Electrostatic treatment of charged interfaces in atomistic calculations

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Abstract

We derive analytic solutions for the electrostatic potential in supercells of atomistic structures containing alternatingly charged lattice planes. The formalism can be applied to both, neutral and charged systems, such as supercells set up for studying properties of surfaces and interfaces like grain boundaries in ionic compounds. The presented methodology allows for the correction of electrostatic artifacts, which are inherent to atomistic simulations of extended structural defects using supercell models with either periodic or open boundary conditions. We demonstrate it for the example of formation energies of charged oxygen vacancies distributed around an asymmetric tilt grain boundary in strontium titanite (SrTiO₃).
1 Introduction

Electrostatics plays a significant role in atomistic simulations of charged structural defects of materials [1–3]. To simulate a charged surface or grain boundary (GB) of a crystal, a supercell is constructed with the majority of atoms in the bulk-like structure of the material, and a few atoms at the two-dimensional (2D) region defining the surface or GB. The application of periodic boundary conditions in the direction perpendicular to the interface plane causes an internal, artificial electric field in the supercell [4–6]. Alternatively, using open boundary conditions may lead to charged surfaces which also lead to an artificial electric field in the interior of the supercell. Such electrostatic effects can influence the crystal structure and the energetics of charged atomic defects considerably [7,8]. Therefore, it is of crucial importance to understand the origins of the electrostatic potential across the supercell in detail, in order to distinguish between the extrinsic contributions arising from the simulation setup, i.e. electrostatic artifacts due to periodic or open boundary conditions, and the intrinsic contributions attributed to the properties of interfaces and atomic defects in crystals.

Atomistic supercells for modelling an ionic crystal can be constructed by considering the crystal as a stack of planes of atoms. There are three possible stacking sequences as illustrated by Tasker [1]: The first type has neutral planes consisting of both anions and cations in stoichiometric composition. The second type contains charged but symmetrically arranged repeat units of planes, as e.g. repeat units of three planes charged in the sequence of $-1$, $+2$ and $-1$, leading to no electric dipole moment. The third type is of particular interest. Its stacking sequence has alternatingly charged planes, resulting in an electric dipole moment perpendicular to the planes. This last scenario is present in various systems, e.g. in supercells of ZnO with (0001) and (000$\bar{1}$) surfaces [9–11], CeO$_2$ with a (001) surface [12,13], Fe$_3$O$_4$ with a (111) surface [14,15], and cubic perovskites with (001) surfaces [16–18].

The electrostatic potentials for such alternatingly stacked structures with surfaces have been addressed in previous studies, mainly in the context of electronic-structure calculations with methods based on density functional theory (DFT):

Meyer and Vanderbilt [4] identified a constant internal electric field inside the supercell used for simulating the (001) surfaces of the perovskite compounds BaTiO$_3$ and PbTiO$_3$. In this reference, periodic boundary conditions were applied, and the repeated supercells, which are charge neutral, were separated by vacuum regions (slab system). To remove the internal field, an external dipole layer was inserted in the vacuum region. This dipole correction was introduced by Bengtsson [3] and has been applied to supercells for simulating various crystal surfaces [19–21]. The correction method was recently generalized to asymmetric slabs by Freysoldt et al. [8].

Charged supercells have been employed for atomistic simulations of charged surfaces, e.g. the (110) surface in Ag [22], the (100) surface in Au [23], and the (110) surface in Pt [24], where the electrostatic effects on the surface reconstruction were investigated. Recently, Rutter [5] studied the electrostatic potentials for a system of four charged layers of graphene (ABAB stacked) with both open and periodic boundary conditions. By using a charge of $+2e$ per unit cell, this system corresponds to a charged conducting slab. In the case of periodic
boundary conditions, a uniform neutralizing background charge was introduced, which induced a spurious non-constant electric field. The author proposed a post hoc correction for the energy only. Recently, a method to directly correct the electrostatics as well as the resulting artificial field in DFT calculations was reported by da Silva et al. [25] using a self-consistent potential, which was included in the Kohn-Sham equation and updated iteratively during the solution of this equation. Note, that the above-mentioned correction methods have been applied to supercells with vacuum regions for simulating surfaces. However, their application to a supercell containing an internal GB but no vacuum region between two external surfaces remains to be explored.

Indeed, limited studies have been undertaken so far which deal with electrostatic artifacts in supercells containing GBs inside materials, although such interfaces repeatedly attracted attention in perovskite materials [26,27]. The surrogate model proposed by Freysoldt and Neugebauer [7] is a useful tool to reproduce the macroscopic electrostatic potential in the repeated supercell with periodic boundary conditions. This is achieved by incorporating point charges into the continuum modeling of space charges close to surfaces. Recently, we extended this method for the application to charge-neutral supercells containing symmetric tilt-grain boundaries (STGBs) in ionic compounds [28]. There, we used the method to correct the internal electrostatic potentials in order to analyze the influence of the GBs on oxygen vacancy formation energies in SrTiO$_3$ (STO).

However, asymmetric tilt grain boundaries (ATGBs) are experimentally more frequently observed than STGBs in polycrystalline STO microstructures [29,30]. An example is the ATGB (430)|(100) whose interface structure has been investigated in detail by transmission electron microscopy [31]. The interaction of grain boundaries with oxygen vacancies under external electric fields is supposed to be the origin of field-assisted grain growth in STO [32,33]. We use the ATGB (430)|(100) in STO as a model GB to describe, explain and demonstrate our procedure to deal with real and artificial electric fields in atomistic supercells. In contrast to the STGB, which can be modelled by charge neutral supercells [31], the simulation of ATGBs may require the use of supercells with non-zero total charge.

In this paper, we extend and generalize our recent study on STGB in STO [28] to correct for the electrostatic artifacts that arise when using charged supercell and derive a general electrostatic formalism for structure models that contain arbitrary stacks of charged atomic planes (Section 2.1). In a systematic way, the derived formalism is applied to specific arrangements of lattice planes with alternating charges (Section 2.2), namely a charge-neutral cell of a crystal with equidistant planes, a charged cell of a crystal with equidistant planes, and a charged cell with grain boundaries between differently oriented crystals. Both open and periodic boundary conditions are considered in each case. The capability of the methodology is demonstrated and discussed for the calculation of formation energies of oxygen vacancies in the vicinity of the unrelaxed (Section 3.1) and the relaxed ATGB (430)|(100) in STO (Section 3.2). In Section 4, we give a summary and concluding remarks.
2 Methodology

2.1 The electrostatic formalism

Following the description of an ionic crystal by Tasker [1], we compose a three-dimensional (3D) atomistic supercell model of a bulk crystal, a system containing surfaces, or a system with grain boundaries, by a sequence of charged lattice planes, which is schematically sketched in Figure 1.

![Figure 1](image)

Figure 1. A two-dimensional sketch of a general atomistic supercell model containing charged lattice planes. Lattice planes at positions $y_i$ are charged with charges $q_i$. The blue dashed box represents the border of the supercell.

Periodic boundary conditions (PBC) are conventionally applied in the directions parallel to the lattice planes (here, the $x$ and $z$ directions) while either periodic or open boundary conditions (OBC) can be applied perpendicular to the lattice planes (here, the $y$ direction). For example, for the simulation of surfaces, we can use supercells with either open boundary conditions (single slabs) or periodic boundary conditions with a vacuum region added in the axial $y$ direction (repeated slabs). Due to the structural discontinuities at an interface, the electrostatic potentials as well as defect energetics vary considerably in this direction in the vicinity of the investigated interface. Hence, we focus on the $x$-$z$-plane-averaged electrostatic potential $V(y)$ in this study. With periodic boundary conditions in the lateral $x$ and $z$ directions, i.e. infinitely extended atomic planes, we can calculate such a plane-averaged potential $V(y)$ by solving the one-dimensional Poisson equation (see the proof in the appendix A of Ref. [34]):

$$\frac{d^2V(y)}{dy^2} = -\frac{\rho(y)}{\epsilon},$$

where $\epsilon$ is the permittivity. Since in the following we are considering a rigid ion model of a crystal, i.e. isolated point charges in vacuum, $\epsilon$ is set equal to the vacuum permittivity $\epsilon_0$. Here, we write the $x$-$z$-plane averaged charge density $\rho(y)$ in the form $\rho(y) = \rho_0 + \rho_1(y)$, where $\rho_0$ is a homogeneous background charge density, such as the neutralizing (charge-compensating) background charge density in the case of charged supercells, while $\rho_1(y)$ is the one-dimensional density profile resulting from the ions at the lattice planes.
For each homogeneously charged plane of a supercell with total charge $q_i$ and cross-sectional area $A$, which is located at a position $y_i$, the $x$-$z$-plane averaged charge density can be expressed with Dirac’s delta function as $\frac{q_i}{A} \cdot \delta(y - y_i)$. Therefore, the charge density across the whole system is a sum over all the $N$ charged planes in the supercell:

$$\rho(y) = \rho_0 + \sum_{i=1}^{N} \frac{q_i}{A} \cdot \delta(y - y_i).$$

(2)

For this charge density, the general solution of the Poisson equation is given as:

$$V(y) = -\frac{\rho_0}{2\varepsilon_0} y^2 - \sum_{i=1}^{N} \frac{q_i}{2\varepsilon_0} |y - y_i| + C_1 y + C_2,$$

(3)

where $C_1$ and $C_2$ are constants of integration which are determined by the choice of boundary conditions. The negative derivative of $V(y)$ with respect to $y$ is the electric field $E(y)$:

$$E(y) = \frac{\rho_0}{\varepsilon_0} y + \sum_{i=1}^{N} \frac{q_i}{2\varepsilon_0} \cdot \text{sgn}(y - y_i) + C_1.$$

(4)

Here, $\text{sgn}(y)$ denotes the sign function, which can alternatively be expressed as a sum of two Heaviside step functions: $\text{sgn}(y) = H(y) - H(-y)$. Differentiating Equation (4) with respect to $y$ and using $H'(y) = \delta(y)$ results in the density given in Equation (2) and thus Equation (1) is satisfied.

We first consider open boundary conditions (OBC) in the $y$ direction of the supercell. Without an external source of charge, there is no need to introduce a neutralizing background charge density ($\rho_0 = 0$), and without an additional external electric field (i.e. $C_1 = 0$), the potential reads

$$V_{\text{OBC}}(y) = -\sum_{i=1}^{N} \frac{q_i}{2\varepsilon_0} |y - y_i| + C_2,$$

(5)

where $C_2$ can be chosen arbitrarily.

Next, we consider the supercell with periodic boundary conditions (PBC) in $y$ direction. Let the total charge of the supercell be $Q_{\text{tot}} = \sum_{i=1}^{N} q_i$. For $Q_{\text{tot}} \neq 0$, the infinite repetition of the supercell results in an undefined electrostatic energy. This problem is commonly treated by adding an averaged compensating background charge density $\rho_0 = -\frac{Q_{\text{tot}}}{V_{\text{cell}}}$ to the system. Here, $V_{\text{cell}}$ is the volume of the supercell. To simplify the following derivations, we select the origin of the $y$ axis as the center of the supercell. The periodic boundary conditions require that the potential is periodic, too, i.e. $V\left(-\frac{L}{2}\right) = V\left(+\frac{L}{2}\right)$, where $L$ denotes the length of the supercell in $y$ direction. From Equation (3), one obtains $C_1 = -\sum_{i=1}^{N} \frac{q_i y_i}{\varepsilon_0 V_{\text{cell}}}$, which effectively describes an internal electric field imposed by the periodic boundary conditions. In general, $C_1$ is non-zero, even for $Q_{\text{tot}} = 0$.

The total potential is then given by:

$$V_{\text{PBC}}(y) = V_{\text{OBC}}(y) + \frac{Q_{\text{tot}}}{2\varepsilon_0 V_{\text{cell}}} y^2 - \sum_{i=1}^{N} \frac{q_i y_i}{\varepsilon_0 V_{\text{cell}}} \cdot y + C.$$

(6)
If $Q_{\text{tot}} \neq 0$, the coefficient of the linear term in $y$ can be written as $-\overline{y}Q_{\text{tot}}/\varepsilon_0 V_{\text{cell}}$ with the “center of charge” given as $\overline{y} = \frac{\sum_{i=1}^{N} q_i y_i}{\sum_{i=1}^{N} q_i}$. Combining this with the quadratic term leads to an alternative formulation of $V_{\text{PBC}}(y)$:

$$V_{\text{PBC}}(y) = V_{\text{OBC}}(y) + \frac{Q_{\text{tot}}}{2\varepsilon_0 V_{\text{cell}}} (y - \overline{y})^2 + C', \quad (7)$$

with a shifted constant $C' = C - \frac{Q_{\text{tot}}}{2\varepsilon_0 V_{\text{cell}}} \overline{y}^2$. In this way it is obvious that periodic boundary conditions in a non-neutral cell lead to an additional quadratic term in the electrostatic potential which is centered around the center of charge $\overline{y}$.

### 2.2 Application to specific scenarios

**A. Charge neutral supercell with equidistant, alternatingly charged planes**

We first consider the electrostatic potential for a cell consisting of equidistant $(d)$, alternatingly charged lattice planes with plane-averaged charge densities $\pm q/A$, as sketched in Figure 2(a).

![Figure 2](image)

**Figure 2.** (a) A sketch of a charge neutral supercell consisting of equidistant, alternatingly charged planes (plane-averaged charge densities $\pm q/A$) indicated by dashed and solid vertical lines. The dashed blue box represents the boundary of the simulation supercell in the case of periodic boundary conditions containing a vacuum region of
arbitrary size in \( y \) direction; (b) the resulting electrostatic potential for open boundary conditions (red line) and periodic boundary conditions (green line) in \( y \) direction. The macroscopic average potentials inside the bulk region are indicated by dotted lines.

Dashed and solid vertical lines indicate positively and negatively charged planes, respectively. In case of the same number of positively and negatively charged planes, such a structure is apparently charge neutral \( (Q_{\text{tot}} = 0) \). This configuration is used e.g. in the atomistic treatment of (001) surfaces of the perovskites \( \text{BaTiO}_3 \) and \( \text{PbTiO}_3 \) [4].

We first consider open boundary conditions in \( y \) direction. The resulting electrostatic potential \( [V_{\text{OBC}}(y)] \) is sketched by the stage-like curve (red line) in Figure 2(b). \( V_{\text{OBC}}(y) \) can further be averaged inside the bulk region along the \( y \) direction. Applying the "macroscopic average" as described by Baldereschi et al. [35], the average values at the positions \( y_i, \bar{V}_{\text{OBC}}(y_i) \), are determined by integrating \( V_{\text{OBC}}(y) \) over an interval \( \alpha \) and dividing the result by \( \alpha \):

\[
\bar{V}_{\text{OBC}}(y_i) = \frac{1}{\alpha} \int_{y_{i-1}}^{y_{i+1}} V_{\text{OBC}}(y) \, dy.
\]

For the configurations with equidistant lattice planes, we chose \( \alpha \) equal to two times the interplanar distance in the following, i.e. the integration interval extends from \( y_{i-1} \) to \( y_{i+1} \). This corresponds to averaging out the microscopic fluctuations inside each unit cell on the order of a lattice parameter [36]. Our values \( \bar{V}_{\text{OBC}}(y_i) \) follow a linear trend and can therefore be extrapolated by a line, which is indicated by the red dotted line in Figure 2(b). Such a linear average potential across the supercell with a non-zero slope corresponds to the presence of a surface dipole [28].

In the case of periodic boundary conditions, a vacuum region of arbitrary size can be added to the region of atomic planes in the supercell, as sketched by the extension of the dashed blue box in Figure 2(a) in \( y \) direction. The internal electric field imposed by the periodic boundary conditions (cf. Section 2.1) ensures the connection of the two end points of \( V_{\text{OBC}}(y) \) extended into the vacuum region to the limits of the supercell (red curve). This transforms the stage-like curve into the zig-zag curve, as sketched by the green solid line in Figure 2(b). There is a resulting internal electric field inside the bulk region, if the slope of the macroscopic average potential (dotted green line) is non-zero. As in the case of open boundary conditions, it has its origin in the surface dipole. Accordingly, the magnitude of this surface dipole depends on the vacuum size.

Two limiting cases for the vacuum size can be considered: in the limit of infinite length \( (V_{\text{cell}} \to \infty) \), the potential curve for periodic boundary conditions is identical to that of open boundary conditions. The other limit is a vacuum length of \( d/2 \) at both ends of the cell. Since this results in no vacuum at all but a periodic bulk structure, there is no surface dipole, resulting in a flat average potential and therefore no internal electric field. In other words, the linear correction term for the potential in the case of periodic boundary conditions and a "vacuum" size of \( d/2 \) is identical to the average potential in the case of open boundary conditions.
B. Charged supercell with equidistant, alternatingly charged planes

Next, we consider the scenario where one further positively charged plane is added as the left termination plane [Figure 3(a)] to the stacking sequence of charged lattice planes treated in scenario A [Figure 2(a)]. In this case, the supercell is charged with $Q_{\text{tot}} = +q$.

Figure 3. (a) A sketch of a supercell consisting of equidistant, alternatingly charged planes with both termination planes being equally (positively) charged; (b) the resulting schematic electrostatic potential for open boundary conditions (red line) and periodic boundary conditions (green line) in $y$ direction. The corresponding macroscopic averages inside the bulk region are indicated by dotted lines. The blue parabola corresponds to the quadratic potential term coming from the neutralizing background charge density, with the minimum located at the center of charge.

Again, we first apply open boundary conditions in $y$ direction. This corresponds to a (single-slab) supercell for the simulation of charged surfaces. Since the system is finite in $y$ direction, a neutralizing background charge density is not needed in this case ($\rho_0 = 0$). The resulting
electrostatic potential is sketched by the zig-zag curve in Figure 3(b) (solid red line). In contrast to the situation in scenario A, the averaged potential is flat (dotted red line), because now there is no surface dipole between the two equal, and therefore equally charged terminating surfaces.

In the case of periodic boundary conditions, i.e. in a periodically repeated slab system of infinite size in y direction, a neutralizing background charge \((-q)\) needs to be included which influences the potential. Such a configuration can be set up to simulate charged surfaces if a vacuum region considerably larger than the interplanar distance is added (periodically repeated slabs). Following Eq. (7), this leads to a quadratic term in the electrostatic potential as schematically sketched by the blue parabola across the supercell in Figure 3(b) with the minimum being in the center of charge, which coincides with the geometric center of the supercell in our setup. Such a quadratic potential was obtained by Rutter [5] for the modelling of graphene sheets. Combining the zig-zag potential \([V_{\text{OBC}}(y)]\) with the quadratic term leads to a total electrostatic potential (shown in green), which is a parabola-like zig-zag curve in the bulk region and a parabola in the vacuum region. Using the averaged line of \(V_{\text{OBC}}(y)\) inside the bulk, one obtains the averaged total potential (green dotted line).

C. Charged cell with interfaces between two grains

Finally, we consider a supercell with two grain regions and a grain boundary [Figure 4(a)]. In our example, both grains, denoted by grain I (with \(N_1\) lattice planes) and grain II (\(N_2\) lattice planes) in the following, are of the form described in the previous example (scenario B), but with different distances \((d_1, d_2)\) and different charges \((\pm q, \pm q')\) of the planes. The total charge of the supercell cell is then \(Q_{\text{tot}} = q + q'\). The distance at an interface between the grains, the grain boundary separation length \(\delta_{\text{GB}}\), is typically a bit larger than the interplanar distances. As we discuss in Section 3, such a configuration reasonably describes a supercell for the simulation of an asymmetric tilt grain boundaries subject to either OBC or PBC.
Figure 4. (a) A sketch of a supercell consisting of two grains (grain I, grain II), each with equidistant ($d_1$, $d_2$) and alternatingly charged ($\pm q$, $\pm q'$) planes. Both grains have equally charged termination planes, and are separated by $\delta_{GB}$ at the grain boundary; (b) the resulting electrostatic potential for open boundary conditions in $y$ direction (red curve, with macroscopic average indicated by the dotted line), together with the linear potential introduced when applying periodic boundary conditions (dashed black line), the quadratic potential originating from the background charge (dashed blue curve), and the shifted parabola (solid orange curve) from combining the latter two terms [cf.
Equation (7)]; (c) the resulting electrostatic potential for periodic boundary conditions in y direction (solid line) and its macroscopic average (dotted line).

First, we consider open boundary conditions in y direction. Similar to the potential in scenario B, a zig-zag potential profile is obtained in this case as sketched in Figure 4(b) (solid red curve). At the position \( y_i \) of each plane, the macroscopic average value \( \bar{V}_{\text{OBC}}(y_i) \) was then calculated following Equation (8). These averaged values follow a linear line in each bulk grain (red dotted lines), which is not flat because of the presence of an interface dipole at the GB. To match the average potential lines of both grains in the GB region, they are extrapolated to \( \tilde{y}_1 = y_1 - \frac{d_1}{2} \), \( \tilde{y}_{N_1} = y_{N_1} + \frac{d_1}{2} \) and \( \tilde{y}_{N_1+1} = y_{N_1+1} - \frac{d_2}{2} \), \( \tilde{y}_{N_1+N_2} = y_{N_1+N_2} + \frac{d_2}{2} \), respectively, where they reach the not averaged stage-like potential curve. Here, we introduced a reference point \( y_B^{\text{ref}} \) somewhere in the bulk region (B) of a grain, with the average potential value \( V_B^{\text{ref}} \) at this point. As a result, the average potential reads:

\[
\bar{V}_{\text{OBC,d}}(y) = V_B^{\text{ref}} + \frac{q_f}{2\varepsilon_0} (y - y_B^{\text{ref}}) \quad \text{for} \quad \tilde{y}_1 \leq y \leq \tilde{y}_{N_1},
\]

\[
\bar{V}_{\text{OBC,d}}(y) = V_B^{\text{ref}} + \frac{q_f-q}{2\varepsilon_0} (y - y_B^{\text{ref}}) + \frac{q}{2\varepsilon_0} (\tilde{y}_{N_1} - y_B^{\text{ref}}) \quad \text{for} \quad \tilde{y}_{N_1} < y < \tilde{y}_{N_1+1},
\]

\[
\bar{V}_{\text{OBC,d}}(y) = V_B^{\text{ref}} - \frac{q}{2\varepsilon_0} (y - \tilde{y}_{N_1}) + \frac{q_f}{2\varepsilon_0} (\tilde{y}_{N_1+1} - y_B^{\text{ref}}) \quad \text{for} \quad \tilde{y}_{N_1+1} \leq y \leq \tilde{y}_{N_1+N_2}.
\]

The second subscript (d) in the potential indicates that the formalism is only valid for a system with equidistant planes in each of the bulk regions. Note, that the length of the GB separation (\( \delta_{\text{GB}} \)) does not influence the slopes of the average potential lines, but only the offset between them.

Next, we consider periodic boundary conditions in y direction. In this case the supercell contains two GBs, or one GB and two surfaces, depending on the vacuum length. If we are only interested in the properties of one specific grain boundary, as e.g. the GB energy, the two GBs must be identical. This defines the supercell dimension [indicated by the blue dashed box in Figure 4(a)]

Following Equation (6), the total potential is obtained as:

\[
V_{\text{PBC,d}}(y) = V_{\text{OBC,d}}(y) + \frac{q+q'}{2\varepsilon_0\varepsilon_{\text{cell}}} y^2 - \sum_{i=1}^{N_1+N_2} \frac{q_i y_{i}}{\varepsilon_0\varepsilon_{\text{cell}}} \cdot y + \mathcal{C}.
\]

Using the “center of charge” as defined in Section 2.1, the above equation can be re-formulated as:

\[
V_{\text{PBC,d}}(y) = V_{\text{OBC,d}}(y) + \frac{q+q'}{2\varepsilon_0\varepsilon_{\text{cell}}} (y - \bar{y})^2 + \mathcal{C}'.
\]

In Eq. (10-a), the quadratic potential term results from the neutralizing background charge density \( \rho_0 = -\frac{q+q'}{V} \) [dashed blue parabola in Figure 4(b)]. The linear potential term (dashed black line) is required by the periodicity, connecting the two ends of the stage-like red potential curve. Combining the linear and the quadratic potential terms leads to one parabola centered
at the center of charge [cf. Equation (10-b)]. Note that this parabola is also vertically shifted with respect to the quadratic term in Eq. (10-a) because of $C \neq C'$. Adding the stage-like potential [$V_{OBC,d}(y)$] to it, we obtain the total potential for the periodic boundary conditions $V_{PBC,d}(y)$ as sketched in Figure 4(c) by the solid green line. The dotted green line results from using the macroscopic average of the stage-like curve including the extrapolation regions [dotted red line in Figure 4(b)] with the formula:

$$V_{PBC,d}(y) = V_{OBC,d}(y) + \frac{q + q'}{2\varepsilon_0 V_{cell}} (y - \bar{y})^2 + C',$$  \hspace{1cm} (11)

with $C' = C - \frac{q + q'}{2\varepsilon_0 V_{cell}} \bar{y}^2$.

By applying the scenario treated in A to both grain regions instead of scenario B, we can obtain a charge neutral supercell. As a specific case for such a GB type, a symmetric tilt grain boundary (STGB) has been investigated in our previous study [28]. Furthermore, the supercell of an interface can also be generated by combining one bulk region of scenario A and another one of scenario B. An example is the heterojunction between the neutral Ge crystal and the (001)-oriented polar GaAs crystal as constructed in Ref. [2]. The authors have investigated the electrostatic potentials inside the supercell by integrating the Poisson equation, which is in analogy to the method described in this section.
3 Results and discussion

The developed methodology is applied to atomistic supercell calculations of formation energies of positively charged oxygen vacancies in the vicinity of an asymmetric tilt grain boundary (ATGB) (430)||⟨100⟩ in SrTiO₃ (STO). The procedure is first applied to an unrelaxed ATGB structure, for both open and periodic boundary conditions in Section 3.1. In Section 3.2, the method is transferred to a relaxed ATGB structure, with the detailed procedure in the case of periodic boundary conditions described in Section 3.2.1, followed by a discussion of the effect of the counteracting depolarization field during the structural relaxation in Section 3.2.2.

As in our preceding study [28], we used the rigid-ion potential model and parameters developed by Thomas et al. [37] to describe the interaction energy between ionic pairs in STO. The effective charges +1.84e, +2.36e and −1.4e are assigned to Sr, Ti and O ions, respectively. For further information on this potential and its capability for atomistic simulations of grain boundaries in STO see Refs. [28, 38] and references therein.

The calculations of the formation energies of oxygen vacancies were performed with the General Utility Lattice Program (GULP) [39]. The formation energy $E_f$ of a vacancy with charge $q^{V_o}$ in the rigid-ion model can be expressed as [40]:

$$E_f = E_{tot} - E_{tot}^{(0)} + E_{\infty} + E_{corr}. $$ (12)

Here, $E_{tot}$ is the total lattice energy of the supercell including the defect. For a charged vacancy and periodic boundary conditions, $E_{tot}$ can be calculated by introducing a compensating background charge density [39]. $E_{tot}^{(0)}$ is the total lattice energy of the supercell without defect. $E_{\infty}$ is the energy of the removed charged ion (or neutral atom), which is isolated and placed at infinite separation from the crystal. $E_{corr}$ denotes the correction of the energy coming from the artificial electrostatic potential induced by the charged lattice planes in the supercells, which can be expressed as [28]:

$$E_{corr}(y) = -q^{V_o}V(y). $$ (13)

We use the formation energy difference $\Delta E_f(y)$ of an oxygen vacancy at an arbitrary position $y$ in the cell with respect to the formation energy of an oxygen vacancy located at a reference point $y_B^{ref}$ inside the bulk, in the form of $\Delta E_f(y) = E_f(y) - E_f(y_B^{ref})$. Combining it with Equations (12) and (13), the corrected $\Delta E_f(y)$ can be re-formulated as:

$$\Delta E_f = E_{tot}(y) - E_{tot}(y_B^{ref}) - q^{V_o}[V(y) - V_B^{ref}]. $$ (14)

Note that, if the same reference point $y_B^{ref}$ is chosen for Equation (14) and for the average potential [e.g. the $V_{OBCd}(y)$ in Equation (9)], the term $V_B^{ref}$ cancels out.

3.1 The unrelaxed ATGB structure

Applying the method developed in Ref. [31], we generated a supercell of STO containing two identical asymmetric tilt grain boundaries with the orientation relationship
(430)[001]||(100)[001]. As in the generic GB supercell sketched in Figure 4(a), the y axis (lattice parameter \(b_{\text{cell}}\)) in this specific ATGB model structure is selected perpendicular to the GB plane. The periodic length in the (430) plane is five times that in the (100) plane, and the cell parameter in x direction (\(a_{\text{cell}}\)) is \(5a_{\text{STO}}\), with \(a_{\text{STO}}\) denoting the lattice constant of STO (3.905 Å). We set the cell parameter in z direction, \(c_{\text{cell}}\), to \(a_{\text{STO}}\). In the coincidence site lattice (CSL) [41], the period length of the (430) plane in y direction is set to four CSL elementary-cell length (20\(a_{\text{STO}}\)), while the period length of the (100) plane in y direction is 12\(a_{\text{STO}}\). These two grains are put together with a GB separation of half the cubic lattice parameter of STO, which leads to the total cell parameter in y-direction, \(b_{\text{cell}}\), of 33\(a_{\text{STO}}\) or approximately 129 Å. This choice of grain sizes ensures sufficiently large bulk regions for the point-defect calculations in the following.

Note that there are two types of possible terminations for both grains: the Sr-O and Ti-O\(_2\) termination planes in the (430) oriented grain, and the (Sr-O)\(_5\) and (Ti-O\(_2\))\(_5\) termination planes in the (100) oriented grain. In the following, we demonstrate the calculation procedure for a cell with Sr-O and (Sr-O)\(_5\) termination planes of the (430) and (100) grains, respectively. The corresponding structure consists of 166 Sr, 160 Ti and 486 O ions, as displayed in Figure 5.

![Figure 5](image-url)

Figure 5. The unrelaxed structure of a supercell containing an ATGB(430)|||(100), viewed from [001] tilt-axis direction. The x-z planes are either positively or negatively charged. The ionic compositions leading to those charges are exemplarily given for the surface planes at the two ends of the supercells. In both grains, several repeated bulk units are omitted, as indicated by the black dots.

Considering the x-z planes in the supercells, the unrelaxed structure is composed of repeated units of two types of atomic layers: a unit containing a Sr-O and a Ti-O\(_2\) plane in the (430) oriented bulk, and a unit containing a (Sr-O)\(_5\) and a (Ti-O\(_2\))\(_5\) plane in the (100) oriented bulk. The surface layers are shown in the x-z plane at the two ends of the supercell. Considering the partial charges of the ionic species in the Thomas potential, the Sr-O plane and the Ti-O\(_2\) plane in the (430)-oriented grain are positively and negatively charged with 0.44 e, respectively. In the (100)-oriented grain, the (Sr-O)\(_5\) and (Ti-O\(_2\))\(_5\) planes are positively and negatively charged by 2.20 e, respectively. Note that such a structure can be treated as a specific case of the model system sketched in Figure 4(a), with the charge values \(q = 0.44\) e and \(q' = 2.20\) e and the interplanar distances \(d_1 = 0.3905\) Å and \(d_2 = 1.9525\) Å.
In this structure, oxygen ions were removed one-by-one from all possible oxygen sites and their respective vacancy formation energies were calculated. First, open boundary conditions were applied in the $y$ direction perpendicular to the interface plane of the ATGB. The formation energies were referenced to the formation energy of a point defect located at a position $y_B^{\text{ref}}$ in the center of the bulk region of the (430) oriented grain. The values obtained without applying the electrostatic correction for this structure are displayed in Figure 6(a) (labeled as “simulation data”). The effect of the electrostatic potential is clearly visible by a strong linear variation of the values around the reference point by about $\pm 150$ eV across the (430) bulk grain, and a weaker linear variation by about $\pm 18$ eV around the midpoint across the (100) bulk grain.

To correct this apparent artifact, we combined Equation (14) with Equations (9-a)-(9-c). For the average electrostatic potential, the same reference point $y_B^{\text{ref}}$ was used as for the formation energies. The defect charge is the charge of the oxygen vacancy ($q_{V^O} = +1.40\ e^-$), and the lattice planes have a cross-sectional area $A = 76.25\ \text{Å}^2$.

Using these parameters, a successful correction was achieved by applying the developed methodology, as demonstrated in Figure 6(a). In the bulk regions, the uncorrected simulation data points deviate from those of the model function on the order of only 0.01 eV, which confirms the validity and capability of the correction approach.

Figure 6. The relative formation energies of oxygen vacancies ($\Delta E_f$) in the supercell containing an unrelaxed ATGB (430)||(100) with (a) open boundary condition and (b) periodic boundary conditions in $y$ direction. The formation energies and the average electrostatic potentials are referenced to their respective values at the position $y_B^{\text{ref}}$. The simulation data shown by the red circles (left energy axis) match the line of the
analytical potential model of Equations (9-a)-(9-c) combined with (14), indicated by the black line. The values corrected for the internal electrostatic potential (purple points) are plotted with respect to the rescaled right energy axis for a better visibility. The dashed vertical lines indicate the GB regions.

Next, periodic boundary conditions were applied in the $y$ direction perpendicular to the interface plane of the ATGB. The "simulation data" in Figure 6(b) show a parabolic behavior in both bulk regions. Here, the model function to correct the formation energies for the electrostatic potential in the bulk grains was obtained by combining Equations (14) and (11). Note that the total charge $q + q' = 2.64 \, e$ is needed as an additional parameter. The values of the other parameters are the same as those used for open boundary conditions.

As plotted in Figure 6(b), the numerical "simulation data" points of the uncorrected formation energies follow the parabolic function of the analytical potential model. The data points in the bulk grain regions deviate from the model on the order of 0.01 eV, indicating the validity and capability of our correction model for supercells with periodic boundary conditions, too.

3.2 The relaxed ATGB structure

3.2.1 Derivation of the potential function

Relaxation of atomic positions in the supercell displayed in Figure 5 was performed at constant volume with both open and periodic boundary conditions in the GB normal ($y$) direction. In the case of open boundary conditions, the grains were found to preserve their bulk structure with only slight displacements of ions close to the surfaces. Therefore, the corresponding correction of the vacancy formation energy values remains largely the same as discussed in Section 3.1 and plotted in Figure 6. In the following, we will focus on the relaxed structure obtained with periodic boundary conditions, which is displayed in Figure 7.

![Figure 7. The relaxed structure of the supercell containing an ATGB(430)||(100), viewed from [001] direction.](image)

In this relaxed structure, the configurations of the $x$-$z$ planes have changed by the ionic displacements. In the two bulk grains, the individual ions deviate by less than 0.1 Å in the GB
normal direction from the center of charge of their respective plane, while some ions close to the GBs deviate by up to 0.2 Å with respect to their unrelaxed positions.

Again, oxygen ions on all possible oxygen sites were separately removed and their corresponding vacancy formation energies were calculated. As before, these energies were referenced to the formation energy of a defect located at a position \( y_B^{\text{ref}} \) in a bulk region, chosen as the midpoint of the (430) grain. The numerical “simulation data” shown in Figure 8 follow a parabola with the depth of \( \sim 12 \) eV across the (430) bulk region and a similar parabola with the depth of \( \sim 6 \) eV across the (100) bulk region. However, such parabolas are not equivalent to the parabola obtained for the unrelaxed structure [cf. Figure 6(b)] because of the displaced (relaxed) ions. Now, each of these ions needs to be treated by a separate charged \( x-z \) plane for the potential summation. In this case, Equation (7) still holds for the averaged total potential \( V_{\text{PBC}}(y) \). But since the planes are not equidistant anymore, the term \( V_{\text{OBC}}(y) \) is not linear and therefore no longer follows Equations (9-a)-(9-c).

To determine an expression for \( V_{\text{OBC}}(y) \) for the relaxed structure, we applied the procedure in the same way as described in Section 2.2 for the unrelaxed structure: we first determined the accurate potential function \( V_{\text{OBC}}(y) \) across the supercell according to Equation (5). At the positions of the planes \( y_i \), the macroscopic average values \( V_{\text{OBC}}(y_i) \) were then calculated following Equation (8), with integration intervals \( \alpha_i \) extending from \( y_i - d_{i,\text{min}} \) to \( y_i + d_{i,\text{min}} \), where \( d_{i,\text{min}} \) denotes the shorter one of the two distances between \( y_i \) and its neighboring planes. In each of the two bulk regions, the values \( V_{\text{OBC}}(y_i) \) obtained in this way showed a quadratic behavior, and we finally obtained the functions \( V_{\text{OBC}}(y) \) by fitting those values to quadratic polynomials, separately for each grain. A qualitative explanation for the quadratic behavior is provided in Section 3.2.2.

Inserting the functions \( V_{\text{OBC}}(y) \) derived in this way into Equation (7) to obtain \( V_{\text{PBC}}(y) \), and using this expression in Equation (14), we arrive at the function for the corrected vacancy formation energies. Again, the same reference point \( y_B^{\text{ref}} \) was selected for the formation energy and for the average potential. The values of the other parameters \((q^{V_0}, A, q + q')\) were identical to those used in Section 3.1.

![Figure 8](image_url)

**Figure 8.** The relative formation energy of oxygen vacancies (\( \Delta E_i \)) in the relaxed structure of a supercell containing an ATGB (430)||(100), with periodic boundary condition in the
direction perpendicular to the GB (\(y\)), before (red circles, numerical “simulation data”, left axis), and after (purple points, right axis) applying the electrostatic correction with the analytical “model function” (black line). The dashed vertical lines indicate the GB regions.

As plotted in Figure 8, the numerical simulation data points of the uncorrected formation energy follow the analytical (parabolic) model function. The data points in the bulk grain regions deviate from the parabola at most by 0.01 eV. This demonstrates the capability and validity of our correction procedure for supercells of relaxed interface structures, too.

### 3.2.2 Influence of the potential on relaxation

As mentioned in Section 3.2.1, the macroscopic average potential \(\overline{\mathcal{V}}_{\text{OBC}}(y)\) in the two bulk grains of the ATGB supercell, which was previously relaxed with periodic boundary conditions, was obtained by fitting the calculated average potential values \(\overline{\mathcal{V}}_{\text{OBC}}(y_i)\) to two quadratic functions, one for each grain. The origin of this parabolic behavior can be understood by considering the repeated units consisting of two oppositely charged ionic groups in the two bulk grains. This is explained here for the case of the (430) oriented grain. As described in Section 3.1, before the relaxation, the positively charged Sr-O plane (+0.44 e) and the negatively charged Ti-O\(_2\) plane (−0.44 e) alternate and are equally spaced by a distance \(d = 0.3905 \text{ Å}\).

Upon structural relaxation, the differently charged ions within each of the above-mentioned planes are displaced due to their experienced electrostatic force originating from the unrelaxed lattice planes. Because the relaxed positions of the individual ions deviate by less than 0.1 Å from their respective unrelaxed positions, we treat the relaxed pair of Sr and O ions and the relaxed triple of Ti and two O ions each as ionic groups and consider the spacings between these groups in the following. We define the position of each of these groups as the mean value of all the individual ions belonging to the group. Let the distance between the Sr-O group and the neighboring Ti-O\(_2\) group in positive \(y\) direction be \(D_1\), and the distance between a Ti-O\(_2\) group and the Sr-O group in the next repeated ionic group in the same direction be \(D_2\).

Considering the parabolic macroscopic electrostatic potential in the bulk grain [cf. Figure 4(c)], a linear electric field is initially present across the supercell in \(y\) direction. Each two oppositely charged ionic groups separated by \(D_1\) left to the potential energy minimum position (and by \(D_2\) right to the potential energy minimum position) correspond to a dipole moment in opposite direction of the respective electrostatic field. Those who experience a larger electrostatic field will get separated with a larger displacement which thereby builds up a stronger counteracting depolarization field against the electrostatic field. However, the electrostatic field will not be fully compensated by the induced depolarization field due to additionally active interatomic forces between the ions. Such rearranged ionic groups further adapt the potential profile which adjusts the positions of the repeated ionic groups in turn, until the structure reaches an energy minimum.

Due to the linear electrostatic field, the distances \(D_1\) and \(D_2\) both are affected linearly as function of the \(y\) coordinate by the relaxation. However, the sum \(D = D_1 + D_2\) is approximately a constant (\(\sim 2d\)) for the repeated ionic groups in the bulk region because the structural
relaxation was employed at constant volume. One such stacked sequence is exemplarily sketched in Figure 9(a) together with the schematically sketched electrostatic potential profile $V_{OBC}(y)$ for this unequally spaced ionic groups in (b) as calculated from Equation (5). The potential increment within each constant distance ($D$) linearly decreases with respect to the $y$ coordinate, which produces a parabolic macroscopic average potential [shown by the dotted red line in Figure 9(b)]. This motivates the choice of quadratic fit functions for obtaining expressions for $\bar{V}_{OBC}(y)$.

![Diagram of stacking sequence and potential profile](image)

Figure 9. (a) An example sketch of the stacking sequence as the one observed in the relaxed ATGB structure, consisting of unequally spaced, alternatingly charged ionic groups with a constant distance $D$, but linearly changing distances $D_1$ and $D_2$ as a function of $y$ (b) the resulting schematic electrostatic potential $V_{OBC}(y)$ (solid red line), and the corresponding macroscopic average function (dotted red line).

The two distances $D_1$ and $D_2$ for the relaxed (430) bulk grain meet the interplanar distance of the unrelaxed structure at positions close to the potential minimum of the unrelaxed structure, i.e. in the center of the grain. This is obvious since no electric force is present there to drive the ions apart.
4 Summary and conclusions

We investigated the origin of electrostatic potentials arising in finite atomistic supercells of ionic crystals from alternatingly charged lattice planes and interfaces, namely surfaces and grain boundaries. Such potentials strongly interact with charged point defects, and therefore need to be corrected to obtain physically reasonable defect energies. Considering both, open and periodic boundary conditions, we analytically derived one-dimensional potential functions and systematically applied them to three generic cases with increasing complexity: a neutral cell with equidistant planes, a charged cell with equal termination planes, and a cell consisting of two different and separated grains. The application of open boundary conditions led to linear potentials across the supercells for each scenario, corresponding to the existence of surface and grain boundary dipoles. With periodic boundary conditions, this applies to neutral cells as well, but in the case of charged cells, a parabolic potential is additionally present arising from the compensating background charge. Since this corresponds to a linearly changing electric field, the ions in the supercell experience artificial, non-constant electrostatic forces and displace accordingly upon relaxation. We validated our formalism by applying it to supercells of the cubic perovskite strontium titanite with an asymmetric tilt grain boundary. The artificial electrostatic potential across the supercell in the direction perpendicular to the grain boundary was probed by positively charged oxygen vacancies, and their formation energies were corrected using our derived potential functions.

The demonstrated methodology offers the possibility of generalizing it to other charged extended defects in ionic crystals, such as the heterojunctions treated in Refs. [2] and [35]. The correction method for the defect calculations can naturally be extended from oxygen vacancies to cationic defects, e.g. strontium vacancies which were reported to be predominant in STO [42]. Even though demonstrated for systems of ions interacting by classical rigid-ion-model potentials in this paper, the gained insight into the origin of electrostatic potentials and the resulting electric fields in supercells with different boundary conditions can be transferred to systems treated by density functional theory as well. Altogether, the analytical correction method presented in this paper extends the family of general correction schemes for charged defects developed so far [43], towards the simulation of both charged point defects and charged extended defects inside polycrystals.

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