been confirmed experimentally [49]. 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 [50, 51, 52, 53, 54]. 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 [55],

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

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 [43]. 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,

$$\begin{aligned}[\vec{a}_{\text{SS}}, \vec{b}_{\text{SS}}, \vec{c}_{\text{SS}}] (V_{\text{SS}}) &= \max_{i_a=1}^n \max_{j_a=-n}^n \max_{\substack{k_a=-n \\ |\vec{a}_{\text{SS}}| > 0}}^n \max_{i_b=-i_a}^{i_a} \max_{j_b=-n}^n \max_{\substack{k_b=-n \\ |\vec{b}_{\text{SS}}| > 0}}^n [\dots \\ &\dots \max_{i_c=-|i_b|}^{|i_b|} \max_{j_c=-|j_b|}^{|j_b|} \max_{\substack{k_c=-n \\ (\vec{a}_{\text{SS}} \times \vec{b}_{\text{SS}}) \cdot \vec{c}_{\text{SS}} = V_{\text{SS}}}}^n \mathcal{O}(\vec{a}_{\text{SS}}, \vec{b}_{\text{SS}}, \vec{c}_{\text{SS}})] .\end{aligned}\tag{2}$$

The volume of the supercell can only be a multiple of primitive cell volume, $V_{\text{SS}} = mV_{\text{P}}$. 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_{min} . In the limit of large m , this will not lead to formation of cubic cells. Rather hexagonal cells with $|\vec{a}_{\text{SS}}| = |\vec{b}_{\text{SS}}| = |\vec{c}_{\text{SS}}|$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ will be favored ‡. 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,

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

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_{max} values of two cells are identical, we select the cell with the larger minimum image distance, d_{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,

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

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

Table 1. Supercells of the fcc structure with 3 atoms per primitive cell, which is needed to calculation of dense, superionic water. N specifies the number of atoms per cell. V_{SS}/V_P is the volume ratio of the supercell and the primitive cell. R_{\max} and d_{\min} are the cell radii and minimum image distances according to Eqs. 3 and 4. The supercells are defined in terms of the integers i, j , and k (Eq. 2), lattice parameters and angles. All dimensional parameters have been normalized with respect to the lattice parameter a . Cubic cells with $V_{SS}/V_P = 4n^3$ are marked by a †.

N	V_{SS}/V_P	R_{\max}/a	d_{\min}/a	i_a	j_a	k_a	i_b	j_b	k_b	i_c	j_c	k_c	$ a_{SS} /a$	$ b_{SS} /a$	$ c_{SS} /a$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
3	1	0.7906	0.7071	1	0	0	1	-1	0	0	0	-1	0.7071	0.7071	0.7071	90.0	120.0	60.0
12	4†	0.8660	1.0000	1	1	-1	1	-1	1	1	-1	-1	1.0000	1.0000	1.0000	90.0	90.0	90.0
21	7	1.1180	1.2247	1	1	0	-1	2	-1	-1	0	2	1.2247	1.2247	1.2247	99.6	80.4	80.4
39	13	1.5000	1.5811	2	1	-1	2	-1	-2	-1	1	-2	1.5811	1.5811	1.5811	72.5	107.5	72.5
69	23	1.7678	1.7321	3	-1	0	-1	3	-1	-1	0	3	1.8708	1.7321	1.8708	90.0	85.9	108.0
78	26	1.7321	1.8708	2	1	0	-2	3	-1	-2	0	3	1.8708	1.8708	1.8708	85.9	94.1	94.1
96	32†	1.7321	2.0000	2	2	-2	2	-2	2	2	-2	-2	2.0000	2.0000	2.0000	90.0	90.0	90.0
114	38	1.8708	2.1213	2	2	-1	-2	3	-2	-2	1	3	2.1213	2.1213	2.1213	93.2	86.8	86.8
150	50	2.1213	2.3452	2	1	1	-2	4	-1	-2	-1	4	2.3452	2.3452	2.3452	97.8	82.2	82.2
210	70	2.4238	2.5495	3	2	-2	-2	4	-3	-2	2	3	2.5495	2.7386	2.5495	90.0	87.8	79.7
276	92	2.5495	2.7386	4	1	-2	-3	4	2	-1	3	-4	2.7386	3.0822	2.7386	88.3	88.1	95.1
288	96	2.5000	2.8284	4	-4	0	-3	-3	3	0	0	-4	2.8284	3.0000	2.8284	90.0	90.0	90.0
300	100	2.6926	2.9155	4	1	-1	-2	5	-1	-1	-1	5	2.9155	2.9155	3.0000	93.3	86.7	79.8
324	108†	2.5981	3.0000	3	3	-3	3	-3	3	3	-3	-3	3.0000	3.0000	3.0000	90.0	90.0	90.0

Table 2. Supercells of the simple cubic pyrite structure with $N = 12$ atoms per primitive cell. All parameters are given in the format of Tab. 1. Cubic cells with $V_{SS}/V_P = n^3$ are marked by a †.

N	V_{SS}/V_P	R_{\max}/a	d_{\min}/a	i_a	j_a	k_a	i_b	j_b	k_b	i_c	j_c	k_c	$ a_{SS} /a$	$ b_{SS} /a$	$ c_{SS} /a$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
12	1†	0.8660	1.0000	1	0	0	0	1	0	0	0	-1	1.0000	1.0000	1.0000	90.0	90.0	90.0
36	3	1.5000	1.4142	1	0	1	1	1	0	1	-1	-1	1.4142	1.4142	1.7321	90.0	90.0	60.0
84	7	2.0616	1.7321	2	0	1	1	2	0	1	-1	-1	2.2361	2.2361	1.7321	105.0	75.0	66.4
96	8†	1.7321	2.0000	2	0	0	0	2	0	0	0	-2	2.0000	2.0000	2.0000	90.0	90.0	90.0
156	13	2.2913	2.2361	2	1	1	1	-2	-1	0	-1	2	2.4495	2.4495	2.2361	90.0	79.5	99.6
168	14	2.2361	2.4495	2	1	1	1	-2	-1	-1	-1	2	2.4495	2.4495	2.4495	99.6	99.6	99.6
288	24	2.5000	2.8284	3	0	0	0	2	2	0	2	-2	3.0000	2.8284	2.8284	90.0	90.0	90.0
324	27†	2.5981	3.0000	3	0	0	0	3	0	0	0	-3	3.0000	3.0000	3.0000	90.0	90.0	90.0
396	33	2.8723	3.1623	3	1	0	1	-3	-1	0	-1	3	3.1623	3.3166	3.1623	90.0	95.7	90.0
456	38	3.2016	3.3166	3	1	1	2	-3	0	-1	-1	3	3.3166	3.6056	3.3166	85.2	95.2	75.5
624	52	3.2404	3.6056	4	0	0	0	3	2	0	2	-3	4.0000	3.6056	3.6056	90.0	90.0	90.0
672	56	3.5000	3.7417	3	2	1	2	-3	-2	-1	2	-3	3.7417	4.1231	3.7417	97.4	98.2	97.4
768	64†	3.4641	4.0000	4	0	0	0	4	0	0	0	-4	4.0000	4.0000	4.0000	90.0	90.0	90.0
876	73	3.9051	4.1231	4	1	1	1	-4	-1	0	-1	4	4.2426	4.2426	4.1231	90.0	80.1	93.2
912	76	3.7417	4.2426	4	1	1	1	-4	-1	-1	-1	4	4.2426	4.2426	4.2426	93.2	93.2	93.2
1116	93	4.0620	4.3589	3	3	1	3	-3	-2	-1	2	-4	4.3589	4.6904	4.5826	92.7	92.9	95.6
1200	100	4.0311	4.4721	5	0	0	0	4	2	0	2	-4	5.0000	4.4721	4.4721	90.0	90.0	90.0

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, $\vec{a}'_{SS} = \vec{a}_{SS}$, $\vec{b}'_{SS} = \vec{b}_{SS}$, and $\vec{c}'_{SS} = \vec{c}_{SS}$ and order the vectors by magnitude such that, $|\vec{a}'_{SS}| \leq |\vec{b}'_{SS}| \leq |\vec{c}'_{SS}|$. Then we successively derive new vectors that point to closer and closer images using the following re-assignments,

$$\vec{b}'_{SS} \rightarrow \vec{b}'_{SS} - \text{round}[\vec{b}'_{SS} \cdot \vec{a}'_{SS} / \vec{a}'_{SS}{}^2] \vec{a}'_{SS}, \quad (5)$$

$$\vec{c}'_{SS} \rightarrow \vec{c}'_{SS} - \text{round}[\vec{c}'_{SS} \cdot \vec{a}'_{SS} / \vec{a}'_{SS}{}^2] \vec{a}'_{SS}, \quad (6)$$

$$\vec{c}'_{SS} \rightarrow \vec{c}'_{SS} - \text{round}[\vec{c}'_{SS} \cdot \vec{b}'_{SS} / \vec{b}'_{SS}{}^2] \vec{b}'_{SS}. \quad (7)$$

We keep re-assigning and re-ordering these vectors until no more changes occur. Then we can derive d_{\min} by setting $n = 1$ in Eq. (4).

Table 3. Supercells of the bcc lattice with one atom per primitive cell. All parameters are given in the format of Tab. 1. Cubic cells with $V_{\text{SS}}/V_{\text{P}} = 2n^3$ are marked by a †.

N	$V_{\text{SS}}/V_{\text{P}}$	R_{max}/a	d_{min}/a	i_a	j_a	k_a	i_b	j_b	k_b	i_c	j_c	k_c	$ a_{\text{SS}}/a$	$ b_{\text{SS}}/a$	$ c_{\text{SS}}/a$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
1	1	0.8292	0.8660	1	0	0	1	-1	-1	0	-1	0	0.8660	0.8660	0.8660	70.5	109.5	70.5
2	2†	0.8660	1.0000	1	0	-1	1	-1	0	0	-1	-1	1.0000	1.0000	1.0000	90.0	90.0	90.0
6	6	1.4790	1.4142	2	-1	-2	-1	2	1	-1	0	-1	1.6583	1.4142	1.4142	90.0	90.0	115.2
9	9	1.4790	1.6583	2	0	-1	1	-2	-2	-1	1	-1	1.6583	1.6583	1.6583	84.8	95.2	84.8
16	16†	1.7321	2.0000	2	0	-2	2	-2	0	0	-2	-2	2.0000	2.0000	2.0000	90.0	90.0	90.0
21	21	2.0616	2.1794	3	-1	-2	-1	3	1	-1	0	-2	2.2361	2.1794	2.1794	87.0	95.9	95.9
25	25	2.2776	2.2361	3	-1	-3	-2	3	1	-1	-1	-2	2.5981	2.2361	2.2361	90.0	85.1	105.0
28	28	2.2361	2.4495	3	0	-1	2	-3	-3	-1	1	-2	2.4495	2.4495	2.4495	80.4	99.6	80.4
35	35	2.2776	2.5981	3	0	-2	-2	3	0	0	-2	-3	2.5981	2.5981	2.5981	87.9	92.1	87.9
48	48	2.5000	2.8284	3	0	-3	2	-4	-2	-2	0	-2	3.0000	2.8284	2.8284	90.0	90.0	90.0
53	53	2.8614	2.9580	3	1	-1	3	-3	-4	-2	3	-1	2.9580	3.0000	3.1623	96.1	83.9	73.6
54	54†	2.5981	3.0000	3	0	-3	3	-3	0	0	-3	-3	3.0000	3.0000	3.0000	90.0	90.0	90.0
65	65	3.0311	3.2787	4	0	-1	3	-4	-4	-1	1	-3	3.2787	3.2787	3.2787	77.9	102.1	77.9
84	84	3.1125	3.3166	4	0	-2	2	-4	-4	-2	3	-2	3.3166	3.3166	3.8406	92.2	87.8	84.8
91	91	3.1125	3.5707	4	0	-3	-3	4	0	0	-3	-4	3.5707	3.5707	3.5707	88.9	91.1	88.9
103	103	3.3448	3.6056	5	-1	-2	-2	5	3	0	-1	4	3.7417	3.6056	3.8406	92.1	94.0	94.3
107	107	3.4187	3.7417	5	-1	-2	2	-5	-4	-1	2	-3	3.7417	3.8406	3.7417	90.0	94.1	86.0
112	112	3.4187	3.8406	5	-1	-1	-1	5	1	-1	1	5	3.8406	3.8406	3.8406	94.9	85.1	85.1
128	128†	3.4641	4.0000	4	0	-4	4	-4	0	0	-4	-4	4.0000	4.0000	4.0000	90.0	90.0	90.0

Table 4. Supercells of hexagonal close packed lattice with the ideal ratio, $c/a = \sqrt{8/3}$. All parameters are given in the format of Tab. 1.

N	$V_{\text{SS}}/V_{\text{P}}$	R_{max}/a	d_{min}/a	i_a	j_a	k_a	i_b	j_b	k_b	i_c	j_c	k_c	$ a_{\text{SS}}/a$	$ b_{\text{SS}}/a$	$ c_{\text{SS}}/a$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
2	1	0.6680	0.5612	1	0	0	1	1	0	0	0	1	0.5612	0.5612	0.9165	90.0	90.0	60.0
6	3	0.9585	0.9165	2	1	0	1	-1	0	0	0	-1	0.9721	0.9721	0.9165	90.0	90.0	60.0
12	6	1.0747	0.9721	2	2	1	1	1	-1	-1	1	0	1.4491	1.0747	0.9721	90.0	90.0	97.7
16	8	1.1225	1.1225	2	0	0	1	2	1	1	2	-1	1.1225	1.3360	1.3360	86.6	90.0	90.0
22	11	1.3651	1.3360	3	1	0	1	2	1	0	-2	1	1.4849	1.3360	1.4491	93.1	81.6	76.2
28	14	1.4760	1.4491	2	-1	1	-2	-2	1	0	-2	-1	1.7449	1.4491	1.4491	95.7	80.4	78.0
32	16	1.4491	1.4849	3	1	0	-1	-3	0	0	0	-2	1.4849	1.4849	1.8330	90.0	90.0	98.2
42	21	1.5540	1.7449	3	1	1	2	3	-1	-1	2	1	1.7449	1.7449	1.7449	85.1	94.9	85.1
54	27	1.7449	1.9170	3	0	1	3	3	-1	0	-3	-1	1.9170	1.9170	1.9170	99.0	81.0	81.0
74	37	1.8963	2.0235	4	1	0	-1	-4	-1	-1	-2	2	2.0235	2.2214	2.0748	87.4	96.5	88.0
78	39	1.9776	2.0748	4	2	1	1	-3	-1	-1	-2	2	2.1494	2.2214	2.0748	93.3	80.5	88.7
84	42	2.0171	2.1494	3	-1	1	-3	-4	1	0	-2	-2	2.2214	2.2214	2.1494	91.3	91.3	82.1
106	53	2.1676	2.2214	4	0	1	3	4	-1	0	-3	-2	2.4248	2.2214	2.4889	97.1	88.0	85.5
124	62	2.2969	2.3590	5	2	0	-1	-4	2	-1	-3	-2	2.4463	2.7303	2.3590	93.3	97.8	95.4
130	65	2.3422	2.4248	4	0	1	3	4	-2	0	-3	-2	2.4248	2.7303	2.4889	81.6	88.0	93.6
138	69	2.2969	2.4463	5	1	0	-2	-5	0	0	0	-3	2.5719	2.4463	2.7495	90.0	90.0	94.3
152	76	2.3976	2.6124	4	2	2	3	4	-2	-2	3	1	2.6720	2.7303	2.6124	89.6	91.7	94.1
160	80	2.3976	2.6720	5	0	0	2	4	2	2	4	-2	2.8062	2.6720	2.6720	86.6	90.0	90.0
176	88	2.4410	2.7303	5	0	1	3	4	-2	-1	-4	-2	2.9520	2.7303	2.7303	90.8	90.7	90.7
180	90	2.4463	2.7495	6	3	0	0	-5	0	0	0	-3	2.9162	2.8062	2.7495	90.0	90.0	90.0
200	100	2.5668	2.8062	5	0	0	3	6	1	1	2	-3	2.8062	3.0569	2.9162	88.0	90.0	90.0

3. Discussion of Cell Design

In Fig. 1, we plotted R_{max} and d_{min} for the supercells that we constructed by starting from the primitive cell of fcc lattice. For every cell size $V_{\text{SS}}/V_{\text{P}}$, we identified the most compact cell according to the optimization criteria that we derived in the previous section. The goal was to construct cells with an R_{max} that is as close as possible to the ideal value of cube, $V_{\text{SS}}^{1/3} \sqrt{3}/2$. For cubic cells with $V_{\text{SS}}/V_{\text{P}} = 4n^3$, this value is recovered. For all other cells, R_{max} is found to reasonably close to the ideal value. The deviations are typically no larger than $0.25a$, where a is the size of the cubic.

The lower panel Fig. 1 shows the minimum image distances for every cell. For a given cell size, this value should be as large as possible in order to minimize the correlation effects between particles during molecular dynamics simulations. One notices that for some cells, the d_{min} falls above the curve for a cubic cell given by $d_{\text{min}}^{\text{cubic}} = V_{\text{SS}}^{1/3}$. This is because hexagonal cells, rather than cubic ones, have the largest minimum image

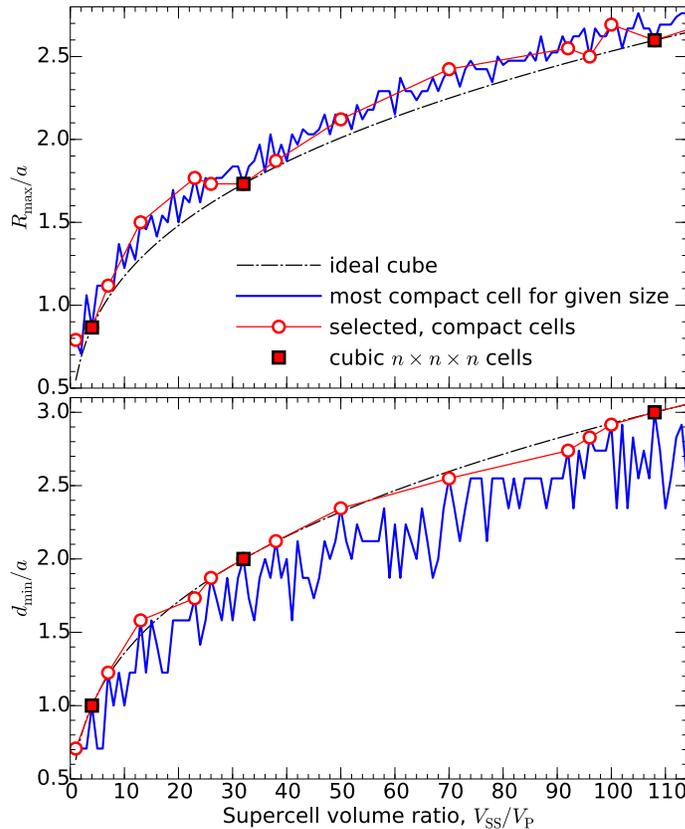


Figure 1. (Color online) Radius, R_{\max} , (Eq. 3) and minimum image distance, d_{\min} , (Eq. 4) of supercells that were constructed from the primitive cell of fcc lattice with lattice parameter a . The solid, blue lines correspond to cells with smallest R_{\max} for a given cell volume. The open circles correspond to a subset of selected, compact cells that have a larger minimum image distance than all smaller cells. The squares denote cubic supercells with $V_{\text{SS}} = 4n^3V_{\text{P}}$ where n is an integer. The dash-dotted line shows R_{\max} and d_{\min} for a cubic cell of arbitrary, non-integer values of n .

distances for given volume.

Furthermore one notices that d_{\min} does not monotonously increase with volume. One would have expected that a larger cell size automatically leads to an increase in the minimum image distance. But the cells differ in shape and in many cases, the minimum image distance of a larger cell is smaller or equal to that of a well-selected smaller one. So it is not obvious why one should invest the computer time into simulating with an larger cell if it does not also lead to an increase in the minimum image distance over all possible smaller cells. For this reason, we constructed a subset of cells where an increase in size also led to a new record in the minimum image distance compared to all smaller cells. We marked the cells in this subset in Fig. 1 and reported their parameters in Tab. 1. The ideal cubic cells are included in the subset. From now on we refer to this subset as set of *compact* cells. All DFT-MD simulations, to be discussed in the next

section, were performed only for such compact supercells. Tables 2, 3, and 4 list the parameters for the compact supercells for simple cubic, bcc, and hexagonal close packed lattices, respectively.

The angles and supercell vector lengths in Tab. 1 show that it becomes easier to construct nearly cubic supercells with increasing cell size. For large supercells there are simply more possibilities to combine the primitive cells to construct supercells with specific size. In the limit of infinite supercells size, one expects the deviations from a cubic shape to disappear completely. Already for $V_{SS}/V_P \geq 13$, one finds that all cell angles deviate from 90° by 10.5° or less. All vector lengths deviate by less than 8.5% from the corresponding value of a cubic cell.

4. Accomodation of Two Crystal Structures

Our optimization scheme in Eq. 2 is general and can be combined with other design criteria, $\mathcal{O}(\vec{a}_{SS}, \vec{b}_{SS}, \vec{c}_{SS})$, for specific applications. We will give one more example in this section where we design supercells that can accomodate two different crystal structures. We will construct supercells that are commensurate with, e.g., an fcc and an hcp lattice, which becomes of interest for crystallization calculations when one wants to eliminate, or at least minimize, the bias from a particular supercell choice. This is of interest for the simulation of materials that show an hcp-fcc transition in their pressure-temperature phase diagrams, such as gold [56], iron at 30 GPa and elevated temperatures [57] as well as at 700 GPa and low temperature [58], iron-nickel alloys at conditions of the Earth's core [59] and many others.

The task of finding a supercell that accomodates two crystal structures shares some similarities with constructing approximate, commensurate cells for incommensurate structures [27, 28] but there is one main difference. In our case there is no need for both structures to be aligned in the supercell. In fact, when we minimize the mismatch between hcp and fcc supercell vectors, we allow for an arbitrary rotation by the Euler angles, ϕ, θ , and ψ . We introduce the rotation matrix, $\mathcal{R}_{\phi, \theta, \psi}$, and define the mismatch parameter,

$$\delta_{\text{fcc-hcp}} = \min_{\phi, \theta, \psi} \left[(\vec{a}_{SS}^{\text{fcc}} - \mathcal{R}_{\phi, \theta, \psi} \vec{a}_{SS}^{\text{hcp}})^2 + (\vec{b}_{SS}^{\text{fcc}} - \mathcal{R}_{\phi, \theta, \psi} \vec{b}_{SS}^{\text{hcp}})^2 + (\vec{c}_{SS}^{\text{fcc}} - \mathcal{R}_{\phi, \theta, \psi} \vec{c}_{SS}^{\text{hcp}})^2 \right]^{1/2}, \quad (8)$$

that measures the deviation between the both sets of lattice vectors. We minimize δ by first determining the 100 most compact hcp supercells for a given size. For each hcp supercell, a pick a random rotation matrix, and identify the closest set of fcc lattice vectors. We use the BGFS algorithm [60] to optimize the Euler angles in order to converge to the closest local minimum of δ . This procedure is repeated many time in an attempt to find the global minimum of δ .

Figure 2 and Table 5 report the best supercells that we constructed. We able to obtain two compact supercells with respectively 156 and 480 atoms that accomodate and hcp and fcc lattices prefectly. Many other supercells with a small mismatch parameter of $\delta < 0.07 a_{\text{hcp}}$ have been identified as well.

We also constructed supercells that can accommodate a bcc as well as an fcc crystal structure, which would be of interest for the simulation of sodium [61], lithium [62], xenon [63], and Yukawa systems [64]. One could expect that accommodating an bcc and an fcc structures in one supercell to be straightforward because both are cubic structures. However, one would want to keep the particle density the same, which implies their bcc and fcc lattice parameters differ by a factor of $2^{1/3}$. Since this is an irrational ratio, we cannot expect to find a supercell that accommodates both crystals perfectly. Still our best cells in Tab. 5 with $N = 160$ and 847 atoms have a small mismatch, δ , of only 0.0455 and 0.0270 a_{bcc} , which means the lattice vectors differ by less than 0.8% and 0.2% respectively. The impact of this deviation may be reduced further by setting the lattice vectors in the simulation to the average of the bcc and fcc supercell vectors so that both structures are affected equally by the constraints of the supercell.

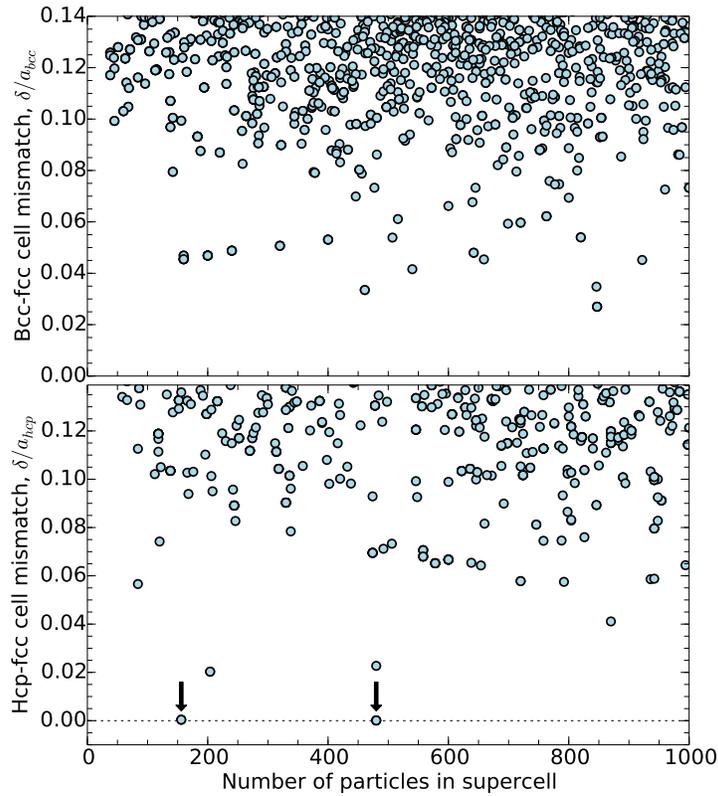


Figure 2. (Color online) Mismatch parameter, δ , (Eq. 8) between bcc and hcp lattices (upper panel) and fcc and hcp lattices (lower panel) for supercells with different numbers of particles. δ is plotted in units of lattice parameter a_{bcc} and a_{hcp} , respectively. The arrows in the lower panel mark cells with 156 and 480 atoms, respectively, that can perfectly accommodate an hcp and an fcc lattice.

Table 5. Supercells that can accommodate hcp and fcc crystals as well as bcc and fcc crystals. N specifies the number atoms per cell. The mismatch parameter, δ , and the supercell vectors are given in units of lattice parameter a_{bcc} and a_{hcp} , respectively.

	N	δ/a	i_a	j_a	k_a	i_b	j_b	k_b	i_c	j_c	k_c	$ a_{\text{SS}} /a$	$ b_{\text{SS}} /a$	$ c_{\text{SS}} /a$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
hcp:	156	0	5	7	0	-3	1	0	0	0	3	6.245	3.606	4.899	90.0	90.0	90.0
fcc:			5	-7	2	-3	-1	4	2	2	2	6.245	3.606	4.899	90.0	90.0	90.0
hcp:	480	0	6	6	3	-4	4	0	-4	-4	3	7.746	6.928	6.325	90.0	90.0	90.0
fcc:			-6	8	-4	0	-4	-4	6	2	-6	7.746	6.928	6.325	90.0	90.0	90.0
bcc:	160	0.0455	5	0	5	4	4	0	0	4	4	5.000	4.000	4.000	90.0	90.0	90.0
fcc:			4	4	-4	2	-2	-4	-4	4	-2	5.040	3.984	3.984	90.0	90.0	90.0
bcc:	847	0.0270	7	-4	2	-6	-8	-7	4	3	-7	7.921	6.225	8.602	88.9	88.3	87.4
fcc:			-7	-3	10	-6	2	-3	4	-11	0	7.918	6.236	8.592	88.7	88.3	87.2

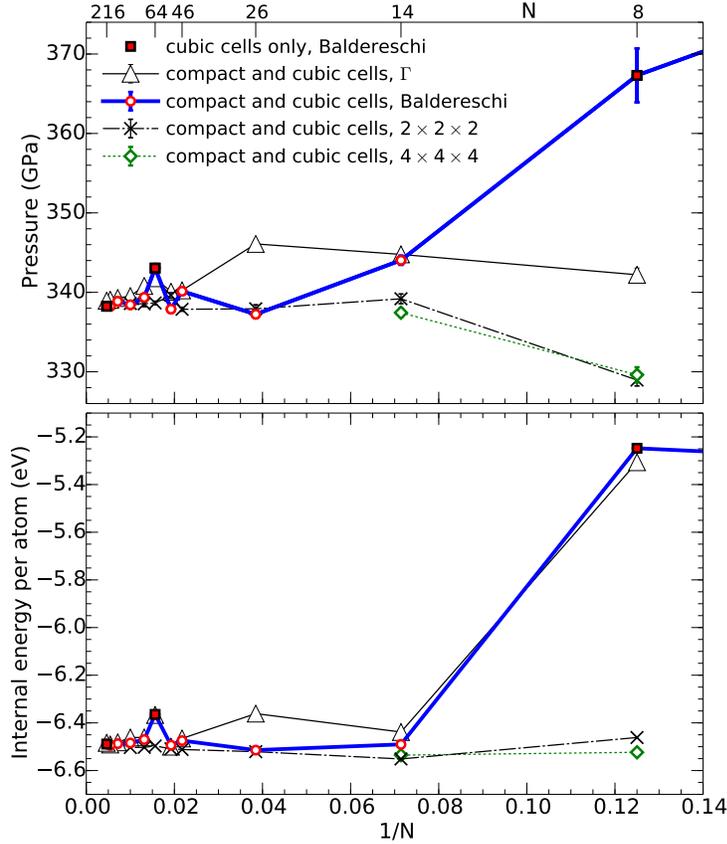


Figure 3. (Color online) Pressure and internal energy of diamond derived from DFT-MD simulations at 5000 K and 5.02 g cm^{-3} using compact supercells with different numbers of atoms, N and k -point grids for the Brillouin zone sampling. Error bars are shown unless they are smaller than the size of the symbols. For zone-average Baldereschi k -point curve, we used squares to mark cases where the constructed, compact cells coincided with the standard, cubic supercells with $N = 8n^3$.

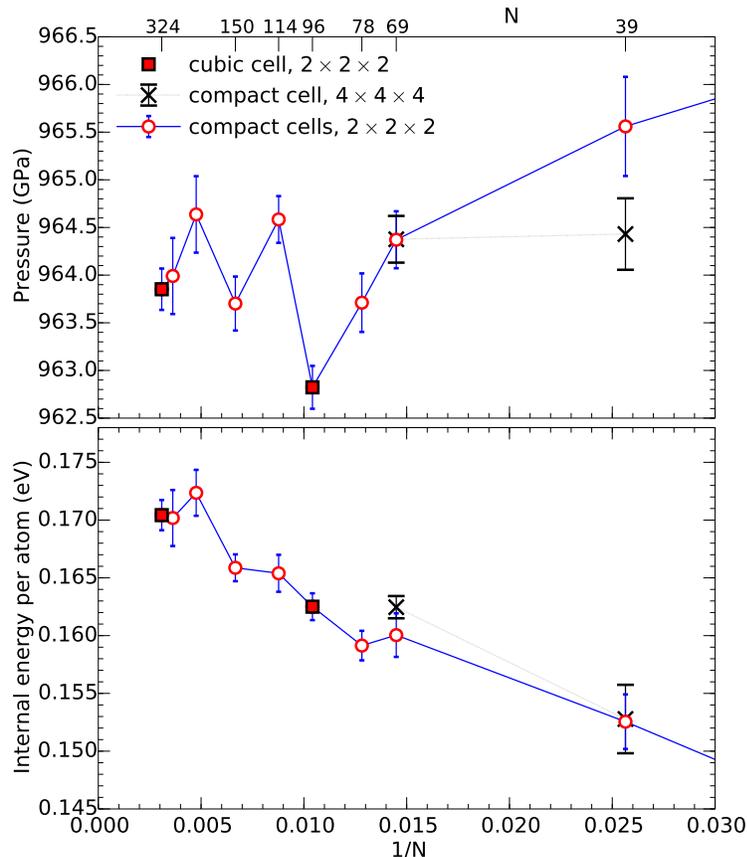


Figure 4. (Color online) Pressure and internal energy of fcc superionic ice from DFT-MD simulations at 4000 K and 6.00 g cm^{-3} using compact supercells with different numbers of atoms, N , and k -point grids for the Brillouin zone sampling.

5. Results from Ab Initio Simulations

In this section, we compare the internal energy and pressure that we obtained with DFT-MD simulations in compact supercells of various sizes. To cover a range of applications, we selected three representative systems with very different character. First we presents results of diamond, a hard, monatomic, covalently bonded solid. As an example for an ionic material, we discuss simulations of SiO_2 silica in the cubic pyrite structure. Finally we compare results for superionic water where the oxygen atoms are arranged on a fcc lattice. Superionic behavior [65] may occur in materials like $\alpha\text{-AgI}$ that are composed of ions with very different radii. The large ions, in this case I^- , remain locked in place and vibrate around lattice site like atoms in a solid while the smaller ions, Ag^+ , move throughout the lattice like a fluid. This behavior has been predicted theoretically to occur in water at megabar pressures [66]. Recent simulations predicted a phase change to an fcc oxygen sub-lattice [39]. Other superionic compounds with H_2O_2 and H_9O_4 stoichiometries has also be studied [67].

All DFT-MD simulations were performed with the VASP code [68]. We used

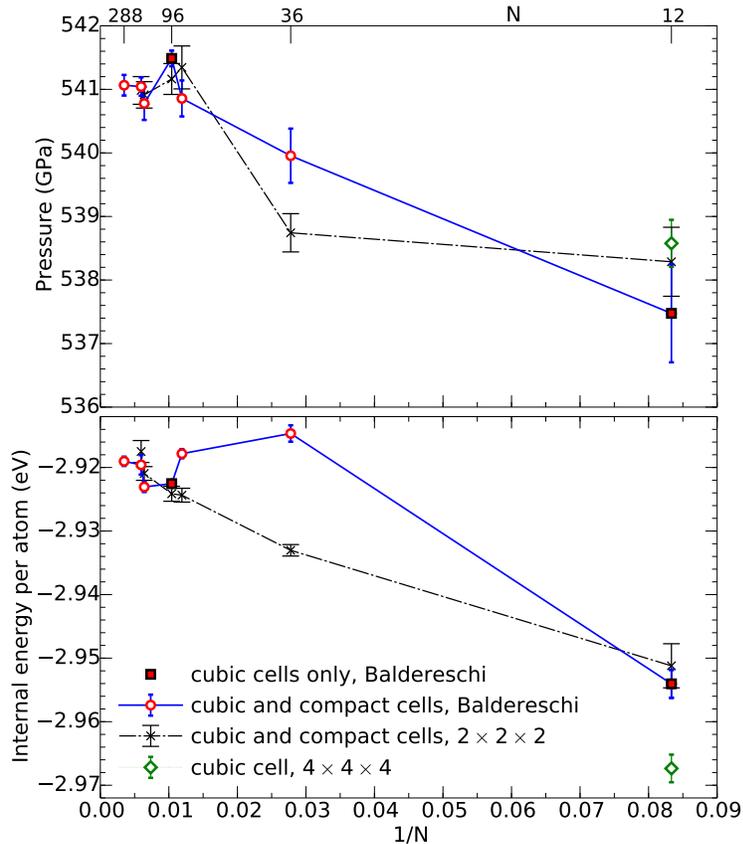


Figure 5. (Color online) Pressure and internal energy of silica, SiO_2 , in the cubic pyrite structure from DFT-MD simulations at 5000 K and 7.56 g cm^{-3} using compact supercells with different numbers of atoms, N , and k -point grids.

pseudopotentials of the projector-augmented wave type [69], the exchange-correlation functional of Perdew, Burke and Ernzerhof [70], and a cutoff energy of 900 eV for the plane wave expansion of the wavefunctions. The Brillouin zone was sampled with the zone-average Baldereschi point [71] as well as with $2 \times 2 \times 2$ and $4 \times 4 \times 4$ Monkhorst-Pack k -point grids [72]. The occupation of electronic states are taken to be a Fermi-Dirac distribution set at the temperature of the ions [73]. The simulation time ranged between 2.0 and 10.0 ps. An MD time step of 0.20, 0.75, and 0.80 fs was used for ice, diamond, and SiO_2 , respectively.

Finite size effects in DFT-MD simulations with periodic boundary conditions do not only arise from a finite number of ions and but also from an incomplete sampling of the Brillouin zone. One cannot completely separate one effect from the other because of k -point folding. When a supercell is constructed using a fixed set of k -points, this already implies a more accurate Brillouin zone sampling compared to the primitive cell. This is the reason why one typically uses a very small number of k -points in DFT-MD simulations and rather invests the available CPU time into simulating more atoms. Earlier simulations of dense carbon used the Γ point but more recent work employed

the Balderesci point [11]. Figure 3 shows pressure and internal energy derived from simulations of various cell sizes. A typical supercell with $64=8\times 2^3$ atoms [11] yielded a pressure of 344 GPa. Relying on cubic supercells alone, would make it very challenging to determine the magnitude of the remaining finite size error (-1.4% in pressure) and correct for it efficiently. One could compare with the results from simulations in a tiny cell with 8 atoms, the only available cubic cell that is smaller, and then linear extrapolation as function of $1/N$. One would not know, however, how reliable such an extrapolation would be unless one obtains results the next larger cubic cell with $216=8\times 3^3$ atoms. As Fig. 3 shows, we were able to perform such large simulations and confirm that the extrapolations for the pressure and energy are reasonably accurate but this test required a disproportionate amount of computer time. For more complex minerals that have unit cells with more atoms, such large supercell calculation may not be feasible.

Fig. 3 also shows simulation results based on our compact supercells that we constructed by starting from a 2 atom primitive cell of the fcc lattice. The supercell parameters are given in Tab. 1. Both pressures and internal energies from simulations with 76, 100, 140, and 184 atoms are in very good agreement with 216 atom results. This highlights the quality of the compact supercells that we constructed. Simulations with smaller cells are significantly faster. This also makes easier to determine how long one needs to run simulation to reach a certain accuracy.

The results from simulations with the Balderesci point in Fig. 3 show an overall trend for pressure and energy to decrease with system size. This is partially due to insufficient sampling of the Brillouin zone. Results from simulation of with $2\times 2\times 2$ and $4\times 4\times 4$ k -point grids converge much faster with system size and pressure and energy tend to increase with system size.

We select superionic water as the next test case for the application of our compact supercells. In each case, we started from a perfect fcc oxygen sub-lattice and then gradually increased the temperature in the DFT-MD simulations until the system reached a temperature of 4000 K where the system is superionic. In Fig. 4, we show results for seven cell sizes in addition to the two cubic supercells with $32=4\times 2^3$ and $108=4\times 3^3$ H_2O molecules used in Ref. [39]. $2\times 2\times 2$ k -point grids was employed in most calculations but two tests with $4\times 4\times 4$ points were performed.

A linear trend in the energy per atoms, N , appears as a function of $1/N$. Our compact cells follow this trend in the same way as the two cubic cells. One finds the energy value of 0.1625 eV/atom from simulations of 32 molecules is not yet converged but that an extrapolated value of 0.173 eV/atom is more realistic. The pressure appears to converge to a value of approximately 964.3 GPa. Simulations with a cubic supercell containing 32 molecules appear to yield a pressure that is slightly too low. The simulations with $4\times 4\times 4$ k -points are broadly consistent with the $2\times 2\times 2$ results, only for simulations with 13 molecules there is a deviation in the pressure.

In Tab. 3, we list 6 intermediate cell sizes that could have been used to study finite size effects in simulations of bcc solids in addition to the cubic cells with $54=2\times 3^3$ and

128= 2×4^3 molecules used in Ref. [40].

Finally, we come to the discussion of the finite size effects in DFT-MD simulations of silicate in the pyrite structure. Since the primitive cubic cell already has 4 SiO₂ molecules, a finite size extrapolations on cubic cells alone would be very challenging. Using the supercell in Tab. 2, we performed simulations with up to 288 atoms. Results in Fig. 5 show that finite size error in cubic simulations 96 atoms with the Balderesci point is already very small. The pressure appears to be overestimated by only 0.4 GPa. The correction to the internal energy is also very small, only on the order of 4 meV per atom.

6. Conclusions

We designed and tested a general algorithm for constructing compact supercells for first-principles simulations of solids. Results for common structures such as sc, bcc, fcc, and hcp lattices were reported. Since we started from the primitive cell, we were able to construct compact supercells of intermediate sizes that cannot be obtained with simple replication of the conventional unit cell. This allowed us to perform a more detailed a finite size analysis of the DFT-MD simulations of diamond, SiO₂, and superionic water. We demonstrate that the compact supercells can be used to estimate finite size effects and in most cases, to extrapolate to thermodynamic limit with good precision. We anticipate this will make predictions from computer simulations more reliable for applications where very large simulation with 1000 atoms or more are still prohibitively expensive. In addition to the presented computation of thermodynamic properties, our algorithm can be used to construct supercells to study systems with defects, solid solutions, magnetic and superionic systems. While we tested our approach only in DFT-MD simulations, future applications will include quantum Monte Carlo calculations where it is even more difficult to study large systems routinely.

References

- [1] M. E. Tuckermann. *J. Phys. Cond. Matter*, 14:R1297, 2002.
- [2] B. Kirchner, P. J. di Dio, and J. Hutter, editors. *Real-World Predictions from Ab Initio Molecular Dynamics Simulations*, volume 307 of *Topics in Current Chemistry*, page 109. Springer Berlin, 2012.
- [3] T. Tsuchiya, J. Tsuchiya, K. Umemoto, and R. M. Wentzcovitch. *Proc. Nat. Acad. Sci.*, 108:1252, 2011.
- [4] K. P. Driver, R. E. Cohen, Zhigang Wu, B. Militzer, P. Lopez Rios, M. D. Towler, R. J. Needs, and J. W. Wilkins. *Proc. Nat. Acad. Sci.*, 107:9519, 2010.
- [5] T. Tsuchiya and J. Tsuchiya. *Proc. Nat. Acad. Sci.*, 108:1252, 2011.
- [6] M. Parrinello. *Solid State Comm.*, 102:107, 1997.
- [7] M.P. Allen and D.J. Tildesley. Oxford University Press, New York, 1987.
- [8] B. Militzer. *Phys. Rev. B*, 79:155105, 2009.
- [9] A. A. Correa, S. A. Bonev, and G. Galli. *Proc. Nat. Acad. Sci.*, 103:1204, 2006.
- [10] D. Alfè, M. Pozzo, and M. P. Desjarlais. *Phys. Rev. B*, 85:024102, 2012.

- [11] L. X. Benedict, K. P. Driver, S. Hamel, B. Militzer, T. Qi, A. A. Correa, E. Schwegler, "A multiphase equation of state for carbon addressing high pressures and temperatures", submitted to *Phys. Rev. B* (2013), available on arXiv:1311.4577.
- [12] S. Baroni, S. de Gironcoli, and A. Dal Corso. *Rev. Mod. Phys.*, 73:515, 2001.
- [13] A. Togo, F. Oba, and I. Tanaka. *Phys. Rev. B*, 78:134106, 2008.
- [14] G. Stapper, M. Bernasconi, N. Nicoloso, and M. Parrinello. *Physical Review B*, 59(2):797–810, 1999.
- [15] Ferenc Tasnádi, M. Odén, and Igor a. Abrikosov. *Physical Review B*, 85(14):144112, 2012.
- [16] Jianpeng Liu and David Vanderbilt. *Physical Review B*, 88(22):224202, 2013.
- [17] a. Lindmaa, R. Lizárraga, E. Holmström, I. a. Abrikosov, and B. Alling. *Physical Review B*, 88(5):054414, 2013.
- [18] M Pesola, R M Nieminen, M J Puska, and S Po. 58(3):1318–1325, 1998.
- [19] Lindsey Munro and David Wales. *Physical Review B*, 59(6):3969–3980, 1999.
- [20] C. Domain, C. Becquart, and J. Foct. *Physical Review B*, 69(14):144112, 2004.
- [21] Adam J. Jackson and Aron Walsh. *Physical Review B*, 88(16):165201, 2013.
- [22] Céline Varvenne, Fabien Bruneval, Mihai-Cosmin Marinica, and Emmanuel Clouet. *Physical Review B*, 88(13):134102, 2013.
- [23] X. T. Trinh, K. Szász, T. Hornos, K. Kawahara, J. Suda, T. Kimoto, a. Gali, E. Janzén, and N. T. Son. *Physical Review B*, 88(23):235209, 2013.
- [24] Johan Pohl and Karsten Albe. *Physical Review B*, 87(24):245203, 2013.
- [25] Filipe Matusalem, Mauro Ribeiro, Jr., Marcelo Marques, Ronaldo Pelá, Luiz Ferreira, and Lara Teles. *Physical Review B*, 88(22):224102, 2013.
- [26] Hannu-Pekka Komsa and Alfredo Pasquarello. *Physical Review Letters*, 110(9):095505, 2013.
- [27] Song Lu, Qing-Miao Hu, Marko P. J. Punkkinen, Börje Johansson, and Levente Vitos. *Physical Review B*, 87(22):224104, 2013.
- [28] Hiroshi Fujihisa, Yuki Nakamoto, Masafumi Sakata, Katsuya Shimizu, Takahiro Matsuoka, Yasuo Ohishi, Hiroshi Yamawaki, Satoshi Takeya, and Yoshito Gotoh. *Physical Review Letters*, 110(23):235501, 2013.
- [29] A. Rohrbach G. Rollmann, P. Entel, and J. Hafner. *Phys. Rev. B*, 69:165107, 2004.
- [30] R. O. Kuzian, I. V. Kondokova, A. M. Dare, and V. V. Laguta. *Phys. Rev. B*, 89:024402, 2014.
- [31] S. Grytsyuk and U. Schwingenschlögl. *Phys. Rev. B*, 88:165414, 2013.
- [32] W. Ching and Paul Rulis. *Physical Review B*, 77(12):125116, 2008.
- [33] D. Alfè. *Phys. Rev. B*, 68:064423, 2003.
- [34] L G.Wang, A. van de Walle, and D. Alfe. *Phys. Rev. B*, 84:092102, 2011.
- [35] S. Aryal, P. Rulis, and W. Y Ching. *Phys. Rev. B*, 84:184112, 2011.
- [36] Y. G. Yu, R. J. Angel, N. L. Ross, and G. V. Gibbs. *Phys. Rev. B*, 87:184112, 2013.
- [37] K. P. Esler, R. E. Cohen, B. Militzer, J. Kim, R. J. Needs, and M.D.L. Towler. *Phys. Rev. Lett.*, 104:185702, 2010.
- [38] L. Shulenburg and T. R. Mattsson. *Phys. Rev. B*, 88:245117, 2013.
- [39] H. F. Wilson, M. L. Wong, and B. Militzer. *Phys. Rev. Lett.*, 110:151102, 2013.
- [40] M. French, T. R. Mattsson, N. Nettelmann, and R. Redmer. *Phys. Rev. B*, 79:054107, 2009.
- [41] L. G. Ferreira, S.-H. Wei, and A. Zunger. *Int. J. Supercomput. Ap.*, 5:34, 1991.
- [42] A. van de Walle and G. Ceder. Automating first-principles phase diagram calculations. *J. Phase Equilib.*, 23:348, 2002.
- [43] G. L. W. Hart and R. W. Forcade. *Phys. Rev. B*, 77:224115, 2008.
- [44] B. Militzer and H. F. Wilson. *Phys. Rev. Lett.*, 105:195701, 2010.
- [45] C. J. Pickard, M. Martinez-Canales, and R. J. Needs. *Phys. Rev. Lett.*, 110:245701, 2013.
- [46] A. R. Oganov and Colin W. Glass. *J. Chem. Phys.*, 124:244704, 2006.
- [47] C. J. Pickard and R. J. Needs. *J. Phys. Condens. Matter*, 23:053201, 2011.
- [48] S. M. Woodley and R. Catlow. *Nature Mat.*, 7:937, 2008.
- [49] Yanming Ma, M. Erements, R. Oganov A, Yu Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle,

- and V. Prakapenka. *Nature*, 458:182, 2008.
- [50] G. A. de Wijs, G. Kresse, and M. J. Gillan. *Phys. Rev. B*, 57:8223, 1998.
- [51] H. F. Wilson and B. Militzer. *Phys. Rev. Lett.*, 104:121101, 2010.
- [52] H. F. Wilson and B. Militzer. *Phys. Rev. Lett.*, 108:111101, 2012.
- [53] B. Militzer. *Phys. Rev. B*, 87:014202, 2013.
- [54] S. M. Wahl, H. F. Wilson, and B. Militzer. *Astrophys. J.*, 773:95, 2013.
- [55] R. A. Evarestov. *Quantum Chemistry of Solids, LCAO Treatment of Crystal and Nanostructures*. Springer Heidelberg New York Dordrecht London, 2012.
- [56] T. Ishikawa, K. Kato, M. Nomura, N. Suzuki, H. Nagara, and K. Shimizu. *Phys. Rev. B*, 88:214110, 2013.
- [57] S. K. Saxena, G. Shen, and P. Lazor. *Science*, 260:1312, 1993.
- [58] C. J. Pickard and R. J. Needs. *J. Phys. Condens. Matter*, 21:452205, 2009.
- [59] A. S. Cote, L. Voadlo, and J. P. Brodhold. *Earth Planet. Sci. Lett.*, 345:185702, 2012.
- [60] D.A.H. (Ed.) Jacobs. *The State of the Art in Numerical Analysis*. Academic Press, 1977.
- [61] E. Gregoryanz, O. Degtyareva, M. Somayazulu, R. J. Hemley, and H. k. Mao. *Phys. Rev. Lett.*, 95:185502, 2005.
- [62] R. G. Munro and R. D. Mountain. *Phys. Rev. B*, 28:2261–2263, Aug 1983.
- [63] B. A. Belonoshko, O. LeBacq, R. Ahuja, and B. Johansson. *J. Chem. Phys.*, 117:7233, 2002.
- [64] R. T. Farouki and S. Hamguchi. *J. Chem. Phys.*, 101:9885, 1994.
- [65] F. A. Karamov, editor. *Superionic conductors*. Cambridge International Science Pub., 2008.
- [66] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, and M. Parrinello. *Nature*, 283:44, 1999.
- [67] B. Militzer, S. Zhang, "Ab initio Simulations of Superionic H₂O, H₂O₂, and H₉O₄ Compounds", submitted to *Phys. Rev. B* (2014).
- [68] G. Kresse and J. Hafner, *Phys. Rev. B* 47, 558 (1993); G. Kresse and J. Hafner, *Phys. Rev. B* 49, 14251 (1994); G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* 6, 15 (1996); G. Kresse and J. Furthmüller, *Phys. Rev. B* 54, 11169 (1996).
- [69] P. E. Blöchl. *Phys. Rev. B*, 50:17953, 1994.
- [70] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865, 1996.
- [71] A. Baldereschi. *Phys. Rev. B*, 7:5212, 1977.
- [72] H.J. Monkhorst and J.D. Pack. *Phys. Rev. B.*, 13:5188, 1976.
- [73] N. D. Mermin. *Phys. Rev.*, 137:A1441, 1965.