# Atomistic Computer Simulations of Dislocations in Strontium Titanate Single Crystals

**Atomistische Computersimulationen von Versetzungen in Strontiumtitanat-Einkristallen** Zur Erlangung des Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.) Genehmigte Dissertation von Arne Jan Klomp aus Dormagen Tag der Einreichung: 1. August 2022, Tag der Prüfung: 22. September 2022

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# Abstract

Thermo-mechanical, functional, as well as processing related properties of ceramics are typically tailored via defect engineering. While zero-, two-, and three-dimensional defects are widely studied, the domain of one-dimensional defects, i.e., dislocations has hardly been exploited to tailor ceramics. The reason is a lack of understanding of dislocations in ceramic crystal structures. Furthermore, effective means of introducing and controlling dislocations in brittle ceramics are not well explored. We expect that once dislocations in ceramics are properly understood, they can also be controlled and finally employed as an engineering framework to enhance mechanical properties such as crack resilience as well as functional properties, such as ferro- and piezoelectricity. However, this requires a fundamental understanding how dislocations work on the microscopic level. Here, we use atomistic computer simulations to shed light on the microscopic structure and properties of dislocations in SrTiO<sub>3</sub> which is a prototype member of the important perovskite family.

In three consecutive sections we explore (I) the equilibrium structure and low temperature configuration of dislocations that can be controlled by external mechanical stress; (II) the behavior of these dislocations under applied load, their tendency to glide, and the imperfections occurring during dislocation glide; (III) the implications of complex dislocation arrangements for the macroscopic plastic behavior of SrTiO<sub>3</sub>.

(I) First, we classify the dislocations reported in literature into five groups and model each of these types explicitly. We find that only dislocations with Burgers vector  $\langle 110 \rangle$  and glide plane  $\{1\overline{1}0\}$  can dissociate into partial dislocations. With the help of analytic estimates we show that this glide dissociation makes them good candidates for easy dislocation glide. However, their structure is very sensitive to the dislocation line orientation as well as the oxygen ion stoichiometry at the dislocation core.

(II) Second, stress is applied to the dislocation configurations identified in (I). We determine the Peierls stress as a function of the dislocation core configuration and stoichiometry and observe that the emission of defects from a gliding dislocation is a prominent feature for certain dislocation configurations.

(III) Third, we study multiple dislocations and their interactions. In doing so, we combine in silico observations of different dislocation arrangements with the results of ex situ electron microscopic characterization. We determine that points of preferential dislocation nucleation and opportunities for dislocation multiplication enable the plasticity of SrTiO<sub>3</sub>. This understanding paves the way to design methods for creating and controlling dislocations.

# Zusammenfassung

Die thermo-mechanischen, funktionellen und Verarbeitungseigenschaften von Keramiken werden gewöhnlich durch die Anpassung von Defekten gesteuert. Während null-, zweiund drei-dimensionale Defekte gut untersucht sind, wurden ein-dimensionale Defekte, d.h. Versetzungen, bisher wenig genutzt, um Keramiken zu optimieren. Dies liegt an einem mangelnden Verständnis von Versetzungen in keramischen Kristallstrukturen. Außerdem sind Mechanismen, um Versetzungen in spröden Keramiken zu erzeugen und zu kontrollieren, bisher wenig untersucht. Mit einem besseren Verständnis von Versetzungen in Keramiken erwarten wir verbesserte Kontrolle über Versetzung und schlussendlich ihre Anwendung, um mechanische Eigenschaften wie z.B. Bruchzähigkeit, aber auch funktionale Eigenschaften wie Piezo- und Ferroelektrizität zu verbessern. Hierfür müssen Versetzungen jedoch auf mikroskopischer Ebene besser verstanden werden. Zu diesem Zweck verwenden wir atomistische Computersimulationen, um die mikroskopische Struktur von Versetzungen und deren Eigenschaften in SrTiO<sub>3</sub>, einem prototypischen Mitglied der wichtigen Perowskit-Familie, zu untersuchen.

In drei konsekutiven Abschnitten untersuchen wir (I) die Gleichgewichtsstruktur und Konfigurationen derjenigen Versetzungen, die sich durch äußere mechanische Spannung bei niedrigen Temperaturen kontrollieren lassen; (II) das Verhalten dieser Versetzungen unter angelegter Spannung, ihre Tendenz zu gleiten und Fehler während der Gleitbewegung; (III) den Einfluss von komplexen Strukturen mehrerer Versetzungen auf das makroskopische plastische Verhalten von SrTiO<sub>3</sub>.

Als Erstes klassifizieren wir die in der Literatur gefundenen Versetzungen in fünf Gruppen und modellieren diese atomistisch. Es stellt sich heraus, dass nur Versetzungen mit einem  $\langle 1\,1\,0 \rangle$  Burgers Vektor und einer  $\{1\,\overline{1}\,0\}$  Gleitebene in Partialversetzungen dissoziieren können. Unter Berücksichtigung analytischer Abschätzungen zeigt sich, dass sie dadurch zu guten Kandidaten für einfaches Versetzungsgleiten werden. Die Struktur dieser Versetzungen hängt jedoch stark von der Orientierung der Versetzungslinie und der Sauerstoffstöchiometrie im Versetzungskern ab.

Als Nächstes wird mechanische Spannung an jene Versetzungen angelegt, von denen eine Gleitbewegung erwartet wird. Neben der Abhängigkeit der Peierls-Spannungen von der Konfiguration des Versetzungskerns wird beobachtet, dass bestimmte Versetzungen während der Gleitbewegung Kristalldefekte zurücklassen. Zuletzt untersuchen wir Strukturen vieler Versetzungen und deren Wechselwirkungen. Dafür kombinieren wir in silico Beobachtungen verschiedener Versetzungsstrukturen mit den Ergebnissen von ex situ Elektronenmikroskopie an mechanisch verformten  $SrTiO_3$  Einkristallen. Es wird gezeigt, dass Nukleationspunkte und Möglichkeiten für Versetzungsmultiplikation entscheidende Faktoren sind, welche die Plastizität von  $SrTiO_3$  ermöglichen.

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# **1** Introduction

 $SrTiO_3$  is an important member of the structural family of oxide perovskites that are of great technological relevance. The importance of this family can only be understood in the light of its basic crystal structure and its variations that enable many of this family's intriguing properties. We address this topic first in Section 1.1. Secondly, just like many metals, the properties of  $SrTiO_3$  can be tailored by defect engineering, which commonly consists of chemical and microstructural approaches, see Section 1.2. However, dislocations add a further defect dimension to this portfolio that has seen little attention thus far. Their understanding requires general knowledge about dislocations, see Section 1.3, as well as the specifics of dislocation configurations in the  $SrTiO_3$  structure, see Section 1.4. These aspects reveal a knowledge gap to be closed and, thus, research questions to be targeted in order to enable the exploitation of dislocations, see Section 1.5.

#### **1.1 Structural Properties of Perovskites**

Perovskites are a family of structures that derives its name from the mineral perovskite, CaTiO<sub>3</sub>, which has an orthorhombic structure [1]. However, the term has become synonymous for compounds of ABX<sub>3</sub> stoichiometry that inherit their structure (hettotype) from the parent  $Pm\bar{3}m$  structure (aristotype) as shown in Figure 1. The structure is composed of B-site cations, here Ti<sup>4+</sup>, that are surrounded by an octahedron of X-site ions, here O<sup>2-</sup> (nominal charges are indicated). The A-site ions, here Ca<sup>2+</sup>, and the B-site ions, form a body-centered configuration and the A-site is itself surrounded by twelve X-site ions. A large structural variety is possible in perovskites due to the breaking of symmetry, e.g., by ordered substitution of A-site or B-site positions [1] or octahedral tilting [2]. This breaking of symmetry explains the plethora of functional properties found in this family, including high temperature superconductivity [3–5], giant magnetoresistance (GMR) [4, 6], catalytic activity [4, 7], piezoelectricity [8, 9], and ferroelectricity [10].

Among the many functional properties of perovskites, dielectric effects are probably most widely used in technological applications, see Figure 2. Exploiting their dielectric properties, perovskites enable applications in electric or micro-electromechanical components [4]. A dielectric is a material that is electrically insulating up to a certain breakdown electric field because charge carriers such as ions or electrons are immobile [11]. Instead, electric fields cause ordering or re-orientation of local dipoles and a polarization that attenuates the electric



Figure 1: The conventional unit cell of the cubic perovskite structure is the aristotype for the family of perovskites displaying A-site cations (green), B-site cation (blue) and oxygen anions (red). Operations breaking the symmetry of this structure lead to a variety of related structures as shown for some simple cases. Atomic radii and distortions are not to scale.

field which is measured by the material's relative dielectric permittivity. This phenomenon enables building capacitors of increased capacitance, or vice versa, decreased dimensions compared to a plate capacitor in vacuum.

Special subgroups of dielectrics, see Figure 2, require restrictions on the crystallographic symmetry [12]. Crystals that exhibit piezoelectricity, i.e., a linear coupling of mechanical strain and polarization, must belong to one of 20 point groups where a center of symmetry is absent. Because the crystal symmetry is reflected in the symmetry of crystal properties [13], cubic  $Pm\bar{3}m$  perovskites do not feature this piezoelectric effect.

Pyroelectricity, in turn, describes the phenomenon that a temperature-dependent spontaneous polarization appears in the crystal [14]. Within the non-centrosymmetric point groups that enable the piezoelectric effect, we find the ten polar point groups necessary to create the pyroelectric effect [12]. In addition to the absence of a center of symmetry these point groups need to possess at least one axis "that is not repeated by any symmetry element" [14]. Put in other words, these are point groups where "every [symmetry] operation leaves more than one common point unmoved" [15].



Figure 2: Dielectric materials and their subgroups symbolizing the necessary conditions for the subgroups.

Finally, a ferroelectric is simply a pyroelectric in the sense that it possesses a permanent polarization. Additionally, a ferroelectric allows the polarization to be switched by the application of an electric field. The switching of a spontaneous polarization has given ferroelectrics their name due to an analogy to ferromagnets [16]. The ability to switch polarization by application of an electric field cannot be determined from crystal structure alone but usually has to be determined empirically. Switching of the polarization P under electric field E in a ferroelectric typically follows a characteristic hysteresis loop P(E). It accounts for the fact, that the material remains in a macroscopically polarized state even after the removal of the electric field.

All of these effects are occurring in perovskites. In fact, ferroelectric perovskites often feature strong pyroelectric and piezoelectric response, too [10, 11]. Therefore, many applications requiring pyroelectrics or piezoelectrics make use of the smaller group of ferroelectric materials. Historically, the use of ferroelectric BaTiO<sub>3</sub> in capacitors for its high dielectric permittivity made this class of crystals technologically relevant [4, 17, 18].

Perovskite structures can be formed by a variety of chemical compositions. This compositional variation is another reason for the popularity of this structural family [4]. It is nicely demonstrated by the structure field maps reported by Muller and Roy [1] showing ranges of stability for different compositions, see Figure 3.

These observations inspired the definition of a tolerance factor *TF* that describes the tendency of a ternary compound ABX<sub>3</sub> to crystallize in a perovskite structure. Taking into account the radii  $R_A$ ,  $R_B$ , and  $R_X$  of A-, B-, and X-site ions, respectively, the tolerance factor is defined as [19]

$$TF = \frac{R_A + R_X}{\sqrt{2} \cdot (R_B + R_X)} \,. \tag{1}$$

*TF* is equal to unity when the ions, represented as hard spheres, are ideally packed in the cubic perovskite structure. Deviations from this factor are allowed to some degree above



Figure 3: "Structure field map for A<sup>2+</sup>B<sup>4+</sup>O<sub>3</sub>". Displays empirically found ranges of stability for different perovskite materials. Re-printed from Ref. [1] with permission from Springer-Verlag GmbH, Heidelberg, Germany.

and below the ideal value resulting in distortions of the crystal lattice and often intriguing functionality [1, 19, 20].

#### 1.2 SrTiO<sub>3</sub> as Model Perovskite

Due to its good tolerance factor strontium titanate (SrTiO<sub>3</sub>) is an almost ideal representative of the perovskite family [19]. It possesses a cubic structure that is stable over a wide range of temperatures and pressures, see Figure 4 [21]. Compared to the technologically important perovskite BaTiO<sub>3</sub> it possesses a rather simple phase diagram [22, 23].

Because the crystallographic symmetry is reflected in the symmetry of crystal properties [13], cubic  $Pm\bar{3}m$  perovskites like SrTiO<sub>3</sub> are not piezoelectric. This simple structure and its stability make SrTiO<sub>3</sub> the ideal ground to study complex defects and their interactions, since the influence of defects is not obscured by piezo-, pyro-, and ferroelectricity. Additionally, many relations found here can be transferred to more complicated perovskites such as BaTiO<sub>3</sub> and PbTiO<sub>3</sub>. Consequently, it is probably the most well studied perovskite material [21, 24].

For most applications, however, ceramics need to be improved for easier processing and better functional performance. This is allowed by the vast configurational space of perovskites,



Figure 4: Schematic phase diagram of SrTiO<sub>3</sub> and BaTiO<sub>3</sub> at ambient pressure [21-23].

which is due to (i) doping and point defect engineering, (ii) the opportunity to form mixed perovskites on the A-site, B-site or both, (iii) the possibility to form ordered and disordered structures in these complex compositions, and (iv) a sometimes extremely large tolerance for off-stoichiometry and structural vacancies [4]. In practice, their functional properties are usually tailored by means of adjusting composition and microstructural features such as grain boundaries. By giving an overview over important aspects of tailoring  $SrTiO_3$  via defect engineering, see Figure 6, we will identify that the field of dislocation controlled properties offers great prospects to further tailor the ceramic properties.

#### 1.2.1 Doping and Alloying

A significant amount of research into defect engineering and doping of SrTiO<sub>3</sub> make this material a "model electroceramic" as highlighted in Refs. [24, 25]. Point defects are always present in a crystal at finite temperature and the most common defect is a pair of strontium and oxygen vacancies (Schottky-like) which is favored due to its low formation energy [24, 26, 27]. Also, oxygen vacancies and the corresponding formation of electron holes are a very common defect reaction, despite some debate about the actual charge state of the vacancy [28–34]. Because oxygen is part of the defect equilibria and oxygen vacancies are very mobile, there is a strong dependence of conductivity on oxygen partial pressure [25, 35–38]. This results in n-type conductivity at low, and p-type conductivity at high oxygen partial pressures [24].

Nevertheless, conductivities of pure or lightly doped  $SrTiO_3$  are generally low and in the range of  $10^{-12}$  S cm<sup>-1</sup> to  $10^{-10}$  S cm<sup>-1</sup> at ambient temperature [28, 39], reaching about 1 S cm<sup>-1</sup> in the vicinity of 1000 K [39]. Note, that low temperatures usually lead to lower conductivity (semiconducting behavior) because ionic motion requires thermal activation and defects tend to associate at low temperatures [24, 40–42]. Especially, the association of rather mobile species like oxygen vacancies with less mobile species such as Fe- or Mn-dopants has been investigated in detail because it can significantly reduce ionic conductivity at low temperatures [28, 38, 43, 44].

The point defect equilibria determining conductivity can be very well controlled using acceptor or donor doping which can occur by substitution on either the Sr- or the Ti-site [24]. While the crystal reacts to the substitution with aliovalent ions by creating vacancies or electronic charge carriers, the formation of interstitials is less common due to the good packing of the perovskite lattice but can be observed, e.g., after irradiation [24, 26, 39, 45]. Thus, doping as well as oxygen partial pressure can be used to induce n- or p-type semiconducting behavior. Nevertheless, as shown for example in the case of Fe-doped SrTiO<sub>3</sub>, conductivity usually remains of ionic nature at ambient temperatures and becomes more and more of electronic character at temperatures exceeding 400 K [28, 40]. The precise tailoring of conduction using, e.g., La-doping has been employed to produce oxygen partial pressure sensors for exhaust gas with superior reaction time and simpler design compared to conventional  $ZrO_2$ -based  $\lambda$ -sensors [28, 46]. Further gases can be selectively detected using various doping strategies as summarized by Szafraniak et al. [47]. Doped SrTiO<sub>3</sub> has also found use as photoelectrode in photocatalytic water splitting [48, 49] or even as a proton conductor [50, 51].

Exceeding the regime of doping by adding larger amounts of substitutes on the Sr- or Ti-site, a variety of solid solutions with different perovskites can be formed. As an example take the random solid solution of  $SrTiO_3$  with  $BaTiO_3$ , which forms a completely miscible system [52–54]. Compared to  $BaTiO_3$  the addition of Sr lowers the Curie temperature until the ferroelectric phase is fully suppressed around  $Sr_{0.96}Ba_{0.04}TiO_3$  [52, 53]. Just like doped  $SrTiO_3$ , the use of  $Sr_{1-x}Ba_xTiO_3$  has been discussed as a gas sensor [47]. Moreover, it is particularly popular as a lead-free dielectric for capacitors due to its high permittivity, low dielectric loss and excellent tunability which is desired in microwave antenna applications [47, 55, 56].

#### 1.2.2 Microstructure Engineering

Adding to the opportunities of doping and alloying, the design of the ceramic microstructure contributes another valuable engineering dimension, since microstructural features – encompassing grains and grain boundaries, inclusions, segregation, and space charge layers – are decisive for many structural as well as functional ceramics [57].



Figure 5: Space charge layers at grain boundaries allow to tailor the band structure spatially and engineer the capacitor's dielectric performance [77, 78]. There are different length scales to this phenomenon: device level (left), grain boundary level (center), and electronic structure (right).

In most applications polycrystalline SrTiO<sub>3</sub> is used, thus, the engineering of grain boundaries is applied extensively to enhance its electric and dielectric properties [24, 58–60]. Depending on their symmetry and coherency, grain boundaries act as sinks for certain defects, especially positive charges [61]. From a thermodynamic point of view, this segregation can be viewed as an alteration of grain boundary energy by defects [62]. The variation of stoichiometry and defect equilibria at grain boundaries can be enforced by doping of SrTiO<sub>3</sub> before sintering or during a separate firing procedure where dopants migrate from the material's surface to its interior along grain boundaries [61, 63–70]. Dopants segregated to grain boundaries hinder electronic and ionic transport, leading to the creation of a space charge layer with oxygen ion surplus [24, 40, 61, 71–76]. Therefore, grain boundaries exhibit p-type conductivity while the grains, especially when reducing sintering conditions are used, exhibit n-type conductivity [67, 70]. This results in Schottky barriers at the grain boundaries, see Figure 5 [77, 78]. By varying the size of the space charge layers the relative permittivity in SrTiO<sub>3</sub> boundary layer capacitors can be tailored in the range from 9400 to 65 000 while exhibiting high resistivity and low dielectric losses [63, 67]. With the delicate interplay of grain boundaries, surface, and space charges even a resistivity tuning by variation of applied voltage can be produced [63, 70, 79]. This phenomenon is commonly employed in variable resistors, so-called "varistors" [80].

Naturally, the control of microstructure is crucial for applications relying on grain boundary dominated properties [64, 67]. Therefore, significant research has been put into understanding grain growth and texture in various synthesis procedures [81–88]. An exceptionally strong influence of grain boundaries is present in thin films and super-lattice structures that have recently attracted significant interest [89]. There, the mechanical interaction of different perovskites with SrTiO<sub>3</sub> is exploited to induce strain and, thus, produce certain dielectric effects or sub-structures inside functional perovskites such as BaTiO<sub>3</sub>, LaTiO<sub>3</sub>, and

PbTiO<sub>3</sub> [90–92]. Also, the use of SrTiO<sub>3</sub> as a substrate for ferroelectric and superconducting thin films falls into this category [93, 94]. Such systems are not only used for their ferroelectricity or superconductivity but also the use as capacitors, resistive switches, and thermoelectrics have been demonstrated [95–97]. Another way to exploit the misfit strain of different perovskites has been explored with ceramic core-shell structures where the core and the shell of a particle are of different composition. The interplay of two different perovskites has been suggested to be beneficial in the context of photochemistry [98], tailoring the transition temperature of ferroelectrics [99], and piezoelectric hysteresis [100].

#### 1.2.3 Dislocation Engineering

The engineering of chemical composition and microstructure as means of tailoring ceramics are a well established field, see Figure 6. In metals the engineering of dislocations adds a further dimension that is used to tailor, e.g., tensile strength [101]. Basically, the study of dislocations in ceramics is as old as the topic of dislocations in metals [102]. Seminal work has been published from the late 1950s to 1980s in crystal structures where single crystals could be conveniently manufactured, e.g., many alkali halides, binary oxides, and few ternary oxides [103–111]. It had already been recognized that dislocations have a strain field associated but are also susceptible to charged dislocation cores enabling charge transport, the interaction with electric fields and charged point defects [103, 106, 110, 112–114]. A peculiarity of dislocations in ceramics is that they can possess charges at imperfect points of the dislocation – e.g., jogs – but can also be "inherently charged" as a result of the Volterra cut made in an ionic structure [103, 112, 115].

In these early works, dislocations were often seen as an artifact of imperfect crystal growth during synthesis [116–120]. Rarely have dislocations been engineered systematically [104], rather they were regarded as detrimental to, e.g., electronic properties [121–124]. Without knowledge about dislocation engineering, a targeted tailoring is hardly feasible. Generally, the literature over the past decades on dislocation engineering and subsequent tailoring of ceramic properties is rather sparse, especially, when compared to chemical or microstructural defect engineering, see Figure 6. We attribute this lack of interest to several reasons including the restriction of dislocation mobility to high temperatures [104, 107, 111, 125], the restriction to single crystals [107, 108], contradictory results about the effect of dislocations on diffusion [110, 126], and the failure to recognize the impact of dislocations on functional properties.

With the discovery of dislocation-based plastic deformation in  $SrTiO_3$  a method for the controlled application of dislocations into (single) crystals became available for a family of highly relevant crystals [127, 128]. On the one hand, it has been argued that the plasticity in  $SrTiO_3$  single crystals marked the overcoming of the paradigm that "ductile ceramics have remained an elusive and perhaps impossible goal, although toughened ceramics have emerged as a reality" [111, 129]. Therefore, novel ceramic processing methods as well as ceramics with improved resistance to fracture have been imagined [129–132]. On



Figure 6: Defects with different dimensions and on various length scales along with some examples of their prominent features. We focus on one-dimensional defects in this thesis because they can be used to tailor a material by their elastic as well as electrostatic fields.

the other hand, it was proposed that dislocations in perovskites could be used to tailor functional effects like electrical conductivity and resistive switching [133–141], thermal conductivity [142, 143], superconductivity [144, 145], and ferroelectric polarization [146–151]. In principle, dislocations were regarded as means of "one-dimensional doping" [140], "autobahns" for diffusion [137], sources of space charge regions [129], and a means of "ferroelectric hardening" [152]. The concepts of considering dislocations as dopants and creating space charge regions have, in fact, been borrowed from early research on dislocations in semiconductors [121–123, 153]. However, these systems are hardly comparable to ceramics due to their covalent bonding which creates the complication of dangling bonds at dislocation cores.

Despite the great hopes, many of the ambitions have not been fulfilled so far. Ductility of  $SrTiO_3$  is still largely limited to single crystals and could not be engineered into polycrystals [132, 154]. Dislocations could hardly be exploited as channels of increased oxygen ion conductivity and the contribution of dislocations to overall conductivity is still debated [137–140]. The expected influence on phonon thermal conductivity could not be demonstrated, probably due to too low dislocation density [143]. The interaction of ferroelectric properties and dislocations in ferroelectric perovskites is still poorly understood [151]. As many phenomena do not play out as expected, there is a demand for a solid theoretical understanding of dislocations at their microscopic level to enable better understanding of the experimentally observed processes as well as a more targeted employment of dislocations. Although some atomistic studies regarding the atomic nature of dislocations in  $SrTiO_3$  are available, see Refs. [137–139, 149, 150, 155, 156], none consistently compares dislocation

structures and elucidates the relation of dislocations and SrTiO<sub>3</sub> plasticity. Here we see the room for improvement and the chance that theoretical studies can explain experimental observations but also guide further theoretical and experimental efforts.

We choose to proceed into the study of the dislocation structure at an atomic level employing atomistic computer simulations. With classical molecular dynamics simulations the elastic as well as electrostatic fields of dislocations in ceramics can be conveniently studied while retaining the discrete atomic nature of the crystal [137–139, 149, 150, 155–157]. A special focus will be put on the relation of microscopic features of different dislocation configurations – Burgers vector, line vector, and dislocation core charge – with the mechanical properties of dislocations. Thereby, we create insights enabling better control over the mechanical response of dislocations, especially at low temperature [141].

The subsequent parts of this thesis start out by addressing some fundamentals about dislocations that are required to understand the findings in literature, simulation setups, and interpretation of simulation results. Then, we will come back to the literature knowledge about dislocations in ceramics and more precisely identify the questions that will be addressed (Section 1.5). Before actually answering these questions, some simulation concepts will be presented to explain why atomistic simulations are well suited for the study of dislocations (Chapter 2). In the main part (Chapter 3), the equilibrium structure (Section 3.1), mobility (Section 3.2), and interactions of dislocations (Section 3.3) in SrTiO<sub>3</sub> will be studied. Ultimately, some concluding remarks are in order to summarize the outcome of this work and guide research to further advance in the field of mechanical control over dislocations in perovskites (Chapter 4).

## **1.3 Theory of Dislocations**

In most solids that exhibit appreciable plastic deformation dislocations are the carriers of this plasticity [158]. Because most research on dislocations was conducted on metals or simple crystal structures [159], we will adopt a general picture on dislocations here and refer to the special case of dislocations in  $SrTiO_3$  in a later section. For now, we will present the typical geometry of a dislocation and how it can be identified in a general crystal.

In their simplest form dislocations are line-like crystal defects that have a one-dimensional periodicity [115]. Their line direction is given by the line vector  $\vec{t}$ . Each dislocation carriers a quantum of deformation called Burgers vector  $\vec{b}$  that describes the magnitude of the crystal fault [160, 161]. When enclosing the dislocation line by connecting neighboring atoms, the vector  $\vec{b}$  describes the mismatch when a symmetric path around the dislocation line is performed, see Figure 7. In essence, this so-called Burgers circuit method will be used by the dislocation extraction algorithm (DXA) to locate dislocations in our atomistic simulations [162, 163].



Figure 7: Schematic models of dislocations in a primitive cubic lattice, adapted from Ref. [164]. (a) and (b) show how the Burgers circuit in the dislocated (a) and in the ideal lattice (b) can identify the Burgers vector. While (c) shows an edge dislocation, (d) shows a screw dislocation in a three-dimensional representation.

As displayed in Figure 7, the Burgers vector can either be parallel or perpendicular to the line direction. These two situations are termed screw and edge dislocations, respectively [160, 161, 164, 165]. Theoretically, a screw dislocation can be constructed by partly cleaving the crystal and shifting one half of the partially cleaved crystal with respect to the other half [160, 161]. In contrast, an edge dislocation results when an extra crystal half-plane is inserted in between two crystal planes [102]. Dislocations where  $\vec{b}$  and  $\vec{t}$  are neither perpendicular nor parallel to each other are, consequently, called mixed dislocations [166]. The Burgers vectors in Figure 7 are conventional Burgers vectors, i.e., they correspond to a linear combination of crystal lattice vectors. If that is not the case, so-called partial Burgers vectors, at least the crystal to one side of the dislocation line must also be faulted [159]. All these situations, i.e., edge, screw, mixed, and partial dislocations do appear in SrTiO<sub>3</sub> and their specific relation is discussed towards the end of this section.

For plastic deformation to occur, the dislocation has to move, e.g., as a result of applied stress [102, 164, 167]. However, the mechanical response of a dislocation is anisotropic and determined by its glide plane with normal  $\vec{s}$ . It describes the plane in which a dislocation moves by dislocation glide and is simply the vector perpendicular to  $\vec{b}$  and  $\vec{t}$  in the case of edge dislocations [168]. The case where edge dislocations do not move within glide plane is referred to as climb or non-conservative motion and typically requires the diffusion of atoms around the dislocation core [169]. For screw dislocations, there is no unique direction in which a screw dislocation can move [169]. In a continuous medium it could in principle move in any direction. Yet, slip is restricted by crystal symmetry along a few specific directions. The modes of motion for a dislocation in SrTiO<sub>3</sub> are investigated in Section 3.2.

#### 1.3.1 Elastic Continuum Description of Dislocations

The construction of a dislocation produces a linear fault which, in turn, results in a mechanical response of the crystal lattice to the defect [102]. Thus, in the next paragraphs, the mechanical fields of edge and screw dislocations will be described in the framework of linear elasticity.

After making the cut-and-shift procedure to create a dislocation, the crystal is left with a discontinuity right at the dislocation line. This region and its immediate vicinity are referred to as the dislocation core. The treatment in conventional continuum mechanics, thus, leads to a technical problem because it entails discontinuous solutions for the displacement field  $u_i$ , the strain field  $\epsilon_{ij}$  and the stress field  $\sigma_{ij}$  that are complicated to solve [170]. However, this discontinuity is only a problem right at the dislocation core [169]. At some distance from the dislocation core (commonly a distance of  $b = |\vec{b}|$  is used) the displacement fields converge to an elastic response. Here, we follow the approach that is presented in common textbooks, for instance Ref. [171], where the continuum solution is restricted to a region outside the dislocation core can be circumvented in atomistic simulations where atomic interactions dictate the actual arrangement at the dislocation core.

If we accept that the displacement field  $u_i$  shows either a jump or a singularity at the dislocation origin, it can be shown that the total deformation tensor  $\beta_{ij}^T$  can be obtained by derivation, using Einstein notation [172, 173]:

$$u_{i,j} = \beta_{ij}^T = \beta_{ij} + \beta_{ij}^P .$$
<sup>(2)</sup>

 $\beta_{ij}^{T}$  consists of an elastic  $\beta_{ij}$  and a plastic contribution  $\beta_{ij}^{P}$ . As we are interested in the elastic description, we continue with the definition of the elastic strain tensor  $\epsilon_{ij}$  which is the symmetric part of the elastic deformation  $\beta_{ij}$  [173]:

$$\epsilon_{ij} = \frac{1}{2} \left( \beta_{ij} + \beta_{ji} \right) \,. \tag{3}$$

To transition from the elastic strain tensor to the stress tensor, material parameters are required. In principle the elastic parameters of any material are given by the fourth rank

Table 1: Mechanical fields produced by screw and edge dislocations [171, 177]. The Burgers vector with length *b* is pointing in *z*-direction for the screw and along *x*-direction for the edge dislocation. The coordinates *x* and *y* are chosen with the dislocation core at the origin and  $r = \sqrt{x^2 + y^2}$  is the distance to the origin. In an isotropic medium only the shear modulus  $\mu$  and the Poisson's ratio  $\nu$  are needed as material parameters.

screw dislocation		edge dislocation		
<i>u<sub>x</sub></i>	0	$\frac{b}{2\pi} \left[ \arctan\left(\frac{y}{x}\right) + \frac{1}{2(1-\nu)} \frac{xy}{r^2} \right]$		
u <sub>y</sub>	0	$\frac{-b}{8\pi(1-\nu)} \Big[ (1-2\nu) \ln r^2 + \frac{x^2-y^2}{r^2} \Big]$		
$u_z$	$\frac{b}{2\pi} \arctan\left(\frac{y}{x}\right)$	0		
$\epsilon_{xx}$	0	$\frac{-b}{4\pi(1-\nu)r^2}y\left[(1-2\nu)+\frac{2x^2}{r^2}\right]$		
$\epsilon_{yy}$	0	$\frac{-b}{4\pi(1-\nu)r^2}y\left[(1-2\nu)-\frac{2x^2}{r^2}\right]$		
$\epsilon_{zz}$	0	0		
$\epsilon_{xy}, \epsilon_{yx}$	0	$\frac{b}{4\pi(1-\nu)r^4}x(x^2-y^2)$		
$\epsilon_{xz}, \epsilon_{zx}$	$\frac{-b}{2\pi}\frac{y}{r^2}$	0		
$\epsilon_{yz}, \epsilon_{zy}$	$\frac{b}{2\pi}\frac{x}{r^2}$	0		
$\sigma_{xx}$	0	$\frac{-\mu b}{2\pi(1-\nu)r^4}y(3x^2+y^2)$		
$\sigma_{yy}$	0	$\frac{\mu b}{2\pi(1-\nu)r^4}y(x^2-y^2)$		
$\sigma_{_{ZZ}}$	0	$\frac{-\mu b}{\pi(1- u)r^2}\nu y$		
$\sigma_{xy}, \sigma_{yx}$	0	$\frac{\mu b}{2\pi(1-\nu)r^4}x(x^2-y^2)$		
$\sigma_{\scriptscriptstyle XZ},\sigma_{\scriptscriptstyle ZX}$	$\frac{-\mu b}{2\pi} \frac{y}{r^2}$	0		
$\sigma_{yz}, \sigma_{zy}$	$\frac{\mu b}{2\pi} \frac{x}{r^2}$	0		

elasticity tensor  $C_{ijkl}$  or the inverse compliance tensor  $S_{ijkl}$  [14, 174]. For simplicity, assume an isotropic material with shear modulus  $\mu$  and Poisson's ratio  $\nu$ . In the case of SrTiO<sub>3</sub> the condition of an isotropic material is fulfilled accurately enough such that we can describe Hooke's law with the two given material parameters [175] and by making use of the Kronecker delta  $\delta_{ij}$  [176]:

$$\sigma_{ij} = 2\mu \left( \epsilon_{ij} + \frac{\nu}{1 - 2\nu} \delta_{ij} \epsilon_{kk} \right) \,. \tag{4}$$

The list of solutions for  $u_i$ ,  $\epsilon_{ij}$ , and  $\sigma_{ij}$  for pure edge and screw dislocations provided in Table 1 is adapted from Cai and Nix [171]. By the application of displacement fields to the atomic lattice, we have an alternative way of constructing dislocations in a simulation.

In the solutions in Table 1 the discontinuity at the dislocation line as a result of the  $\delta$ distribution-like dislocation core is apparent [171]. Additionally, note that the displacement field  $u_i$  decays with  $\ln(r)$  and, thus,  $\epsilon_{ij}$  and  $\sigma_{ij}$  are proportional to  $\frac{1}{r}$ . Therefore, these fields decay rather slowly with increasing distance from the dislocation core compared to, e.g., charge defects where Coulomb force decays proportional to  $\frac{1}{r^2}$ . Consequently, the study of dislocations in a computer simulation requires means to avoid finite size effects, such as using realistic distances between dislocations, large simulation volumes or Green's function approaches [169].

The divergence at *r* close to zero and the slow convergence at large *r* are also a problem when the excess defect energy of a dislocation shall be calculated because the integral in Equation (5) does not converge. To alleviate this problem finite boundaries  $r_0$  and *R* are chosen for the integration of the elastic self-energy  $E^{el}$  of a dislocation [171]:

$$E^{\rm el} = \frac{1}{2} \int_{L_0}^{L_1} \int_{r_0}^R \sigma_{ij} \epsilon_{ij} dR' dl , \qquad (5)$$

$$\Gamma(R) = \begin{cases} \frac{\mu b^2}{4\pi(1-\nu)} \left[ \ln\left(\frac{R}{r_0}\right) - \frac{1}{2} \right] & \text{for edge dislocation,} \\ \frac{\mu b^2}{4\pi} \left[ \ln\left(\frac{R}{r_0}\right) - 1 \right] & \text{for screw dislocation.} \end{cases}$$
(6)

Note that the first integral in Equation (5) runs along the line vector of the dislocation and the second integral is orthogonal to it. For convenience  $E^{\text{el}}$  is usually normalized by the dislocation length and sometimes referred to as the line energy  $\Gamma$ , see Equation (6) [159]. The elastic energy does neither converge for infinitely large crystals (large *R*) nor close to the dislocation core (small  $r_0$ ). For the latter boundary  $r_0$  an energy contribution termed "dislocation core energy" [159] is used to account for the energy in the inner core region, where linear elasticity breaks down [169]. The extent of the upper integration boundary, *R*, is limited by other dislocations or surfaces of the crystal [159].

#### 1.3.2 Dislocation Glide

Deformation by dislocations occurs incrementally: Each dislocation carries a quantum of deformation, the Burgers vector. By motion of the dislocation through the crystal a deformation of magnitude b is realized. The cumulative motion of many dislocations ultimately leads to macroscopic plastic deformation.

Dislocations can either move within their glide plane (conservative motion) or out of their glide plane (non-conservative motion). Glide motion is usually the easiest mode of dislocation motion where the dislocation line moves step by step from one lattice plane to the next [102]. This motion is driven by mechanical load, i.e., stress and strain. The action  $\vec{f}^{\rm PK}$  of an external applied stress  $\sigma^{\rm ext}$  on a dislocation line is connected to the orientation of the dislocation via

the Peach-Koehler formula [168], given in Einstein and vector notation making use of the Levi-Civita symbol  $\epsilon_{ijk}$ :

$$f_i^{\rm PK} = \epsilon_{ijk} \sigma_{li}^{\rm ext} b_l t_k , \qquad (7)$$

$$\vec{f}^{\rm PK} = \left(\vec{b} \cdot \vec{\sigma}^{\rm ext}\right) \times \vec{t} . \tag{8}$$

Equation (8), therefore, describes the geometry of optimal loading of a dislocation. In the simulations of dislocation glide in Section 3.2 we will always use this optimal loading geometry.

As  $f_i^{\text{PK}}$  is increased by raising  $\sigma_{lj}^{\text{ext}}$  there will be a stress level where the dislocation starts to glide at 0 K. This stress level is commonly referred to as the Peierls stress  $\tau_m$  [178]. Its origin is the Peierls energy, i.e., the energy barrier that has to be overcome to move a dislocation on its respective potential energy landscape, see Figure 8. In equilibrium a dislocation stays in a minimum on this energy landscape (Peierls valley). During motion, it surmounts an intermediate maximum (Peierls hill) and moves into the adjacent valley. By moving from Peierls valley to Peierls valley the dislocation moves step-wise [179]. At finite temperature, the motion of a dislocation line is also thermally activated reducing the average stress needed to overcome the Peierls hill. Since information about the dislocation motion can be drawn from the energetic configuration, we will make use of the stacking fault energy hypersurface which describes the energetic relation of different displacement in the glide plane, thus, allowing conclusions about the dislocation structure [180], see Section 3.1.

In any macroscopic crystal, a dislocation does not surmount the Peierls barrier as a straight line [181]. This would require a large amount of activation energy. Instead, it is common that only a segment of the dislocation surmounts the Peierls barrier and moves to the adjacent Peierls valley, see Figure 8. This segment is bounded by two kinks which gives this process



Figure 8: Schematic model of a simple energy landscape for an edge dislocation indicating its important features.

its name "kink pair formation". Subsequently, these kinks move to the side and thereby drag the full dislocation line over the Peierls barrier.

### 1.4 Overview of Dislocation Types in SrTiO<sub>3</sub>

So far dislocations have been discussed in a qualitative and quantitative framework for general crystals. However, dislocations in ceramics such as  $SrTiO_3$  are especially interesting and relevant for the improvement of ceramic properties. Different slip systems are available in  $SrTiO_3$ , which are commonly labeled by their Burgers vector in angular brackets and slip plane in curly braces. On the one hand, the "soft" slip system  $\langle 110\rangle \{110\}$  features easy dislocation glide even at and below room temperature. On the other hand, the "hard"  $\langle 100\rangle \{001\}$  system can only be activated at high temperatures [127, 128, 132, 182–184]. This general feature is known from other perovskites [185, 186]. Thus, we focus on dislocations of  $\langle 110\rangle \{110\}$  orientation and only shortly discuss dislocations of other orientations that were found experimentally at low temperatures. For conciseness, we classify the dislocations with letters  $\mathcal{A}$  to  $\mathcal{E}$  ordered by their relative importance and not by their historic appearance.

The early works (before 1996) on dislocations in perovskites, including SrTiO<sub>3</sub>, have been summarized by Mao and Knowles [114]. In their transmission electron microscopy (TEM) studies of dislocations after high temperature synthesis they find  $\langle 0\bar{1}1 \rangle \{0\bar{1}0\}$  dislocations. We will consider this to be dislocation type  $\mathcal{E}$ , see Figure 9. It appears dissociated into two equal and collinear partial dislocations,  $\frac{1}{2}\langle 0\bar{1}1 \rangle \{0\bar{1}0\}$ , either in the glide plane (glide dissociation) or out of the glide plane (climb dissociation). This is in contradiction to the then known dislocations in other perovskites [182, 185, 186], but no satisfactory explanation could be given. We note that the dislocations observed in this study have experienced a strong influence from the high temperatures of the synthesis procedure as well as heavy doping. Later, however, this dislocation type was also reported in Nb-doped SrTiO<sub>3</sub> after Vickers indentation and investigated theoretically [187, 188]. None of the these studies, however, show notable plastic deformation or expect to control the arrangement of dislocations mechanically.

As already mentioned, the revived interest into dislocations in  $SrTiO_3$  goes back to the studies by Brunner et al. [127]. By compressing  $SrTiO_3$  single crystals along a crystallographic [001] direction they produce the maximum shear stress on  $\{1\overline{1}0\}$  planes. Dislocation formed on these  $\{1\overline{1}0\}$  planes possess a  $\langle 110 \rangle$  Burgers vector and are seemingly dissociated. Details of their line orientation and the type of splitting, however, have often been neglected in literature [127, 128, 140, 189].

Despite the ductility itself, also the temperature-dependence of the yield strength was surprising [127, 128, 184]. As displayed in Figure 10, the stress at which SrTiO<sub>3</sub> either yields in a ductile ( $\tau_0$ ) or brittle fashion ( $\tau_{\rm fr}$ ) is low at temperatures less than about 1000 K. Exceeding 1000 K the material shows brittle fracture at increasing fracture stresses. Only when temperature exceeds a certain threshold, the behavior is ductile and yield stress



Figure 9: Crystallographic orientation of defining vectors for dislocation type  $\mathcal{E}$ . Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple).

decreases again. At first, there was no convincing explanation to this behavior. However, the dependence on crystallographic orientation, see Figure 10, suggests that different glide systems need to be involved in the different regimes.

Regarding the arrangement of these mechanically controlled dislocations in the (110){110} system it was suggested by Taeri et al. [184] that they can be of edge or of screw character. We will refer to the former edge type as type  $\mathcal{A}$  dislocations and the screw type as type  $\mathcal{B}$  dislocations, see Figure 11. For the edge dislocation  $\mathcal{A}$ , Sigle et al. [190] later specified that they were predominantly found at temperatures of 1700 K in a climb dissociated configuration, i.e., with  $\frac{1}{2}(110)$  Burgers vector. At temperatures exceeding 1000 K sufficient activation energy for such a climb should be present. Note, that climb dissociated type  $\mathcal{A}$ dislocations are generally immobile at temperatures where not sufficient activation energy for climb is available [190, 191]. The climb dissociation was also verified after low temperature deformation but after the influence of ultra-high voltage TEM [156]. It is probable that the sample preparation procedures for the microscope and its strong electron beam have a similar activating influence as high thermal energy [192, 193]. Climb dissociated partials of (110){110} edge dislocations have also been constructed in bi-crystal experiments. It was found that two corresponding partials feature different ratios of Sr and Ti at the dislocation core suggesting that the two partial dislocations are actually not identical [194]. However, the climb dissociation is not a natural feature but has been enforced by the way of constructing the bi-crystal. The results are, therefore, of limited use in determining the equilibrium structure of these dislocations.

In contrast, screw type  $\mathcal{B}$  dislocations were present after deformation at room temperature and below [190, 195, 196]. While this suggests a low mobility at low temperatures, there is also evidence of type  $\mathcal{B}$  dislocations to be more mobile at room temperature that type  $\mathcal{A}$ dislocations [197]. Also, the experimental results regarding the splitting of this dislocation



Figure 10: Yield stress ( $\tau_0$ , filled symbols) and fracture stress ( $\tau_{fr}$ , empty symbols) of SrTiO<sub>3</sub> at different temperatures and loading directions (color coded) [184]. Regimes A and C are the regimes of ductility at low and high temperatures, respectively. In the intermediate temperature regime B samples fail in a brittle fashion. Therefore, not the yield stress but the fracture stress is given for these samples.

type into partial dislocations are contradictory [184, 190, 195, 197, 198]. Nevertheless, from a theoretical standpoint it is expected that type A and B are both able to dissociate in their glide plane [149, 188]. Hirel et al. [149] used the calculation of the stacking fault energy hypersurface ( $\gamma$ -surface) to show that there is a metastable configuration that stabilizes the stacking fault appearing between two equal and collinear partial dislocations.

The metastable stacking fault configuration could also enable climb dissociation of type  $\mathcal{A}$  dislocations, which was confirmed in MD simulations at extremely high temperatures and pressures [149, 155]. The climb dissociation immobilizes type  $\mathcal{A}$  dislocations. Therefore, SrTiO<sub>3</sub> might become brittle at elevated temperatures that are high enough for type  $\mathcal{A}$  to climb dissociate but too low to activate the hard slip system. Only when temperature is increased even further the high temperature ductility regime is reached where dislocations with  $\langle 100 \rangle$  Burgers vector dominate [127, 128, 155, 184]. While so much evidence exists on climb dissociated configurations of  $\mathcal{A}$  dislocations, we, surprisingly, found hardly any experimental proof of glide dissociated type  $\mathcal{A}$  dislocations [199]. Rather full and climb dissociated type  $\mathcal{A}$  dislocations dominate the electron microscopic findings [156].

In the soft slip system  $\langle 110 \rangle \{1\overline{1}0\}$  that hosts the edge and screw dislocations, i.e., types  $\mathcal{A}$  and  $\mathcal{B}$ , a third dislocation line orientation was also observed. Instead of dislocation line vectors perpendicular ( $\langle 001 \rangle$ ) or parallel ( $\langle 110 \rangle$ ) to the Burgers vector, the line vector of this third dislocation type is  $\langle 111 \rangle$  leading to the mixed type  $\mathcal{C}$  dislocation, see Figure 12. It



Figure 11: Crystallographic orientation of defining vectors for dislocation types A and B. Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). The full Burgers vector has been split into two equal parts to indicate glide dissociation.

was first mentioned in bulk compression of  $SrTiO_3$  [199] and described in more detail in Refs. [129, 136, 156]. This dislocation type was also reported to glide dissociate into two equal and collinear partials [136].

In addition to C-type dislocations, Jin et al. [136] also reported a type D dislocation that can be formed from two type C dislocations, see Figure 13. Since it also has a  $\langle 110 \rangle$  Burgers vectors like dislocation types A, B, C, and E, we will include it into the list of dislocations related to the soft slip system studied here.

We have now established that many types of dislocations have been proposed in literature. Mainly, dislocations of Burgers vector  $\langle 1\,1\,0 \rangle$  that are part of the soft  $\langle 1\,1\,0 \rangle \{1\,\overline{1}\,0\}$  slip system or related to it are found in experiments where dislocation-based plasticity was observed. Therefore, the dislocation types summarized in Table 2 are the ones that are susceptible to mechanical tailoring of dislocation arrangements in SrTiO<sub>3</sub>.

Table 2: Summary of the vectors corresponding to dislocation types  $\mathcal{A}$  to  $\mathcal{E}$  and the according references.

	$\vec{b}$	ť	ñ	type	configuration	Refs.
$\mathcal{A}$	$a\langle 110\rangle$	$\langle 001 \rangle$	$\{1\overline{1}0\}$	edge	full/glide/climb	[200]
${\mathcal B}$	$a\langle 110\rangle$	$\langle 110\rangle$	$\{1\overline{1}0\}$	screw	full/glide	[201]
$\mathcal{C}$	$a\langle 110\rangle$	$\langle 111\rangle$	$\{1\overline{1}0\}$	mixed	full/glide	[202]
$\mathcal{D}$	$a\langle 110\rangle$	$\langle 1\overline{1}1\rangle$	$\{1\overline{1}\overline{2}\}\$	edge	full/climb	[203]
${\mathcal E}$	$a\langle 110\rangle$	$\langle 100 \rangle$	{001}	mixed	full/glide/climb	[204]



Figure 12: Crystallographic orientation of defining vectors for dislocation type C. Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). The full Burgers vector has been split into two equal parts to indicate glide dissociation.

Regarding the charge state of dislocations and dislocation cores with  $\langle 1\,1\,0 \rangle$  Burgers vector, information is very limited. Some indirect observations from the interaction with point defects and interactions with electric and dielectric properties are available, but generally the dislocation types have not been specified. Adepalli et al. [140] perform tracer diffusion experiments in different atmospheres and find that  $\langle 1\,1\,0 \rangle$  dislocations possess a positive charge due to oxygen deficiency. The resulting negative space charge layers around the dislocations overlap significantly at high dislocation densities strongly inhibiting oxygen tracer diffusion. In addition to the interaction with oxygen vacancies, Refs. [205–207] find that a slight stoichiometric imbalance in favor of Sr and reducing conditions, increasing the oxygen vacancy concentration, ease dislocation nucleation. At the same time dislocation mobility is reduced [206, 207].

With respect to the motion of  $\langle 1\,1\,0 \rangle$  dislocations, theoretical investigation based on the kink pair theory have been conducted [208–210]. They basically confirm that experimental observations are the result of kink formation and migration, and that kink formation on corresponding pairs of partial dislocations are probably correlated at low temperature. Correlated formation of kinks has been discussed for a long time as a mechanism that significantly reduces the required force to move a dislocation [211]. We note, that the dislocation migration by kink formation for these dislocation types as visualized by electron microscopy in Refs. [197, 199] leads to significantly reduced stresses required to actually move the dislocation in a macroscopic crystal at finite temperature compared to microscopic simulations at 0 K. Experimentally, Javaid et al. [212] estimated the stress required to move a dislocation at 25 °C to 350 °C from dislocation pile-ups after nanoindentation. They report the required stress level to be in the range of 89 MPa to 36 MPa. At 0 K, however, the Peierls stress for type A and B to rigidly overcome the Peierls hill was estimated from



Figure 13: Crystallographic orientation of defining vectors for dislocation type  $\mathcal{D}$ . Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple).

simulations of continuous straining of dislocation monopoles to be around 1.5 GPa and 2.64 GPa, respectively [150].

The presence of dislocations in the SrTiO<sub>3</sub> crystals before mechanical load seems to be an important factor to enable plastic deformation [198]. In general, feasible dislocation densities in SrTiO<sub>3</sub> vary by synthesis method and loading procedures. The upper limit in single crystal compression seems to be around  $10^{13}$  m<sup>-2</sup> as verified by various microscopy and diffraction techniques [129, 189, 213]. Via rough polishing of single crystal surfaces, however, local dislocation densities of  $10^{15}$  m<sup>-2</sup> and higher can be achieved [129, 136].

In summary, experimental investigations have contributed great efforts to identify means of mechanical dislocation control and measure the effect on microscopic and macroscopic properties. However, the research community is well aware that, in order to understand the transport, electronic, and mechanical properties of dislocations in more detail, more detailed investigations of the relevant dislocations is required. Therefore, numerous publications are requesting research on the atomistic structure of dislocations in SrTiO<sub>3</sub>, the ultimate goal being to facilitate dislocation-based or -enhanced functionality [129, 141, 207].

## 1.5 Research Questions

The preceding literature review has revealed that even in a well investigated system like  $SrTiO_3$ , a conclusive understanding of dislocation structure and mechanics are lacking. Without understanding their microscopic properties and the relation of dislocation structure and mechanical properties, a targeted engineering of dislocations and, ultimately, tailoring of

material properties is hardly possible. At the same time, we have identified that dislocations in engineering ceramics have great potential. To leverage this potential, this thesis aims to reduce this knowledge gap in three consecutive sections.

Section 3.1 aims to understand the dislocation structure in their equilibrium configuration by performing static simulations and simulations at very low temperature. In these simulations the relaxation of particles and structures as well as the atomic motion is easily controlled and observed. The following questions are addressed:

- 1. Analytical and continuum theories of dislocations are mostly based on observations made in metals or are deduced from mathematical models. Can these theories be employed to predict the behavior of dislocations in perovskites?
- 2. Type  $\mathcal{A}$  dislocations are reported in literature as the prime carrier of plasticity in SrTiO<sub>3</sub> [190]. What microscopic structure of this dislocation type is responsible for easy glide, and how does it relate to the ductile-to-brittle transition [128, 155]?
- 3. Type *B* dislocations are the screw analog of type *A* edge dislocations. How does the different alignment of dislocation line and Burgers vector affect the dislocation core structure and its ability to glide?
- 4. Type C dislocations mark an important mixed type between type A and B dislocations [136]. Do these mixed dislocations rather behave like edge or screw dislocations or do they show entirely new characteristics?
- 5. It has been suggested that type  $\mathcal{D}$  dislocations can form through a reaction of two type  $\mathcal{C}$  dislocations [136]. However, it differs from type  $\mathcal{C}$  by the line direction. How does this different line direction influence the structure of the dislocation and its core?
- 6. Type  $\mathcal{E}$  dislocations have a  $\langle 110 \rangle$  Burgers vector and  $\{001\}$  glide plane [114]. Despite having a different glide plane than types  $\mathcal{A}$  to  $\mathcal{C}$ , can  $\mathcal{E}$  type dislocations also glide dissociate and contribute to plasticity?

Section 3.2 extends the static picture of dislocations towards the motion of dislocations. Based on the equilibrium structure we make predictions about the mobility of the various dislocation types. These predictions are then checked by application of stress to the dislocations. Our studies will, thus, answer these questions:

- 1. What is the Peierls stress of dislocation types A, B, and C?
- 2. How does kink formation and migration affect the stress level required to move dislocations?
- 3. What is the mode of motion of the dislocations, and how do they interact with point defects?
Finally, multiple dislocations are required for the macroscopic plastic deformation of crystals. Therefore, Section 3.3 addresses the question if we can relate experimental observations to simulations of large dislocation arrangements.

- 1. In bulk deformation experiments by Porz et al. [156] dislocations were created by nucleation at a stress concentrator and dislocation multiplication. How does dislocation multiplication occur when dislocations move through the sample over longer distances?
- 2. It has been shown, e.g., in Refs. [132, 198], that already existing dislocations strongly influence the plasticity of  $SrTiO_3$  at a microscopic level. Does there need to be an arrangement of pre-existing dislocations in order to facilitate macroscopic plasticity up to high strain?

# **2** Computational Methods

In order to study dislocations on an atomistic level we require three ingredients: (i) A model for the physical interactions of the particles, (ii) methods using these interactions to simulate the material's response, and (iii) a proper setup of the atomic arrangements and boundary conditions such that we can reveal the properties of interest. Therefore, we first discuss which model of the microscopic interactions is appropriate and what parameters are used. Next, the computational methods for static and dynamic simulations are explained shortly. Here, we add a section on the software implementations that are actually used in executing the computations. And last, the specific structures of our setups will be explained as they connect the observable properties and their meaning, e.g., critical stress, to the atomic arrangement, e.g., a pair of dislocations.

# 2.1 Modeling of Interatomic Interactions

In this thesis we want to study the static and dynamic behavior of dislocations in  $SrTiO_3$ . The behavior of any system we study is determined by its tendency to achieve a state of minimum energy [214]. The type of energy relevant depends on the boundary conditions of the system. More generally, the combination of a system with its constituents and the applied boundary conditions are called "ensemble" [215].

In the easiest case, the energy under consideration is the potential part  $E^{\text{pot}}$  of the inner energy E [215]. Thus, we require a model that allows to calculate the potential energy in dependence on the system's configuration. Three models are commonly employed on the length scales that are appropriate for studying the configuration of dislocations and dislocation cores, see Figure 14.

At the lowest level are a group of models relying on density functional theory (DFT). The energy  $E^{\text{pot}}[n(\{\vec{r}_k\})]$  of an ensemble of atoms is obtained based on the electron density  $n(\{\vec{r}_k\})$ , which in turn depends on the position of all atoms  $\{\vec{r}_k\}$  [219, 220]. The electron density is obtained by treating the valence electrons of the atoms explicitly [221]. Therefore, they are computationally very demanding which currently restricts the number of atoms N that can be treated simultaneously to a few hundred [216]. Nevertheless, they have the advantage of requiring little a priori knowledge about the atomic interactions and providing



coarse-graining, increasing computational efficiency

Figure 14: Comparison of the ways to calculate potential energy  $E^{\text{pot}}$  from different microscopic models in materials science. The basic quantities described, typical length scales, and an example for a software implementation are also given [216–218].

some of the most exact results in solid state physics [222]. We will use the DFT-approach for the calculation of  $\gamma$ -surfaces where we desire results with as little as possible assumptions about the atomic interaction while requiring the treatment of few atoms only. The  $\gamma$ -surface is a useful descriptor for accessing the energetics of dislocation motion in a crystal [180, 223, 224].

At a coarser level the interactions between particles are described by analytic formulae called classical interatomic potentials. The interatomic potential is a description of energy or force that one atom exerts onto another atom allowing the calculation of  $E^{\text{pot}}(\{\vec{r}_k\})$  directly as a function of the atomic positions [225]. Therefore, simulations using interatomic potentials can currently be employed to study up to 10<sup>9</sup> atoms, although simulations up to a few million atoms are more common [217]. Efficiency comes at the cost of generality of the interatomic potentials. The study of a certain material usually requires the time-consuming design of a new interatomic potential for each material and its applicability is often restricted to a range of boundary conditions, such as certain crystal phases [225].

The most basic variant of interatomic potentials features only pair-wise interactions of particles [226, 227]. While classical pair-wise potentials are easy to implement and analyze, more complex alternatives have been developed for more accurate material descriptions. Popular examples include potentials with fixed ionic charges (rigid ion potential) [157, 228], separate core and shell particles for each ion [26, 27, 54, 229], variable ionic charge (charge transfer models) [230], and embedding terms for electron density (embedded atom method)

[231]. Recently, interatomic potentials derived from machine learning approaches have gained popularity and demonstrated accurate results for a variety of materials [232–234]. Typically, these machine learning potentials such as the Gaussian Approximation Potentials [235, 236], Moment Tensor Potentials [237], and Atomic Cluster Expansion [238] take into account higher order interactions, i.e., interactions are derived from a group of neighboring particles instead of pair-wise interactions.

Because we are concerned with one certain material,  $SrTiO_3$ , and require samples of several nanometers in size to capture the elastic fields of dislocations an interatomic potential is the method of choice. For the study of  $SrTiO_3$  rigid ion [157, 228] as well as core-shell potentials [26, 27, 54, 229] have been proposed. The selection of the model used in this thesis is discussed in Section 2.1.2.

As an even more coarse-grained level the effective Hamiltonian framework neglects the atomic nature of the crystal and represents the solid on a unit cell basis. The energy is calculated based on effective quantities that are important for the phenomena of interest such as phase transformations [239]. For studying ferroelectrics, for example, each unit cell can be well described by one vector for strain  $\vec{e}_k$  and one vector for the local optic mode  $\vec{p}_k$  which is responsible for the local polarization [240, 241]. Potential energy  $E^{\text{pot}}(\{\vec{e}_k\},\{\vec{p}_k\})$  is then a function of these two vectors. In the case of a perovskite this reduces the positional degrees of freedom from 15 per formula unit in the interatomic potential (5 atoms with 3 positional coordinates) to 6 in the effective Hamiltonian approach (2 vectors with 3 entries each). This increase in efficiency comes again at a trade-off: only systems where unit cells are complete and on fixed positions can be evaluated. Therefore, this approach is not appropriate for studying dislocations.

In the following sections we will elaborate on the models and methods employed in more detail. First, we describe the models that are used to represent the physical behavior of an ensemble of atoms, i.e., the DFT approach as well as interatomic potentials. Second we focus on means to optimize, molecular statics, or sample the finite temperature behavior, molecular dynamics, of our ensembles. Third, as an ensemble includes boundary conditions, they will also be touched upon shortly. After a short note of the software employed for our purposes, we finally discuss the construction of the simulated samples.

## 2.1.1 Density Functional Theory Simulations

The idea of applying density functional theory in materials science is based on the observation that many quantities of physical systems are a consequence of their electronic structure [222]. If, therefore, we have a tool to reliably obtain a good approximation for the electronic structure one can in principle derive many quantities of interest. Note, that exact solutions are not available for any relevant physical system and numerical approximations need to be made [219, 220].

The name DFT derives from the theorem that for any system of interacting electrons with a density  $n(\{\vec{r}_k\})$  that is a function of the ionic positions, the minimum energy state – called ground-state – has an energy that is described solely by the electron density. Electron density n is described in terms of a set of electron wave functions  $\{\psi_i(\vec{r})\}$ . Therefore, the ground-state energy depends only on the functional Hamiltonian  $\hat{H}$  of the electron wave functions  $\{\psi_i(\vec{r})\}$  [219]. In practice the Hamiltonian is evaluated by numerical integration on a grid in reciprocal space [216].

At the core of DFT calculations is a method to obtain  $n(\{\vec{r}_k\})$  for the ground state in a self-consistent scheme [220]. The self-consistent scheme (also called self-consistent field calculations, SCF) iteratively computes the electron density  $n(\{\vec{r}_k\})$  from which all other quantities are derived. This cycle requires some knowledge about the Hamiltonian  $\hat{H}$  in order to assess the energy of a certain electronic configuration. At this point the energy contributions from the exchange interaction of paired electron, the correlation between electrons, and the electronic self-interaction are not exactly known [220, 222, 242]. Different schemes have been devised for an accurate description of this so-called exchange correlation energy  $\epsilon_{xc}$ , but its contribution still remains the main obstacle in modern DFT calculations [243]. Ultimately, the user has to decide on the trade-off between accuracy and computational effort – a choice which may vary depending on the system under study.

In the following we use a specific variant of DFT that makes use of projector-augmented electron wave functions (PAW) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [244–246]. In practice, the use of PAW functions reduces the necessary energy cut-offs of the wave functions that are needed to obtain accurate results, while the PBE formulation of the exchange-correlation functional is a good compromise of computational efficiency and accuracy.

Note, that DFT per se only results in the ground state's electron density. Yet, energy and forces on atomic nuclei can be readily derived with any modern software package, e.g., Refs. [216, 247, 248]. Following the Born-Oppenheimer approximation [249] the treatment of the motion of atomic nuclei is separated from the distribution of the electron density. Once the electron wave functions have been obtained, the forces on the nuclei can be calculated directly [250, 251]. Therefore, the integration of DFT forces as the basis of molecular statics and molecular dynamics calculations is possible, despite at large computational cost.

## 2.1.2 Classical Interatomic Potentials

In the particle description of classical potentials [215] atoms are represented as mathematical mass points, see Figure 14. In the simplest form, a pair potential  $\phi_{ij}$  describes the energy of one particle *i* interacting with other particles *j* in a functional or tabulated form. For solids, a potential typically defines the interactions between two particles such that it possesses a large positive value at very close distances (repulsion), a small minimum at a close to intermediate distance (equilibrium distance in a two particle system), and reduces to zero

for very large distances. The potential energy of a system of atoms is then obtained by summation over all pair-wise interaction,

$$E^{\text{pot}} = \frac{1}{2} \sum_{i} \sum_{j} \phi_{ij}(r_{ij}) , \qquad (9)$$

where *i* encompasses all atoms, *j* runs over all neighbors of atom *i*, and  $r_{ij} = |\vec{r}_i - \vec{r}_j|$  is the absolute distance between atoms *i* and *j* at positions  $\vec{r}_i$  and  $\vec{r}_j$ , respectively. The factor  $\frac{1}{2}$  accounts for the double counting of each interaction. Because of the form of  $\phi_{ij}$ , the largest contributions to  $E^{\text{pot}}$  for each atom come from the other atoms at close to intermediate distances. Therefore, it is common practice to design and use potentials in a way that truncates the interactomic interactions after a finite distance. This keeps the computational effort limited, creates close-to-linear scaling of computational effort with number of atoms *N*, enables efficient parallelization of the simulation over multiple processing units, and ultimately is the reason why large ensembles of atoms can be studied using this approach.

Simple interatomic potentials that feature only simple functional forms of short-range interaction, e.g., the Lennard-Jones potential [226, 227], are not sufficient to model more complex materials like  $SrTiO_3$ . In addition to the short-range interaction, the ionic charges have been included by Thomas et al. [157] and Pedone et al. [228]. This adds long-range electrostatic fields to the potential. The complete potential for  $SrTiO_3$  from Thomas et al. [157], which we employ in this thesis, combines a Born-Mayer term with the electrostatic interactions:

$$\phi_{ij} = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} .$$
<sup>(10)</sup>

Here  $r_{ij}$  is the distance between two particles and  $q_i$  is the ionic charge. Because the electrostatic contributions decay only very slowly with distance, a cut-off can hardly be chosen for the electrostatic part of the potential. In order to study large ionic systems, the electrostatic interactions are only calculated up to a distance of 10 Å in real space. Beyond that a more efficient Fourier-space calculation is used [252].

This interatomic potential has been used in a variety of studies about point defects [45], dislocations [138, 149, 150, 155, 253], and diffusion [138, 139], just to name a few. Its reliability has, therefore, been shown in several cases. Such a formulation of an interatomic potential is called rigid ion potential because atomic polarization and charge transfer are not included [254]. For materials that exhibit more complex phenomena such as ferroelectricity, the atomic polarizability may be required [255]. In this context core-shell interatomic potentials as proposed by Mitchell and Fincham [256] have proven very useful. The added degree of freedom comes from partly lifting the Born-Oppenheimer approximation. Each ion is regarded as a couple of particles, one representing the positively charged ionic core and one representing the negatively charged electronic shell. The charges of core as well as shell particles are fit parameters, i.e., they do not correspond to the actual charges of the nuclei or the valence electrons. Instead, they are usually adjusted to reproduce macroscopic material characteristics [255, 257]. For SrTiO<sub>3</sub> such potentials have been published in Refs. [26,

27, 54, 229]. Despite their complexity it has been found that these models do not lead to more accurate prediction of material characteristics, e.g., grain boundary energy [254, 258]. However, including shell particles creates a set of very light particles and reduces the integration time step for molecular dynamics calculations. Thus, they would lead to an unnecessary rise in computational effort for the scenario of dislocations in SrTiO<sub>3</sub>.

# 2.2 Modeling of Atomic Configurations

So far we have discussed the models that mathematically describe the interactions within a material. Next, we need an approach that makes use of these interactions to extract the material behavior for the desired situations [169]. To this end we distinguish three methods: molecular statics, molecular dynamics, and Monte Carlo simulations. Molecular statics are a way of optimizing the structural arrangement of the atoms without the influence of temperature [169, 215]. In molecular dynamics, atoms move due to their thermal energy while positions and interactions are calculated as they evolve over time [259, 260]. In contrast, Monte Carlo simulations follow a statistical approach of optimizing an arrangement of atoms. Monte Carlo simulations are a great method of finding optimum configurations but are not suited for extended defects such as dislocations [169, 261]. Thus, in the following, we will describe the principles of molecular statics and molecular dynamics simulations.

### 2.2.1 Molecular Statics Simulations

Molecular static (MS) simulations are a way of iteratively finding the local energy minimum of a group of particles:

$$E = \min E^{\text{pot}}(\{\vec{r}_k\}). \tag{11}$$

As the name suggests, MS solves this problem without the regard of time, temperature, and mass and, therefore, gives insights about the 0K structure of a material. To optimize the structure, the particles are iteratively displaced from their initial arrangement towards an arrangement of lower energy [169]. Therefore, as basic ingredients an initial arrangement of particles, a way of obtaining the energy and forces of such a configuration, and a method for propagating the system to a state of lower energy are needed.

The MS recipe works as follows [169]. Starting from an initial arrangement the energy of this configuration is calculated. DFT and classical interatomic potentials for this purpose have been discussed Sections 2.1.1 and 2.1.2. As the initial atomic arrangement is likely not to be the system's optimum it needs to be adjusted to come closer to the energetic minimum. In its simplest form, one can now compute the gradient in energy with respect to the displacement of each of the particles. In practice, this gradient might be calculated directly if there is a functional form for the energy and the gradient [215] or can be obtained

from the electron wave functions in DFT [250, 251]. When the particles are now moved slightly along the direction of the negative gradient, one can expect the overall energy to be reduced. Subsequently, the energy and gradients (equivalent to forces) are evaluated again, and the process repeats. It is only aborted when a predefined stopping criterion (commonly number of cycles, maximum force, minimum energy change) is met.

This so-called steepest descent algorithm has the disadvantage that it is usually not the most efficient way of reaching the next energy minimum. A very popular and often much more efficient strategy to attain a minimum is the conjugate gradient minimization scheme [262]. For a comprehensive introduction, see Ref. [263]. Note, that there are a variety of further algorithms to (quasi-)statically move an ensemble of particles to its optimum, such as the FIRE [264, 265] or the BFGS [266–269] algorithm, that each perform well in particular situations.

It is important to keep in mind that all static methods rely on a continuous reduction of the objective function (potential energy). Therefore, they continuously move the system towards decreasing energy and never upwards in energy, i.e., activation barriers cannot be overcome. Consequently, the initial configuration of particles decides which local minimum is found by the minimization procedure. It is up to the user to decide if this local minimum is also the physically sensible state. Other methods, such as molecular dynamics simulations can overcome energy barriers and assist in finding the global minimum (ground state).

### 2.2.2 Molecular Dynamics Simulations

Molecular dynamics (MD) simulations treat particles as classical point masses that move over time according to their velocities and forces. The basic structure of the algorithm in MD is shown in Figure 15.

It relies on describing the movement of an individual particle i by Newtonian equations of motion [270]. The force on an atom is related to its gradient in energy,

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{f}_i = -\vec{\nabla}_i E(\{\vec{r}_k\}), \qquad (12)$$

which can be integrated to track a particles motion over time. It is assumed that the Born-Oppenheimer approximation is valid [249] and the motion of particles can be described by a single point mass  $m_i$  per particle (e.g., atomic nucleus). Again, as initial conditions an arrangement of particles needs to be chosen. Instead of just positional coordinates also masses and momenta (or velocities) of the particles are required to propagate the system in time. In practice positions and masses are usually assigned based on the desired setup while velocities are initially assigned randomly in compliance with the desired temperature. As a system of particles is described in terms of its dynamic properties, i.e., an ensemble of positions { $\vec{r}_k$ } and velocities { $\vec{v}_k$ }, a procedure is required to obtain the temporal evolution of these properties for all N particles in time. This trajectory is approximated by an iterative



Figure 15: Flow chart of an MD procedure adapted from Ref. [271]. After initialization the MD loop is started and physical quantities are computed based on a physical model and on boundary conditions. After each MD loop it is checked if a predefined stopping criterion is met. If true, the simulation is stopped and results are output.

integration of the classical Newtonian equations of motion, see Equation (12). With each iteration the positions and velocities are propagated (calculated) for an increment in time  $\Delta t$ .

**Time Integration** The numerical integration of the trajectory is the central part of the MD routine and several algorithms for integration have been proposed. Some prominent examples are called Verlet [272], velocity-Verlet [273] or leap frog algorithm [252]. The default integration scheme in the program LAMMPS (see Section 2.3) is the velocity-Verlet algorithm.

The velocity-Verlet algorithm requires the calculation of the forces  $\{\vec{f}_k\}$  that act on each particle as the only physical input that is calculated for each time step. Because the mass m of a particle is fixed, the acceleration of a particle can be simply obtained by  $\vec{a} = \vec{f}/m$ . Based on the velocity and the acceleration at time t the positions at a consecutive point in time  $t + \Delta t$  are calculated for every particle (indices are dropped for readability):

$$\vec{r}(t+\Delta t) = \vec{r} + \Delta t \vec{\nu}(t) + \frac{1}{2} \Delta t^2 \vec{a}(t) .$$
(13)

Next,  $\vec{a}(t + \Delta t)$  is calculated with the new position  $\vec{r}(t + \Delta t)$  and velocity is updated using the mean of the acceleration at point *t* and  $t + \Delta t$ :

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{1}{2} \Delta t \left[ \vec{a}(t) + \vec{a}(t + \Delta t) \right] \,. \tag{14}$$

If thermodynamic or average quantities are of interest, they need to be obtained from the ensemble of positions and velocities, e.g., by means of statistical thermodynamics [215]. When these optional calculations are finished the stopping criteria (usually maximum number of cycles or one of the physical quantities) are checked, and the next iteration can begin. Outside this basic loop also several control procedures like thermostats can be added. A multitude of such algorithms is implemented in common MD programs. The most basic ones that allow for control of temperature and pressure are referenced below.

The choice of the time step  $\Delta t$  is crucial for the accuracy of MD simulations. It should be as large as possible for fast calculations but must be small enough to conserve energy during integration. In practice, this is tested by simulations over many time steps (on the order of 10<sup>5</sup>) by monitoring the total energy using the *NVE* ensemble (see below). If total energy drifts, i.e., its average does not stay constant, the time step is too large.

**Velocity Initialization** For the very start of an MD simulation the choice of velocities is somewhat arbitrary. Because of equipartition the initial kinetic energy will evenly distribute among all degrees of freedom [274]. Also, the velocity distribution naturally assumes a Maxwell-Boltzmann distribution in thermal equilibrium [275]. It should be kept in mind, that the temperature will often shift dramatically in the initial simulation steps due to redistribution of the kinetic energy into potential energy. Sufficient time steps should, therefore, be allowed to reach an equilibrated state [215]. Additionally, a thermostat can help to adjust the temperature to a desired value.

**Thermostat** A thermostat in an MD simulation is a separate control loop that adjusts the particles' velocities to come closer to a target temperature. Here we use the so-called Nosé-Hoover thermostat [276–279] for the MD simulations with the classical interatomic potentials. It introduces a kind of damping parameter to the forces and therefore drives the system to a target temperature (if the damping parameter is chosen appropriately). This formulation, however, requires a modification of the equations of motion in order to correctly include the damping parameter in the velocity-Verlet time integration scheme [279].

**Barostat** A barostat – like a thermostat – is a control loop that takes care to keep the stress tensor in a simulated cell at the target value [280]. It does so by comparing the inner pressure tensor of the simulation cell with the external stress tensor (target value) and adjust the system size if they do not match. Therefore, volume and shape of the simulation cell may change. The barostat features a damping parameter, too. Again the equations of motion are modified accordingly [279, 281]. A barostat can be applied as the only thermodynamic control loop, but also the simultaneous application of a thermostat is possible. However, the two damping parameters for thermostat and barostat are coupled and cannot be chosen independently when both are applied to a system simultaneously [281].

**Ensembles** Ensembles classify the thermodynamic conditions of an arrangement of atoms. There exist a variety of ensembles for a variety of physical situations to study but the most important are the micro-canonic (NVE), canonic (NVT), isenthalpic (NpH), and isobaric-isothermal (NpT) ensembles [280, 281]. The quantities in brackets indicate that these quantities are controlled quantities, namely N for number of particles, V for volume and shape, E for inner energy, T for temperature, p for pressure tensor, and H for enthalpy. Other quantities result from the definition of the system using these quantities.

#### 2.2.3 Boundary Conditions

Just like the thermodynamic conditions, the spatial boundary conditions (BC) are an important practical ingredient to particle-based simulations. The particles under observation are placed in a confined space called simulation cell. There are different ways this confinement can behave. The simplest case are open boundaries in which case particles are surrounded by vacuum. Thus, in case of the simulation of condensed matter, the boundaries act as surfaces. If surfaces are to be avoided periodic boundaries can be used. A periodic simulation cell now virtually repeats the system infinitely across the corresponding opposite boundary. For example, if a particle were to cross the boundary it would simply re-appear at the opposite boundary. Likewise, interactions are continued across a periodic boundary. Applying different types of boundary conditions to different sides of the simulation cell is also possible. Note, that the approach of periodic boundary conditions (PBC) only produces quasi-infinite systems. As the system interacts with itself across a periodic boundary, the surface is eliminated, but finite size effects will still occur.

Because a dislocation is a fault in the periodic arrangement of the crystal lattice it also affects periodic boundaries. For the construction of dislocations in a fully periodic simulation cell, care must be taken that the so-called Nye's tensor  $\vec{\beta}$  amounts to zero [172, 282]:

$$\vec{\beta} = \frac{1}{V} \int_{L} \vec{b} \times \vec{t} \, \mathrm{d}s \equiv 0 \;. \tag{15}$$

Here the integral runs over the full dislocation line lengths L in the simulation cell volume V. It basically ensures that there is no incompatible step at the surfaces of the cell violating the

periodic boundaries. When we construct dislocations in simulation cells this means that there must be an antagonistic dislocation for each dislocation we introduce. Therefore, we will resort to dislocation dipoles in the following [283, 284]. In contrast, the study of dislocation monopoles requires the breaking of periodicity, manual fixation of atoms at the surface of the simulation cell, and can also introduce an electric field, see Ref. [150].

We note that the setup of dislocation dipoles in periodic simulation cells technically creates an infinite array of dislocations. To avoid finite size effects due to the self interaction of dislocations two approaches can be taken. On the one hand, the setup of a dislocation quadrupole leads to a full cancellation of the mechanical fields inside the simulation cell [285, 286]. However, it requires large simulation cells, and the application of shear stress to the simulation cell for moving dislocations leads to a quick annihilation of the moving dislocations. On the other hand, finite size effects can be studied systematically in a dipole setup. Here, we take up this second approach and systematically vary the simulation cell size until the results no longer depend on it. Further details on the setup are given in Section 2.4.

# 2.3 Software Implementations

# 2.3.1 LAMMPS

For the MS and MD simulations based on classical potentials the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is employed [217, 287]. Its main features include very efficient time integration schemes for a large bandwidth of classical and more elaborate interatomic potentials. The potential forms used here can be easily implemented and the velocity-Verlet integration schemes for temporal evolution and Ewald summation for long-range electrostatic interactions are already included. Also, the application of boundary conditions, thermostats, barostats, and the calculation of thermodynamic quantities is straightforward.

Another major advantage of this software package is its excellent scaling when calculations are distributed over multiple processing units. The simulations performed in the context of this thesis commonly use anything from two compute cores up to more than a thousand individual CPUs simultaneously.

## 2.3.2 Abinit

The DFT calculations are performed using the software package ABINIT [216, 247, 248]. It performs the SCF calculations based on the PAW method and also has basic structure

optimization, i.e., MS capabilities. Besides these calculations it is also possible to obtain a multitude of derivative quantities such as stresses, energies, and forces on atoms.

In addition to the atomic structure, DFT calculations require the input of per-atom basis sets that contain the wave functions for the PAW method. They have been calculated using ATOMPAW [288, 289]. Although it is claimed that the PAW functions are not very sensitive to the exchange-correlation functional use, we take care to only use PAW data sets that use the same exchange-correlation functional as in the actual calculations.

## 2.3.3 OVITO

As the major post-processing and visualization tool the algorithms implemented in the software Open Visualization Tool (OVITO) are widely used. First, it allows the visualization of structures containing large numbers of atoms like the ones that are contained in the output of LAMMPS as well as the manipulation of these structures, e.g., to focus on certain regions or quantities. Second, we make use of the common neighbor analysis (CNA) and polyhedral template matching (PTM) as implemented in OVITO [290, 291]. These algorithms reliably identify the local crystal structure of a group of particles. Third, the dislocation extraction algorithm (DXA) that is used to identify dislocations is also part of this software package [163].

The two latter algorithms require a trick to work with perovskite structures. In the current implementation they are only able to handle simple structures like fcc, bcc, hcp, diamond, and icosahedral motifs. To make the algorithm recognize the structural backbone of the perovskite structure, we apply it only to the A-site and oxygen particles. Without the central B-site particle and in ignorance of the species, the perovskite structure becomes an fcc structure. So essentially, when identifying crystal structure and dislocations we rely on the structural  $SrO_3$ -backbone.

# 2.4 Computer Setups

## 2.4.1 DFT Stacking Fault Energy Calculation

We use DFT to calculate stacking fault energy hypersurfaces ( $\gamma$ -surfaces) of SrTiO<sub>3</sub>. The  $\gamma$ -surface is an important parameter to judge if dislocations can dissociate into partial dislocations [180]. When partial dislocations move or full dislocations split into partial dislocations, they require the formation of a stacking fault, because the partial Burgers vector does not replicate the lattice onto itself. A stacking fault is only feasible if the atomic arrangement across the plane of the fault does not constitute an energetic maximum. Rather it should be a (local) minimum if it is not to collapse immediately.



Figure 16: (a) The two halves of the simulation cell are shifted along  $\vec{x}$  and  $\vec{y}$  in the stacking fault plane with normal  $\vec{z}$  (colored) to sample the stacking fault energy surface. (b) Stacking fault plane for the {110}  $\gamma$ -surface, see Figure 20. Only strontium (green) and titanium cations (blue) are schematically displayed. Particles in the foremost layer are displayed as large and solid, while particles in the layer below are small and light. The shift in the stacking fault plane only needs to be done for one quarter of the unit cell (orange area) due to the two mirror planes intersecting the central titanium ion.

The  $\gamma$ -surfaces are obtained from a simulation cell that is of size  $1 \times 1 \times 6$  u.c.<sup>3</sup> (unit cells) for the {100}  $\gamma$ -surface with the long direction perpendicular to the stacking fault. For the {110}  $\gamma$ -surface the dimensions are  $1 \times \sqrt{2} \times 6\sqrt{2}$  u.c.<sup>3</sup>. Before production runs the unit cell volume of the cubic cell, energy cut-off and reciprocal space mesh have been checked for convergence. Although the distance between the two stacking faults is only 3 u.c. and  $3\sqrt{2}$  u.c., respectively, due to the periodic boundaries along all axes, the general shape of the  $\gamma$ -surface can be confidently reproduced [149]. The  $\gamma$ -surface is then sampled by shifting one half of the simulation cell with respect to the other on a grid within the stacking fault plane, see Figure 16. The cubic lattice parameter and ionic coordinates are fixed for the in-plane directions, but the ionic positions and simulation cell size are relaxed perpendicular to it using the BFGS procedure.

### 2.4.2 Setup of Dislocation Pairs

If not mentioned otherwise, the simulation cells for the dislocation simulations are stoichiometric, i.e., we use only multiples of  $SrTiO_3$  formula units. This way we avoid creating an infinite array of charged cells through periodic boundary conditions. Alternatively, one could adjust the ionic charges of certain ions to balance net charges in the simulation cell, as discussed by Marrocchelli et al. [138].

**Edge Dislocations** Edge dislocations are defined by three linearly independent vectors: Burgers vector  $\vec{b}$ , line vector  $\vec{t}$ , and slip plane normal  $\vec{s}$ . All three are orthogonal to each other and suitable to define corresponding orthogonal simulation cells in an orthogonal crystal class. Therefore, the three axes  $\vec{x}$ ,  $\vec{y}$ , and  $\vec{z}$  of the simulation cells containing dislocation pairs in SrTiO<sub>3</sub> are oriented in such a way that  $\vec{t}$  aligns with  $\vec{z}$ . Moreover,  $\vec{b}$  aligns with  $\vec{y}$ and  $\vec{s}$  with  $\vec{x}$ . A schematic representation of the simulation cell and the simulation cell axes is shown in Figure 17.

To create the simulation cell, the simple cubic  $SrTiO_3$  unit cell is repeated periodically in accordance with the crystallographic axes needed for the dislocation setup. While the simulation cell is large along  $\vec{x}$  and  $\vec{y}$  (on the order of 80 nm to 110 nm), direction  $\vec{z}$  is initially rather short. Because the dislocation line is periodic along  $\vec{z}$  it is sufficient to only simulate e.g. 3 u.c. along this direction for (quasi-)static simulations. As we will see in Section 3.2.4, the finite size effects along  $\vec{z}$  are, however, relevant for moving dislocations. Therefore, we vary the thickness  $L_z$  for the loading simulations up to 60 u.c..

An edge dislocation can be thought of as the removal or insertion of a half-plane of atoms. We choose to delete a half-plane of atoms in the center of the simulation cell, i.e., between the two dislocations. The removed half-plane is stoichiometric and, therefore, also the simulation cell without half-plane is charge neutral. Now, there is a ribbon of atoms missing in the simulation cell.



Figure 17: Schematic drawing of the simulation cell setup for simulations with dislocation pairs [283, 284]. The directions  $\vec{x}$ ,  $\vec{y}$ , and  $\vec{z}$  are indicated and the positions of the dislocations are represented by "T"-shaped symbols [159]. The dislocation line vector  $\vec{t}$  is always aligned with the  $\vec{z}$ -axis. Careful static and subsequent dynamic relaxation at low temperature (around 20 K) is needed to close this gap slowly without unphysical sudden displacements of atoms. For the static relaxation we chose to constrain the atomic motion such that atoms relax into the gap first before relaxing along  $\vec{x}$  and  $\vec{z}$  to avoid motion of ions along the surface of the gap. Once the gap has closed and relaxed we are left with a simulation cell containing two dislocations of identical type with opposite orientation of  $\vec{b}$  (alternatively one could speak of oppositely oriented  $\vec{t}$ ).

The simulation cells are chosen large enough that the stress fields by the dislocations have decayed significantly at the fully periodic boundaries of the simulation cell. Although the setup technically creates an infinite array of evenly spaced dislocations, we can, thus, assume that the dislocations are independent of each other. Finally, simulation cells containing between 390 000 and 800 000 atoms of cubic SrTiO<sub>3</sub> containing two antiparallel dislocations are created.

**Screw Dislocations** The procedure for setting up dislocations of screw type differs slightly from the recipe for edge dislocations. Since  $\vec{b}$  and  $\vec{t}$  are parallel for a screw dislocation, the third axis for the simulation cell setup has to be constructed. This can be done by a simple cross product from  $\vec{b}$  and  $\vec{s}$ .

Instead of a cut-and-remove procedure to introduce the dislocation a cut-and-shift procedure would be needed. In practice, we find it more simple to use the analytic displacement field of a screw dislocation from Table 1 and apply it to the atomic positions [171]. Because the anisotropy factor of  $SrTiO_3$  is close to unity the isotropic continuum solutions for the mechanical fields are sufficient [292, 293].

**Mixed Dislocations** In mixed dislocations the angle between  $\vec{b}$  and  $\vec{t}$  is neither 0° nor 90°. However, by projection of  $\vec{b}$  onto  $\vec{t}$  the Burgers vector can be decomposed into a screw and an edge contribution. Also, the construction of this dislocation type is a combination of the procedures for screw and edge dislocation. The three axes of the simulation cell are pre-defined by the edge part of dislocation. It is again created by a cut-and-remove procedure. For the screw component the analytic displacement fields are applied with a center at the exact location the half-plane terminates.

**Climb Dissociated Edge Dislocations** Dislocations can split into partial dislocations if crystal structure and local energy landscape permit. For both edge and screw dislocations in SrTiO<sub>3</sub> dislocation splitting is possible, as we will show in Section 3.1.1. However, there are two  $\langle 110 \rangle$  directions that can serve as planes of dislocation splitting.

In the case of screw dislocations the displacement field is symmetric about the dislocation line, and it is thus oblivious in which plane splitting occurs. However, in the case of edge



Figure 18: (a) A full  $\langle 1\,1\,0 \rangle$  layer is removed to create a full A-type dislocation. (b) The two sub-layers of one  $\langle 1\,1\,0 \rangle$  layer are removed in slightly shifted positions creating a climb dissociated dislocation.

dislocations, one plane is the glide plane while the other is orthogonal to it. Splitting in the glide plane is commonly called glide dissociation and splitting in the orthogonal plane is called climb splitting. While the former requires dislocation glide to occur, the latter requires diffusion-assisted dislocation climb. Therefore, it is typically associated with large activation barriers only occurring at high temperatures or pressures [155].

We avoid annealing for very long times and extreme conditions by a priori creating this type of climb dissociated edge dislocation, see Figure 18. In the construction of the full edge dislocation we remove a half-plane with  $a\langle 110\rangle$  thickness. Actually, an  $a\langle 110\rangle$  half-plane consists of two stoichiometric sub-layers, one terminating with SrO and one with TiO<sub>2</sub>. In the climb dissociated configuration these sub-layers are shifted against each other. Consequently, the climb dissociated configuration can be created by removing first one of the two sub-layers and then removing an adjacent sub-layer of the half-plane at a location slightly shifted orthogonal to the glide plane. Examples of this will be shown later in Section 3.1.4 on dislocation type A.

**Dislocation Types and Measurements** Following the above recipes for the alignment of dislocation vectors and simulation cell axes, we choose the crystallographic directions for the simulation cells as given in Table 3.

Often, the static and low temperature properties of dislocations are measured using MS calculations at 0 K. Due to the complex and shallow energy landscape the system may be trapped in local energy minima, and the large number of degrees of freedom in the dislocated system can lead to convergence issues of the conjugate gradient scheme. Thus, we use MD instead of MS and allow the system to leave very shallow local energy minima and avoid trapping the system in an unrealistic configuration with small energy barriers. The thermodynamic quantities are measured as averages from dynamic simulations at very low temperatures between 10 K and 50 K while the anisotropic pressure on the boundaries is kept at zero. Additionally, to obtain reliable averages and check for consistency, each dislocation configuration is simulated multiple times using independent random velocity

Table 3: Crystallographic orientations for the simulation cell directions  $\vec{x}$ ,  $\vec{y}$ , and  $\vec{z}$  as defined in Figure 17. Axis  $\vec{z}$  is always aligned with the dislocation line vector  $\vec{t}$  (or a permutation thereof).

	$\vec{x}$	ÿ	$\dot{z}$
$\mathcal{A}$	[110]	[110]	[001]
${\mathcal B}$	[001]	$[1\overline{1}0]$	[110]
$\mathcal{C}$	$[1\overline{1}0]$	$[11\overline{2}]$	[111]
$\mathcal{D}$	$[11\overline{2}]$	$[\bar{1}10]$	[111]
${\mathcal E}$	[100]	[010]	[001]

initializations. Finite-size effects perpendicular to the dislocation line have been excluded by achieving convergence of structural features with respect to varying simulation cell size [294].

## 2.4.3 Mechanical Properties of Dislocation Pairs

Testing for the stress necessary to move a dislocation is performed on the simulation cells with dislocation pairs that have been relaxed in the quasi-static arrangement. We perform loading for dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  because they are expected to be mobile. The exclusion of other dislocation types will be justified in Section 3.1. These dislocation types include edge, screw, and mixed dislocations in different configurations. For all dislocation types the glide plane is well-defined. We use applied shear stress on the periodic boundaries in such a way that the full stress acts on the dislocations as Peach-Koehler force. For the mixed dislocation type we chose to study the two extreme scenarios where either the edge part or the screw part experiences the loading.

As a first approximation we continuously ramp up the stress by modifying the barostat until motion or de-pinning of the dislocations is observed. The continuous increase in load could lead to an overestimation of the Peierls stress because loading is performed in a dynamic setup. To confirm the results, we also keep the samples at a constant stress level for 24 ps so that we are in a static equilibrium configuration. If the dislocation does not move, the applied stress is less than the Peierls stress. If at least one dislocation moves the system departs from static equilibrium and the Peierls barrier has been surpassed. The results are carefully checked against observations from literature where applicable [150] confirming the validity of our approach.

As detailed in Section 3.2.3, when simulation cells are very thin along the dislocation line direction, the curvature on dislocations is constrained. This effect needs to be mitigated by studying the dislocation motion in simulation cells of different length along  $\vec{z}$ , ranging from

2 u.c. to 60 u.c.. In comparison with experimental observations we expect this size to be sufficient because it is larger than the typical wavelength of kinking in  $SrTiO_3$  [199].

## 2.4.4 Simulations with Natural Dislocation Structures

The simulation setups discussed so far are very valuable as they allow to study the properties of isolated dislocations in very much detail. In a real crystal, however, the arrangement does not necessarily follow these well-defined geometries. Therefore, we study large arrangements of dislocations in setups that are closer to experiment; for an overview see Figure 19.

In the first setup from Porz et al. [156] a large simulation cell featuring a block of SrTiO<sub>3</sub> with  $360 \times 720 \times 5 \text{ u.c.}^3$  is chosen (approx. 6.5 million atoms). The *x*-dimension is not periodic and a (stoichiometric) sharp notch is introduced on one of the two surfaces of the crystal, see Figure 19 left. The  $\langle 100 \rangle$  crystal axes are aligned with the simulation cell axes and compressive loading is applied along the long *y*-axis. Thus, the slip system for type  $\mathcal{A}$ 



Figure 19: Representation of experimental and modeled samples for the notched samples (left) and the micropillar scenario (right). All samples have been subjected to uniaxial compression and typical length scales are indicated. Additionally, the observed quantities reveal how experimental and theoretical investigations supplement each other.

dislocations lies at the optimal angle of 45° to the loading direction and experiences maximum shear stress. With the notch a stress concentration is created such that type  $\mathcal{A}$  dislocations are forced to nucleate at the tip of the notch. The analog setup was tested in experiment and led to very controlled arrangements of dislocations. However, the major difference is the restriction to type  $\mathcal{A}$  dislocations by the short *z*-dimension which is not applicable to experiment.

In the second series of setups we intentionally lift the constraint on dislocation type by expanding the simulated volume of  $SrTiO_3$ . The goal is to explain the results from mechanical compression testing of micro- and nanopillars of  $SrTiO_3$ , see Figure 19 right. Therefore, we also perform compression testing in MD simulations on slabs that resemble a cut through such a pillar. These slabs contain more than 25 million atoms and are prepared in two sizes each with two configurations. For the two different sizes a thin and a thick slab are compared. While the thin slabs restrict the dislocations to be predominantly of type A, there is more variety of dislocation types in the thick slabs because of reduced image interactions. For the two configurations, pristine samples without dislocations and samples with dislocations are compared. These dislocations are introduced by homogeneous dislocation nucleation during uniaxial compression of fully periodic simulation cells. In total this gives four different combinations of scenarios (two sizes and two dislocation structures) which are subjected to compressive as well as tensile loading.

During compression testing we use open boundaries along the x-axis such that dislocations are able to leave the crystal and, thus, realize plastic deformation. Because of the ionic structure, surfaces are usually charged and can create large electric fields inside the material. The results of the simulations shown in Section 3.3 do indeed suffer from this effect. In order to exclude that this alters the observed material behavior we conduct additional calculations where surface charges are compensated. We do so by changing the ionic charges of the ions at the surface prior to compression such that the electric field between the surfaces vanishes. The implications are discussed below.

# **3 Results**

# **3.1 Equilibrium Dislocation Structure**

Aiming for an in depth understanding of the behavior of dislocations in perovskites we start with the most fundamental scenario: the static equilibrium configurations of dislocations. Thus, we chose to first perform static simulations and simulations at very low temperature of the perovskite  $SrTiO_3$ . In these simulations the relaxation of particles and structures as well as the atomic motion are easily controlled and observed. The following questions are addressed:

- 1. Analytical and continuum theories of dislocations are mostly applied to describe dislocation-based plasticity in metals. For ceramics these equations have found less application because they are lacking electrostatic fields. Before diving into simulation, we try to make predictions regarding the behavior of different dislocation types and then validate them using simulations.
- 2. Type  $\mathcal{A}$  dislocations are reported in literature as the prime carrier of plasticity in SrTiO<sub>3</sub> [190]. Their configuration is supposed to be a glide dissociated state that lowers the Peierls barrier. However, the ductile-to-brittle transition found by Gumbsch et al. [128] suggests a mechanism rendering these dislocations immobile, at least at elevated temperatures. Therefore, we search for the glide dissociated structure as well as for hints why this dislocation type may become sessile [155]. Additionally, the strong impact of dislocation core charge on the dislocation structure will be revealed.
- 3. Type  $\mathcal{B}$  dislocations are the screw analog of type  $\mathcal{A}$  edge dislocations. Screw and edge dislocations possess different stress fields, therefore, they are expected to behave differently. Because screw dislocations do not have a terminated plane at their dislocation core it is uncharged. Thus, we will investigate if this edge-screw analogy holds true in the case of SrTiO<sub>3</sub> crystals.
- 4. Type *C* dislocations mark an important combination of type *A* and *B* dislocations that have been reported in TEM studies [136]. Because it is a mixed dislocation it is not immediately clear if this dislocation can also form dissociated configurations and what

role dislocation core charges play. Type C dislocations are also put into context as a species competing with type A and B dislocations.

- 5. It has been suggested that type  $\mathcal{D}$  dislocations can form through a reaction of two type  $\mathcal{C}$  dislocations [136]. However, type  $\mathcal{D}$  dislocations differ from type  $\mathcal{C}$  by the line direction. How does this different line direction influence the structure of the dislocation and its core?
- 6. Also, type & dislocations have a (110) Burgers vector and are of mixed type. However, the glide plane is the more simple {001} plane. Since dislocation splitting has been suggested for this dislocations type [114] we want to see if splitting is plausible and if this dislocation type also contributes to plasticity.

#### 3.1.1 Elastic Energy of Full and Dissociated Dislocations

A dislocation carries excess energy because it disturbs the perfect crystal lattice. According to Equation (6) the elastic line energy in an isotropic continuous medium depends on the magnitude of the Burgers vector [171]:

$$\Gamma \propto \left| \vec{b} \right|^2 = b^2 \,. \tag{16}$$

Possible Burgers vectors in a cubic crystal system are  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$ . If we compare the squared Burgers vectors, see Table 4, it is noted that the line energy doubles for  $\vec{b} = a \langle 110 \rangle$  and triples for  $\vec{b} = a \langle 111 \rangle$  compared to the  $a \langle 100 \rangle$  Burgers vector. The high energy of a dislocation with a  $\langle 111 \rangle$  Burgers vector makes this type improbable. We have performed separate calculations verifying that this type is unlikely and carries high elastic energies [293].

Besides a short Burgers vector, a dislocation's glide plane favorably resides on a close packed plane [159]. The degree of packing in a solid with more than one species is not as obvious to define as it is in crystals consisting only of one species in the glide plane. We estimate the packing  $\rho_{hkl}$  of a lattice plane by normalization of the number of atoms in a unit cell  $n_{atoms}^{uc}$  (which is five for cubic SrTiO<sub>3</sub>) by the projected area of that unit cell onto the glide plane  $A_{hkl}^{uc}$ ,

$$\rho_{hkl} = \frac{n_{\text{atoms}}^{\text{uc}}}{A_{hkl}^{\text{uc}}}.$$
(17)

Because the areas  $A_{100}^{uc}$ ,  $A_{110}^{uc}$ , and  $A_{111}^{uc}$  are  $a^2$ ,  $\sqrt{2}a^2$ , and  $\sqrt{3}a^2$ , respectively, the loosest packing is on the {111} plane. Thus, we also exclude this plane from further discussion. The two available Burgers vectors (100) and (110) and the two glide planes {100} and {110} can be combined in four different ways. We expect that these configurations are the most favorable in cubic SrTiO<sub>3</sub> [188].

Table 4: Relevant slip systems in SrTiO<sub>3</sub> with the Burgers vector in angular brackets and the slip plane normal in curly braces. The square of the Burgers vector  $|\vec{b}|^2$  is computed using the unit cell parameter *a*. It is proportional to the elastic line energy of a dislocation, see Equation (16). A  $\langle 110 \rangle \{1\overline{1}0\}$  dislocation which is split into two equal collinear partials has the same elastic line energy as a full  $\langle 100 \rangle \{001\}$  dislocation.

dislocation	$\left \vec{b}\right ^2$
$\langle 100 \rangle \{ 001 \}$	$a^2$
$\langle 110\rangle \{001\}$	$2a^2$
$\langle 0 0 1 \rangle \{1 \overline{1} 0\}$	$a^2$
$\langle 110 \rangle \{ 1\overline{1}0 \}$	$2a^2$
$2 \times \frac{1}{2} \langle 1  1  0 \rangle \{ 1  \overline{1}  0 \}$	$2 \times \frac{1}{2}a^2$

The actual behavior of a defect depends on its energy landscape. In the case of a dislocation in a glide plane the relevant energy landscape is the  $\gamma$ -surface (stacking fault energy hypersurface) [180, 295, 296]. It relates the potential energy to a rigid shift of two surfaces in the glide plane with respect to each other. Put in other words, it determines what energy is needed to create a given displacement in the glide plane. The relevant glide planes here are the {100} and {110} planes [149, 188].

The procedure for calculating an accurate shape of the  $\gamma$ -surface is explained in Section 2.4.1. We use the analog procedure with the interatomic potential for SrTiO<sub>3</sub> in order to check for the correct reproduction of the  $\gamma$ -surface by the interatomic potential [157]. The  $\gamma$ -surfaces for the interatomic model and from the DFT calculations are qualitatively identical, see Figure 20. For the metastable stacking fault energy on the {110}-surface we find a value of 0.795 J m<sup>-2</sup> from DFT while Hirel et al. [149] report 0.925 J m<sup>-2</sup>. However, they did not relax the atomic displacement normal to the stacking fault plane which naturally increases the energy of the stacking fault. In fact, the experimentally reported value of 0.606±0.077 J m<sup>-2</sup> by Jin et al. [136] is in fair agreement to our theoretical values considering that the DFT calculations are computed for the 0 K configuration. It is, however, in contrast to results by Ferré et al. [188] who do not show an intermediate minimum in their  $\gamma$ -surface calculated by DFT.

Following the reasoning by Vítek [180] we deduce that the intermediate minimum (metastable state) in the {110}  $\gamma$ -surface along the  $\langle \overline{1}10 \rangle$  direction could allow a full dislocation of type  $\langle \overline{1}10 \rangle$ {110} to split into two equal and collinear partial dislocations. Thus, dislocation splitting is relevant for types A, B, and C. Their partial dislocations would be separated by a stacking fault that corresponds exactly to the  $\frac{a}{2}\langle \overline{1}10 \rangle$  shift displayed in the  $\gamma$ -surface. For other combinations of directions and slip planes the energy landscape is indicated as red



Figure 20: Stacking fault energy hypersurfaces calculated using the empirical pair potential by Thomas et al. [157] (left) and DFT with PBE GGA exchange correlation functional (right). Top: {110} surface with a distinct local minimum for shifts along the  $\langle 110 \rangle$  direction. Bottom: {100} surface with shifts along  $\langle 010 \rangle$  and  $\langle 001 \rangle$ direction yield no metastable stacking faults. Although the numeric values differ between the models the general features are very well re-produced.

lines in Figure 20. Such dislocations cannot split and motion of these dislocations requires steps of full a(001) vectors.

The full dislocation with  $\langle 110 \rangle$  Burgers vector carries twice the elastic energy compared to a  $\langle 100 \rangle$  dislocation, see Equation (16). As a consequence of the  $\gamma$ -surface two partial dislocations with  $\frac{a}{2}\langle 110 \rangle$  Burgers vector that are connected by a stacking fault can be created instead. Therefore, we need to re-consider the energy balance for this dislocation type (corresponds to  $\mathcal{A}$ ,  $\mathcal{B}$ , or  $\mathcal{C}$ ) [295, 296]. For clarity, we write the dislocation splitting as [295]

$$\langle 110 \rangle \rightarrow \frac{1}{2} \langle 110 \rangle + SF_{\{1\overline{1}0\}} + \frac{1}{2} \langle 110 \rangle , \qquad (18)$$

and obtain for the energy of the full and the split configuration:

$$\Gamma^{\text{full}} = \Gamma^{\text{full}}_{\text{elast}} + \Gamma^{\text{full}}_{\text{core}}, \qquad (19)$$

$$\Gamma^{\text{split}} = 2\Gamma_{\text{elast}}^{\text{partial}} + 2\Gamma_{\text{core}}^{\text{partial}} + \gamma d .$$
(20)

The energy per unit length of dislocation line  $\Gamma^i$  has been decomposed into its elastic, core, and stacking fault energy contributions  $\Gamma^i_{elast}$ ,  $\Gamma^i_{core}$ , and  $\gamma d$ , respectively. *d* is taken to be the distance between the partial dislocation cores.

So far we implicitly assumed that the partial dislocations do not interact, i.e., the overlap of their mechanical fields can be neglected because they are far apart. In fact, this assumption will later be lifted in the atomistic simulations, see Section 3.1. Let us assume, for now, that the elastic energy dominates Equations (19) and (20) [111, 297]. Again, we compare the four dislocation types with respect to their line energy based on Burgers vector  $\vec{b}$  and glide plane  $\vec{n}$ , see Table 4.

The split dislocation has an elastic line energy in the same range as the  $\langle 100 \rangle \{001\}$  dislocation. This is a reduction by a factor of two compared to the full dislocation. A splitting of a full  $\langle 110 \rangle \{1\overline{1}0\}$  dislocation into partials is, thus, expected for energetic reasons. Because there is also the energy contribution  $\gamma d$  by the stacking fault the dislocation splitting distance is finite.

#### 3.1.2 Analytic Considerations on Dislocation Mobility

Since we are interested in dislocations relevant to plastic deformation and introduced by mechanical force, the dislocations need to be mobile. For the low energy dislocation types  $(100)\{001\}, (001)\{1\overline{1}0\}, \text{ and split } (110)\{1\overline{1}0\}$  we, therefore, compare their mobility qualitatively.

The Peierls stress  $\tau_m$  is the "minimum stress to keep a dislocation moving" [211]. It can be estimated from analytical formulae based on mechanical and crystallographic characteristics of a solid, as has been extensively discussed by Hull and Bacon [159] and references therein. As we do not compare different materials but only different dislocation types in the same material, we only consider the proportionality with regard to crystallographic parameters [164]:

$$\tau_m \propto \exp\left(\frac{-2\pi h}{b}\right).$$
 (21)

Here *b* and *h* refer to the Burgers vector magnitude and distance between equivalent lattice planes, respectively. This so-called Peierls-Nabarro formula is often used as a first approximation for  $\tau_m$  [132, 164]. Strictly speaking Equation (21) is valid for screw dislocations, but edge dislocations behave analog.

Table 5: For the slip systems indicated in Table 4, the Burgers vector length *b*, the distance between glide planes *h*, the proportionality factor of the Peierls stress (see Equation (21)) and the reduced Peierls stress  $\tau_m/\tau_m^0$  are given. Here  $\tau_m$  has been normalized to the Peierls stress of the  $\langle 100 \rangle \{001\}$  slip system. Dislocations with glide dissociation (see last line) can have strongly reduced Peierls barriers.

dislocation	b	h	$\exp\left(\frac{-2\pi h}{b}\right)$	$\tau_m/\tau_m^0$
$\langle 100 \rangle \{ 001 \}$	a	a/2	0.043	1
$\langle 110 \rangle \{001\}$	$\sqrt{2}a$	a/2	0.108	2.5
$\langle 001 \rangle \{1\overline{1}0\}$	a	$a/\sqrt{2}$	0.012	0.27
$\langle 110 \rangle \{ 1\overline{1}0 \}$	$\sqrt{2}a$	$a/\sqrt{2}$	0.043	1
$\frac{1}{2}\langle 110\rangle \{1\overline{1}0\}$	$a/\sqrt{2}$	$a/\sqrt{2}$	0.002	0.043

The values for *b* and *h* for the relevant dislocation types are presented in Table 5. Also, the exponent from Equation (21) has been evaluated and for clarity it has been normalized in the last column labeled  $\tau_m/\tau_m^0$  (normalized Peierls stress). From Table 5 we see that it is the split dislocation type that is most easily moved under applied load. Our considerations are confirmed by experimental studies that have investigated and characterized dislocations in plastically deformed SrTiO<sub>3</sub>, see Refs. [127, 128, 184] and our own work [156]. Note that the dislocation nucleation does not necessarily follow the same trend [153, 298].

### 3.1.3 Lattice Structure of Dislocations and Dislocation Splitting

In classical homogeneous metals, Burgers vectors can be on the scale of next-neighbor distances. However, in ionic structures such as perovskites, the ionic nature enlarges the unit cell and limits possible Burgers vectors [111]. In Figure 21 this situation is illustrated by two-dimensional lattices occupied with one or two species.

The large Burgers vector is often given as the reason why ceramics are brittle [299]. As we have seen in Section 3.1.1, the Burgers vector may, however, be decreased by dislocation splitting. An additional complication arises in ionic substances due to the charges on each ion. In Figure 21 we see that it is easy to think of a crystal that has charged dislocation cores despite being stoichiometric and macroscopically charge neutral. If such dislocations arise simply from the way a dislocation is created in a cut-and-remove procedure they are called "inherently charged" [112]. Because such a charge originates from the way an atomic plane at the dislocation core terminates, it occurs only in edge or mixed dislocations. We will discuss its implications in the corresponding sections on type  $\mathcal{A}$  and  $\mathcal{C}$  dislocations.

In ionic crystals anions and cations usually occupy different sub-lattices. Of course this alternating ionic arrangement increases the Madelung sum because ions of equal sign would



Figure 21: Edge dislocations in different materials. In metals, Burgers vectors are usually short and dislocations cannot be charged in pure materials. Because of the ionic structure, unit cells and Burgers vectors are often larger in ceramics. Due to the termination at the dislocation core, dislocations in ceramics can be inherently charged even if stoichiometry is preserved.

tend to repel each other. As a rule of thumb it has been established that at least one of the sub-lattices of a cation or anion species should retain its periodicity across a stacking fault [111]. This is exactly the case for the stacking fault in SrTiO<sub>3</sub> that is responsible for dislocation splitting as discussed Section 3.1.1. The intermediate minimum of the {110}  $\gamma$ -surface in Figure 20 is commensurate with the anion sub-lattice. The atomic arrangement of this stacking fault is displayed in Figure 22 (a). In Figure 22 (b) an example for a stacking fault that is not stable is shown. Stability and instability have been checked with separate atomistic simulations.

We have now consistently established that dislocations in SrTiO<sub>3</sub> with a  $\langle 1 1 0 \rangle$  Burgers vector should be favored because they can dissociate into partial dislocations lowering elastic energy as well as Peierls barrier. Also, we have addressed some basic concepts, for instance the retained oxygen sub-lattice, that serve as general rules to judge dislocation configurations. In Section 1.4 we have already reviewed literature and identified dislocation types with  $\langle 1 1 0 \rangle$ Burgers vectors that might be relevant in SrTiO<sub>3</sub>. Next, we will study them one after another from  $\mathcal{A}$  through  $\mathcal{E}$ .



Figure 22: Stacking faults in ceramics are usually only stable if at least one sub-lattice of the ionic crystal is retained [111]. While the {110} stacking fault conserves the oxygen sub-lattice (a), the hypothetical {112} stacking fault breaks the stacking sequence completely (b). Thus, only the former variant is stable. Orientation corresponds to the type C setup.

# 3.1.4 Dislocation Type $\mathcal{A}$

The investigation of the A-type dislocations is structured as follows. First, we revisit some essential literature that highlights the framework and relevance of this dislocation type. Second, we make qualitative statements and analytical estimates about glide and climb dissociated dislocations. Third, the charged configuration of this dislocation type is highlighted. Finally, the type A dislocation is modeled with an interatomic potential to reveal a more accurate picture of the dislocation splitting and the charge state at the dislocation core.

**Literature on and Connection of Types** A, B, and C We start with analyzing dislocation type A from Table 2. It possesses a Burgers vector  $\vec{b} = a\langle 110 \rangle$ , a dislocation line direction  $\vec{t} = \langle 001 \rangle$ , and a slip plane normal  $\vec{n} = \{1\overline{1}0\}$  which are illustrated in Figure 23. It is probably the most investigated dislocation type in SrTiO<sub>3</sub>. This dislocation is of pure edge character (the angle between  $\vec{b}$  and  $\vec{t}$  is 90°) but with types B and C the screw and a mixed analog also exist.

In several publications this dislocation type is described as the one that enables plasticity [127, 128, 184]. These references compressed  $SrTiO_3$  single crystals along  $\langle 100 \rangle$  at temperatures between 110 K and 1000 K. The glide dissociated form was expected to be the



Figure 23: Crystallographic orientation of defining vectors for dislocation type A. Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). The full Burgers vector has been split into two equal parts to indicate glide dissociation. Reproduced from Figure 11 for convenience.

most relevant dislocation type. Yet, a pure glide dissociated type  $\mathcal{A}$  has rarely been observed experimentally [199]. Only the climb dissociated configuration was created in experiments where two crystals are joined in a bi-crystals setup designed to yield climb dissociated type  $\mathcal{A}$  grain boundary dislocations [194]. However, we note that we require the glide dissociated configuration to enable plasticity in SrTiO<sub>3</sub>. It is, therefore, important to address if the glide or the climb dissociated form is the equilibrium configuration of type  $\mathcal{A}$  dislocations.

Besides the discussion about the dissociation, the edge character of the  $\langle 1 1 0 \rangle \{ 1 \overline{1} 0 \}$  dislocation type is a matter of debate, too. Continued work by Sigle et al. [190] suggests that the nature of the  $\vec{b} = \langle 1 1 0 \rangle$  dislocations varies strongly with temperature. Because types  $\mathcal{A}$  and  $\mathcal{B}$  are interchangeable within the kink pair theory [197, 208, 209], they can easily convert into each other. Possibly, type  $\mathcal{B}$  (screw) dominates below room temperature while type  $\mathcal{A}$  exists above [190]. Also, an intermediate configuration (type  $\mathcal{C}$ ) was found in literature without any account which dislocation type might be the most favorable [199].

As dislocation types  $\mathcal{A}$  (edge),  $\mathcal{C}$  (mixed), and  $\mathcal{B}$  (screw) naturally form a group because they have identical Burgers vectors and vary only by their line vector, we will start with the limiting cases  $\mathcal{A}$  and  $\mathcal{B}$ , before turning to type  $\mathcal{C}$ .

**Glide vs. Climb Dissociation** We discussed in Section 3.1.1 how glide dissociation can reduce the elastic energy as well as the Peierls barrier of a dislocation. From the  $\gamma$ -surfaces we found the glide dissociation feasible and explained its stability by an undisturbed anion-cation stacking sequence. In fact, it is expected that the dissociation occurs spontaneously for type  $\mathcal{A}$  and  $\mathcal{B}$  dislocations [149].

The thermodynamic/entropic stability of this configuration is, however, in question. Under the influence of extremely high temperatures and pressures, glide dissociated dislocations studied by MD simulation re-associated into a full dislocation and subsequently showed climb dissociation [155]. With nudged elastic band calculation this climb configuration was found to be actually the energetically favorable configuration.

The climb dissociation has been used as a possible explanation for the loss of ductility that occurs at high temperatures in  $SrTiO_3$  [184]. In that case embrittlement (ductile-brittle transition) is the consequence of dislocations becoming sessile. This "glissile to sessile" [155] transition is specific to an edge type dislocation, as pure screw dislocations (type  $\mathcal{B}$ ) cannot show climb dissociation.

In essence, it is of fundamental interest to clarify the exact structure of this dislocation type which was suggested to be the result of mechanical deformation. It is also not entirely clear how the different dislocation configurations (full, glide dissociated, climb dissociated) are related to each other, see the schematic drawing in Figure 24. A full dislocation can split into either a glide dissociated or a climb dissociated configuration. Both paths will need different activation energies. The transition from glide to climb dissociated configuration, however, is not directly possible but requires the preceding constriction of the glide dissociated configuration.



Figure 24: Schematic representation of different dislocation configurations with the stress fields of opposite sign symbolized by red and blue dumbbells. For glide (center) and climb dissociated dislocations (right) the stacking fault is indicated by a dotted line and the decreased size of the dumbbells represents a reduced magnitude of the elastic fields compared to the full dislocation (left). Glide dissociation can be a spontaneous and/or a thermally activated process. In contrast, the transition from the full or the glide dissociated to the climb dissociated variant requires activation.

Before we start with the actual simulation of the glide and climb dissociation of dislocation type  $\mathcal{A}$  we try to make some analytical prediction of the splitting distance. Since the energy of a single dislocation in linear elasticity is divergent (Equation (5)), we need to consider force balance criteria to estimate the splitting distance. Assume that the first partial in a glide dissociated configuration is at a fixed position. Through its stress field, see Table 1, it exerts a force on the second partial that tends to increase the distance between the partials. However, an increase in stacking fault area is counteracting this force. We can write the force  $\vec{f}_2$  that the second partial experiences as

$$\vec{f}_2 = -\gamma + \vec{f}_2^{\rm PK}$$
, (22)

where  $\vec{f}_2^{\text{PK}}$  is the Peach-Koehler force from Equation (8) caused by the stress field  $\vec{\sigma}_1$  of the first partial dislocation [168]:

$$\vec{f}_2^{PK} = \left(\vec{b}_2 \cdot \vec{\sigma}_1\right) \times \vec{t}_2 . \tag{23}$$

The index refers to either the first or the second partial dislocation. The first term in Equation (22) is the force caused by the stacking fault which ties the partial dislocations together. While we can take the stacking fault energy  $\gamma$  from Figure 20, the force  $\vec{f}_2^{\text{PK}}$  acting due to the linear elastic interaction of the partials can be adapted from common textbooks [159, 171]. For the special dislocation orientation of two identical parallel edge dislocations along *z*-direction with a Burgers vector along *x*-direction, we find:

$$f_x = \frac{\mu b^2}{2\pi (1-\nu)} \frac{x \left(x^2 - y^2\right)}{\left(x^2 + y^2\right)^2} , \qquad (24)$$

$$f_{y} = \frac{\mu b^{2}}{2\pi (1-\nu)} \frac{y \left(3x^{2}-y^{2}\right)}{\left(x^{2}+y^{2}\right)^{2}},$$
(25)

$$f_z = 0$$
 . (26)

 $f_x$ ,  $f_y$ , and  $f_z$  are the force components of  $\vec{f}_2^{\text{PK}}$  along the three cartesian coordinates. For the case of glide splitting into two equal partial dislocations y = 0. Thus,  $f_y$  vanishes and  $f_x$  reduces to:

$$f_x^* = \frac{\mu b^2}{2\pi (1-\nu)} \frac{1}{x} \,. \tag{27}$$

In equilibrium  $\vec{f}_2 \equiv 0$  must be valid. By re-arranging we arrive at a solution for the dislocation glide dissociation *d* in force equilibrium [176, p. 112]:

$$0 = -\gamma + f_x^*, \qquad (28)$$

$$d = \frac{\mu b^2}{2\pi (1 - \nu)\gamma} , \qquad (29)$$

$$d = \frac{\mu a^2}{4\pi (1 - \nu)\gamma} . \tag{30}$$

In the last step we used the condition  $b = \left| \vec{b}^{\text{partial}} \right| = \left| \frac{1}{2} \langle 110 \rangle \right| = \frac{a}{\sqrt{2}}$ . The equilibrium distance can, however, only be realized if there is no Peierls barrier adding a periodic force contribution to the equations and preventing the partial dislocations from gliding to their equilibrium positions. We insert the values from the interatomic potential of SrTiO<sub>3</sub>, a = 3.905 Å,  $\mu = 107 \text{ GPa}$ ,  $\nu = 0.26$ , and  $\gamma = 1.225 \text{ Jm}^{-2}$  and obtain  $d = 1.43 \text{ nm} \approx 3 - 4 \text{ u.c.}$ . Compared to stacking faults in fcc metals this result is on the same order of magnitude which appears reasonable, cf. e.g. Ref. [300] and references therein.

For the climb dissociation the situation is more complicated. The considerations about the elastic self-energies of the dislocations are equally true for the climb splitting, therefore, we expect that there is an energetic benefit from a climb dissociated dislocation compared to a full dislocation. Moreover, from Figure 24 (right) we see that the regions of compressive (red) and tensile (blue) stress and strain partly overlap when partial dislocations are in a climb configuration. In a linear elasticity framework the strain/stress should, thus, be reduced between the partials. Less strain results in decreased elastic energy which in turn affects the splitting distance and complicates predictions about  $d^{\text{climb}}$ . However, the analytical treatment based on the far-field solutions for the elastic forces, see Equations (24) to (26), contradicts a climb dissociation. For climb splitting, the edge dislocations are at the same x coordinate, i.e., x = 0 and  $f_x$  vanishes. Because  $\gamma$  as well as  $f_y$  have the same sign, they both tend to collapse the two climb dissociated partial dislocations. In summary, while dislocations should climb dissociate from the viewpoint of elastic energy of the dislocations, the linear elastic solution of the forces seems to favor a full dislocation. We conclude that the linear elastic solutions breaks down here and that non-linear effects of the dislocation core region might be of considerable importance. Therefore, the self-consistent calculation of a numeric MS or MD scheme are required to make predictions on dislocation climb splitting distances.

At this point we note that the stacking faults for glide and climb dissociated dislocations are identical for this dislocation type. For illustration, we plot the  $\gamma$ -surface alongside the quasi-statically relaxed glide dissociated dislocation as well as the manually created and quasi-statically relaxed climb dissociated dislocation, see Figure 25. Only for the former case the stacking fault is on the glide plane. The partials can, therefore, either move one by one, i.e., by expanding and collapsing the stacking fault consecutively [150], or simultaneously in a correlated fashion [297]. In the climb dissociated case the stacking fault is also in a {110} plane with a shift of  $\frac{a}{2}\langle \overline{1}10\rangle$ . The crystallographic situation is, thus, almost identical but the partials terminating the stacking fault have a glide plane different from the stacking fault plane. If such a partial was to move by dislocation glide it would drag behind the stacking fault, a process that generally is energetically unfeasible because it requires massive diffusion. We expect that such a configuration cannot be moved by applied external stress and becomes sessile.

**Dislocation Core Charge** After the analytic discussion of the glide and climb dissociation there remains the issue about the dislocation core charge, which we will discuss qualitatively, first. In Figure 26 excerpts from the simulation cell before relaxation without the atoms of



Figure 25: As predicted by the  $\gamma$ -surface, there is a metastable stacking fault configuration for a shift in the {110} plane along the  $\langle \overline{1}10 \rangle$  direction. This enables the glide dissociation of the shown type  $\mathcal{A}$  dislocation and holds equally true for type  $\mathcal{B}$  and  $\mathcal{C}$  dislocations. Inside the stacking fault the Sr- and Ti-sub-lattices are shifted with respect to each other. Thus, the stacking fault can be identified by the connectivity of the blue oxygen octahedra. The crystallographic situation of the stacking fault is identical for the climb dissociated type  $\mathcal{A}$  dislocation.

the missing half-plane are shown. This is the setup for the creation of type  $\mathcal{A}$  dislocations. The subsequent relaxation of the atoms from the top and bottom into the void create the desired edge dislocation at the end of the cut. In this representation the termination of the dislocation can be most easily observed. As the cut has been made in a  $\{1\bar{1}0\}$  plane, i.e., the glide plane, it always separates O<sup>2–</sup>-layers from (SrTiO)<sup>4+</sup>-layers. The dislocation with oxygen surplus (Figure 26 left) is negatively charged. Correspondingly, at the other end (Figure 26 right) there is a surplus of positively charged cations. As a result, any dislocation that forms from such a cut-and-remove procedure will have a charged core, although overall stoichiometry is preserved, see also Ref. [138].

For a quantitative picture refer to Figure 27 where the smoothed cumulated charge is plotted along the *x*-direction of the simulation cell. Per unit cell dislocation line there is an excess/deficit of one oxygen ion at each dislocation line. The insets have been added to highlight that this is simply an effect of the termination of the dislocation cut.



Figure 26: Center: Schematic drawing of the simulation cell viewed along the dislocation line with indications of the regions for the shown atomic structure. Left/Right: A layer of Burgers vector thickness has been cut out of a perfect and fully periodic crystal. The length of the cut is half the length of the simulation cell (dotted line in inset) such that the ends of the cut plane create an edge dislocation. The left core terminated by oxygen ions while the right core has a cation surplus.

**Simulation of Splitting Distance** The void from the removed half-plane of the dislocation construction slowly closes during the relaxation and the opposite faces of the cut re-associate. In between the dislocations the ideal lattice is, thus, restored. Even though the relaxation only requires MD runs at very low temperatures the dislocations glide dissociate. Consequently, this is a spontaneous process without any relevant energy barrier and the as-created full dislocations are not stable. The driving force for the splitting is the reduction of elastic energy.

The splitting distance of the spontaneously dissociated dislocation is in the range of 1.56 nm—2.05 nm and, thus, in good agreement with the value of 1.43 nm obtained by the analytical force-based approach. In multiple simulations with different minimization/relaxation procedures and varying seed velocities for the low temperature dynamic relaxations, the dislocations always glide dissociate but never climb dissociate. The latter is, therefore, not a spontaneous process. This meets the expectations that thermally activated diffusion is required for climb motion of a (partial) dislocation.

In literature, we find one example by Hirel et al. [155] where the problem of thermally activated diffusion has been overcome by brute force calculations. Extremely high temperatures and presumably equally unrealistic stresses have been used to enable climb motion of a type  $\mathcal{A}$  dislocation. We circumvent this problem by a priori constructing dislocations in their climb dissociated configuration. For illustration, refer to Figure 18 where the layer sequence of the removed planes can be deduced. The removal of a layer of  $\sqrt{2a}$  thickness corresponds to the removal of two stoichiometric sub-layers. Shifting one of these layers incrementally to the right or the left creates the desired climb stacking fault because it shifts the partial dislocations orthogonal to the glide plane. A relaxation of these cuts automatically


Figure 27: Charge density in a simulation cell containing a type  $\mathcal{A}$  dislocation dipole. In order to obtain a smooth charge density that can be binned along the *x*-direction, the nominal ionic point charges have been smeared out be a Gaussian distribution. Additionally, the integrated charges *q* for each dislocation and a representation of the terminal layer of the dislocation cut are given.

generates to climb dissociated dislocations and the size of the climb stacking fault  $d^{\text{climb}}$  can be adjusted by the size of the shift. The stability of the different configurations is judged based on the simulation cell's potential energy in Figure 28.

This plot confirms the expectations our expectations that climb splitting is indeed a favorable configuration due to reduction of the burgers vector magnitude and the overlap of the stress/strain fields for small climb splitting distances. An optimum appears at  $d^{\text{climb}} \approx 3 \text{ u.c.} - 4 \text{ u.c.}$  where the overlap of mechanical fields is large enough to cancel significant portions of themselves reducing elastic energy and small enough to avoid large energy contributions from the stacking fault. Even though the Peach-Koehler forces in the elastic far-field tend to attract the partial dislocations, see Equation (25), the non-linear mechanical effects in the dislocation core region stabilize a splitting of finite size.

It can be concluded that the glide dissociated dislocation is not thermodynamically stable but kinetically favored. The stable configuration of type  $\mathcal{A}$  dislocations is the climb dissociated configuration when provided with enough thermal activation. These dislocations are then sessile. With regard to experimental procedures we note, that besides thermal activation



Figure 28: Comparison of energies of as-created type A dislocations for different climb splitting distances. Each point represents the average of at least three independent samples. A growing stacking fault and decreasing elastic interactions increase energy at high splitting distances.

also other forms of activation energy must be considered. Especially in imaging techniques such as high voltage TEM the samples under investigation are irradiated by high intensity electron beams. These provide high amounts of activation energy that can possibly alter the dislocation structure significantly [156, 192, 301]. Therefore, it might be difficult to observe glide dissociated dislocations since the electron beam supplies sufficient activation for dislocations to constrict and climb dissociate.

**Simulation of Dislocation Core Charge** The type  $\mathcal{A}$  dislocation in the as-created state is charged, see Figure 27. In fact, this has a direct consequence for the dislocation glide dissociation. We observe that the splitting distance for the positively charged dislocation is generally larger (about 5 u.c.) than at the negatively charged dislocation (about 4 u.c.).

It is known that the charge as well as the stress fields of dislocations alter the local defect equilibria [138, 140, 293]. Variations of point defect concentrations around the dislocation can either raise or lower the Peierls barrier [103]. Because oxygen vacancies are the mobile species in SrTiO<sub>3</sub>, they can build up space charge layers and compensate the dislocation core charge [129, 140]. Of course the removal of the electrostatic dipole goes hand in hand with a reduction in energy and will, therefore, occur if activation energy for oxygen diffusion is available. We mimic this process by manually shifting oxygen ions from the negatively charged dislocation core to the positively charged dislocation core [138]. As indicated in Figure 27 shifting one oxygen ion per unit cell dislocation line length balances the charges completely. We do this charge balancing prior to relaxation and otherwise continue with the procedure as before including the simulation of the climb dissociated configurations.

Surprisingly, the dislocations do not show glide splitting when they are charge neutral. Although splitting is very effectively suppressed, the potential energy is still lowered compared to the charged state because of the reduced electrostatic contribution, see Figure 29. As expected, the climb dissociation is still effective at further reducing energy.

The glide dissociated configuration of the dislocation is the one expected to make the major contribution to the plastic deformation. So it is also the type of dislocation that is probably introduced into  $SrTiO_3$  when it is plastically deformed. During glide motion, dislocations move rather quickly. If they do not sweep up or leave behind any defects, this dislocation type can be mobile. However, as soon as the charge on the dislocation is allowed to equilibrate, the more favorable dislocation configuration is the full dislocation. Such a charge equilibration could also just happen due to enhanced diffusion at elevated temperatures. Then the full dislocation is more stable than the glide dissociated variant, but also less mobile because of the larger Burgers vector. Only if it would be forced to dissociate into two partials at very high stresses it could further contribute to plastic deformation.

Thus, the reason for the ductile-to-brittle transition between 1000 K and 1500 K is two-fold [128]. Firstly, the constriction of the dislocation due to charge balancing raises the Peierls barrier. Charge balancing in turn is enabled by diffusion which is facilitated by increasing temperature. Secondly, a full dislocation can climb dissociate, which is also a process that depends on thermal activation. During climb all species, i.e., Sr, Ti, and O need to diffuse. A climb dissociated dislocation is not only thermodynamically the most stable form but also expected to be permanently sessile. Our findings, thus, support earlier studies that have suspected such a mechanism [128, 155, 184]. For easier reference Figure 30 shows a schematic energy landscape for the type  $\mathcal{A}$  dislocation.

**Outlook** As we will show in Section 3.3.2, the climb instability is closely related to processes of dislocation multiplication [156]. Furthermore, it is one ingredient to a possible multiple cross-glide dislocation multiplication that has been observed in other ceramics [104–106]. Experimental evidence for our findings in literature is indirect but promising. More indirect experimental evidence could include the study of ductility in very pure  $SrTiO_3$  at varying temperatures and oxygen partial pressures. Significant changes in ductility are expected when pre-existing dislocations are treated in a way that allows charge balancing of dislocations.

Another aspect would be to revisit the importance of this dislocation type for the plastic deformation of SrTiO<sub>3</sub> altogether. As the glide dissociated state is not energetically stable it should not appear in equilibrium. Indeed, close examination of the available published experimental evidence suggests the presence of the climb dissociated configuration of type  $\mathcal{A}$  dislocations [184]. Climb dissociated type  $\mathcal{A}$  dislocations can, however, also be the result of a reaction of two type  $\mathcal{C}$  dislocations that are discussed below [136]. This alternative route, that explains the presence of climb dissociated type  $\mathcal{A}$  dislocations and avoids the unstable glide dissociated configuration, is, in fact, deemed probable.



Figure 29: Comparison of energies of type A dislocations with and without charge balancing for different climb splitting distances. Each point represents the average of at least three independent samples. The charged full dislocation spontaneously decays into its glide dissociated configuration and is not (meta-)stable. By balancing the charge on the dislocations the energy can be decreased. An equilibrium climb splitting for charged and charge balanced dislocations of three unit cells is evident. A growing stacking fault and decreasing elastic interaction increases energy at high climb splitting distances.



configurational space

Figure 30: Schematic map for the relation of different configurations of type A dislocations. Dislocations with their symbolic elastic fields and possible charges are indicated as well as possible paths between the configurations. The vertical ordering is according to the potential energy as measured in simulation (not to scale). The horizontal ordering is somewhat arbitrary and only used to depict relations schematically. The configurational space may be either sampled by temperature or by time, especially if activated processes are necessary.

# 3.1.5 Dislocation Type $\mathcal{B}$

Next, we turn to type  $\mathcal{B}$  dislocations which differ from type  $\mathcal{A}$  dislocations by their line orientation. Just like for the  $\mathcal{A}$ -type dislocation we first review important aspects from literature and make an analytic estimate of the splitting distance. Then we turn to the atomistic study of dislocation core structure which is significantly more simple than the edge dislocation core.

**Literature** Dislocations of type  $\mathcal{B}$  represent the screw analog of type  $\mathcal{A}$  dislocations. Thus, they also possess a Burgers vector  $\vec{b} = a\langle 110 \rangle$  and a glide plane  $\vec{n} = \{1\overline{1}0\}$ , but the line vector  $\vec{t} = \langle 110 \rangle$  is aligned with  $\vec{b}$ , see Table 2. The defining vectors are illustrated in Figure 31.



Figure 31: Crystallographic orientation of defining vectors for dislocation type  $\mathcal{B}$ . Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). The full Burgers vector has been split into two equal parts to indicate glide dissociation. Reproduced from Figure 11 for convenience.

Types  $\mathcal{A}$  and  $\mathcal{B}$  represent the pure edge and screw cases of  $\langle 110 \rangle \{110\}$  dislocations and are interchangeable during dislocation motion [190, 197, 208]. Dislocations move by the so-called kink mechanism, see Figure 8. A small segment is bowing-out and moving into the adjacent Peierls valley where it is expanding. Eventually, the dislocation has moved by on Burgers vector. If the dislocation is of edge type and the kinks form a 90° angle with the dislocation line, the kink is of screw type. Vice versa, kinks in a  $\mathcal{B}$  type dislocation are of  $\mathcal{A}$  type. This is why we regard  $\mathcal{A}$  and  $\mathcal{B}$  as limiting cases and type  $\mathcal{C}$  as a special intermediate case.

As mentioned before, the predominance of type  $\mathcal{B}$  over  $\mathcal{A}$  depends on temperature [190, 195, 209]. Experimentally type  $\mathcal{B}$  is observed to be in a glide dissociated state with splitting distances of about 4.2 nm. Additionally, they appear in arrangements where two split dislocations reside next to each other in parallel glide planes that are separated by several nanometers at room temperature [195]. The screw dislocation type was also found in nanoindentation experiments on {001} surfaces [196]. However, such experiments, especially when observations rely on very thin samples that have been prepared for TEM, are strongly influenced by surface effects as well as the electron beam [156, 192, 301].

Previous MD simulation studies on type  $\mathcal{B}$  dislocations showed that this dislocation indeed spontaneously glide dissociates in its {110} glide plane. Splitting distances are about 25% less than for the edge type dislocation [150]. In fact, this difference was expected from linear elasticity theory [176, pp. 59 & 110]. Adapting Equation (30) for type  $\mathcal{B}$  dislocations leads to:

$$d = \frac{a^2 \mu}{4\pi\gamma}.$$
(31)



Figure 32: Charge density map for type  $\mathcal{B}$  dislocations using nominal charges. Dislocation cores are uncharged. See Figure 27 for comparison.

Because the elastic fields of the screw dislocations differ from the edge dislocation (see Table 1) we need to modify these equations by omitting the factor (1 - v) [176, pp. 59 & 110]. With v = 0.26 the splitting distance reduces by 26% compared to the edge type dislocation. Therefore, we expect a splitting distance of  $d \approx 2 - 3$  u.c.. Apparently, this is smaller than the experimentally measured value since the stacking fault energy  $\gamma$  is overestimated by the interatomic potential [150].

Furthermore, simulations have shown that type  $\mathcal{B}$  dislocations have a lower mobility than type  $\mathcal{A}$  dislocations at low temperatures [150]. This explains the experimental observation of screw dislocations at low temperatures [195]. The less mobile species remains in the crystal after deformation while the mobile species migrates and easily reaches surfaces or reacts with other dislocations.

**Charge at Dislocation Core and Splitting** Pure screw dislocations are not charged by construction. Nevertheless, we check for charge imbalance in the same manner as for type  $\mathcal{A}$  dislocations, see Figure 32. The charge density map for a type  $\mathcal{B}$  dislocation proves the absence of charged dislocation cores.

Also, this dislocation type exhibits spontaneous glide dissociation, see Figure 33. While the glide plane is a  $\{1\bar{1}0\}$  plane, a climb dissociation would require a splitting in the perpendicular  $\{001\}$  planes, see Table 3. Because there is no intermediate minimum in the corresponding  $\gamma$ -surface (Figure 20) a climb dissociated configuration does not exist for



Figure 33: Type  $\mathcal{B}$  dislocation in its glide dissociated form. Sr is displayed in green, oxygen octahedra around Ti in blue, and oxygen in red. The dislocation lines and Burgers vectors are added as a guide to the eye.

the  $\mathcal{B}$ -type dislocation. A motion along this direction can be excluded because a dislocation would not move perpendicular to the plane of its glide dissociation.

Our calculations confirm the findings of other studies [149, 150]. Similar to type  $\mathcal{A}$  the splitting is into two collinear partial dislocations and the stacking fault is in a {1 1 0} plane. Because the dislocations are charge neutral the splitting distance is identical at both dislocations in the simulation cell with an average of approx. 1.9 nm. Correcting for the overestimation of the stacking fault energy in the interatomic potential compared to DFT [149], we obtain an adjusted splitting distance of 2.5 nm which is lower than the 4.2 nm observed experimentally [195]. In fact, we were expecting even lower values from the analytical estimate as well as from the results of the edge dislocation. A direct comparison of types  $\mathcal{A}$  and  $\mathcal{B}$ , however, is obscured by the dislocation core charge of the former type. Remember that glide dissociation only occurred for the scenarios where charged type  $\mathcal{A}$  dislocation cores were introduced.

Just like for A-type dislocations, the Peierls stress for the type B dislocations is reduced by the glide dissociation of the dislocation [159]. But because a re-association of the partial dislocations is not initiated by charge balancing the dislocation core and climb dissociation is not relevant either, this dislocation type is more robust in retaining its mobility under varying conditions. Because they do not become sessile as easily, their impact on plasticity and toughness may even be greater than that of type A dislocations.

**Non-equilibrium Dislocation Splitting** As we will discuss in Section 3.2.4, the screw dislocation can move by dislocation glide when external load is applied. A peculiarity of this glide motion is that the splitting distance between the partial dislocations increases during loading (Figure 54), which was already noted but not explained by Hirel et al. [150]. In fact, if we load the dislocation only the leading partial moves initially and the glide dissociation distance increases before the trailing partial follows. However, after removal of the load the pair of partial dislocations stays in the extended configuration. In short, there are multiple force-free configuration with different glide dissociation distances. Comparing the energies of simulation cells with different glide dissociation distances *d* we find that the lowest energy is indeed found for the smallest splitting distance, see the 1.9 nm from above. For larger metastable splitting distances of up to 5.6 nm the energy is increased.

In order to explain why several splitting distances can be observed, we schematically construct the force balance for the situation at hand, see Figure 34. We take the first partial to be fixed at position zero and then plot the repulsive and attractive forces acting on the second partial dislocation. First, there is the elastic repulsion of the two partial dislocations displayed in red. The repulsive forces have to be balanced by forces tieing the partial dislocations together, i.e., the force exerted by stacking fault. This force displayed in blue is independent of splitting distance. For the edge dislocation type A this situation leads to a single point where forces are in equilibrium and, thus, to a unique splitting distance as described by Equation (30). In contrast, the Peierls stress for the screw dislocation is a significant contribution, and it has to be added to Equation (22). The difference between the edge and the screw dislocations' Peierls landscape is evident from the different energy landscapes for the respective glide directions in Figure 20. For our graphic representation we add the sinusoidal course of the Peierls stress (orange) to the attractive side of the force balance resulting in the black curve combining the stacking fault energy forces and the Peierls stress landscape.

Now it is clear that there are multiple points where the repulsive (red) and attractive forces (black) for the screw dislocation partials are in balance. Therefore, different splitting distances can be realized where the forces acting on the partial dislocations exactly cancel. Nevertheless, the energetically most favorable configuration is the smallest splitting distance, since it has the smallest contribution from the stacking fault energy as revealed by the atomistic simulation.



Figure 34: Force *f* acting on the second partial dislocation segment of length *l* as a function of splitting distance *d* between the two connected partial dislocations. At points where the solid black curve (SF & Peierls) and the red curve (dislocation interaction) intersect, the forces on the second partial dislocation are in equilibrium.

### **3.1.6** Dislocation Type C

**Literature** Type C dislocations are an intermediate variant between type A and type B dislocations and, therefore, possess a mixed character. Despite identical Burgers vector  $\vec{b} = a\langle 110 \rangle$  and glide plane  $\vec{n} = \{110\}$ , the line vector is  $\vec{t} = \langle 111 \rangle$ , see Table 2. The defining vectors are illustrated in Figure 35.

Any mixed dislocation can be decomposed into an edge and a screw component by projecting  $\vec{b}$  onto  $\vec{t}$ . The total Burgers vector then simply is a linear combination of these two contributions:

$$\vec{b} = \vec{b}_{edge} + \vec{b}_{screw}$$
, (32)

$$a\langle 1\,1\,0\rangle = \frac{a}{3}\langle 1\,1\,\overline{2}\rangle + \frac{2a}{3}\langle 1\,1\,1\rangle.$$
(33)

Actually, this dislocation type has only been investigated some time after the original discovery of ductility in SrTiO<sub>3</sub> [136]. However, a close re-examination of older studies reveals that this dislocation type may also have played a role in many other compression experiments of single crystals [127, 128, 184, 199]. Not many details are known about the nature of type C dislocations and their connection to other dislocation types. However, it has been proposed that the climb dissociated type A dislocations originate from a reaction of two type C dislocations [136]. Moreover, stacking of dislocations and the arrangement of antiparallel dislocation lines on parallel slip planes has been discussed for this configuration [136]. Evidence from nanoindentation experiments and MD simulations support the importance of type C dislocations. Here also a preferential dislocation alignment along  $\langle 111 \rangle$  directions was found [198]. Yet, no dislocation dissociation was observed. Because there are hints



Figure 35: Crystallographic orientation of defining vectors for dislocation type C. Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). The full Burgers vector has been split into two equal parts to indicate glide dissociation. Reproduced from Figure 12 for convenience.

that type  ${\cal C}$  dislocations play an important role in  $SrTiO_3$  plasticity, they are modeled in the following.

**Dislocation Core Charge and Splitting** The creation of this dislocation type is a combination of the cut-and-remove procedure for the edge component and the application of the analytic displacement field for the screw component. The cut for the edge contribution results in a charged dislocation core. In Figure 36 the charge distribution is shown for the situation where the cut is made exactly according to  $\vec{b}_{edge}$ .

The simplest simulation cell investigated for type C dislocations is only 2 u.c. thick along the dislocation line direction. Therefore, the oxygen terminated layer in Figure 36 (a) contains 4 oxygen ions in the periodic cell. A charge balanced configuration is achieved when half of the oxygen ions in the terminal plane are shifted to the other dislocation. As a result, each dislocation is terminated with a half-occupied layer of oxygen ions, see Figure 36 (b). Note, that in principle also incomplete charge balancing is possible, e.g., by shifting only one quarter of the oxygen ions from the negative to the positive dislocation.

Dislocations of type C in their as-created charged state spontaneously glide dissociate into two equal and collinear partial dislocations with  $\vec{b} = \frac{1}{2}\langle 110 \rangle$  on a  $\{1\overline{1}0\}$  plane. An example for a glide dissociated dislocation is shown in Figure 37 (a). The stacking fault between the partials is equivalent to the one between dissociated type A and B dislocations as the shift along  $\langle 1\overline{1}0 \rangle$  is in an  $\{110\}$  plane, cf. local minimum in on the stacking fault energy hypersurface in Figure 20. Also, the separation distance of the partials is of similar magnitude of about 1.9 nm or 4 u.c. – 5 u.c.. Correcting for the overestimation of the stacking fault energy



Figure 36: Charge density in a simulation cell containing a type C dislocation dipole. In order to obtain a smooth charge density that can be binned along the *x*-direction, the ionic point charges have been smeared out be a Gaussian distribution. Additionally, the integrated charges q for each dislocation and a representation of the terminal layer of the dislocation cut are given. (a) Charge at the dislocation core is high in the as-created dislocation. (b) The dislocation cores are charge balanced when the oxygen ions of the terminal plane are equally distributed among the two dislocations.

in the interatomic potential compared to DFT [149], we obtain an adjusted splitting distance of 2.5 nm which compares well to the value of 2.5 nm reported in TEM studies [136].

For charge balanced dislocations we find a similar behavior: they also glide dissociate by the same distance. Nevertheless, the total energy still depends on the presence of the dislocation core charge. Generally, the uncharged glide dissociated dislocation is lower in energy than the charged glide dissociated variant due to the absence of the electrostatic dipole.

However, comparing charged full dislocations with charged glide dissociated dislocations of type C we find that the glide dissociated variant is favored by  $1.18 \text{ eV } \text{Å}^{-1}$ . In the case of uncharged full versus uncharged glide dissociated dislocations the glide dissociated variant is only favored by  $0.52 \text{ eV } \text{Å}^{-1}$ . Consequently, the splitting into glide dissociated partials is less favorable when the dislocation cores are not charged. Thus, it is easier for an uncharged dislocation to re-associate into a full dislocation. This trend is identical to the type A

dislocation where charge balancing also destabilizes the split configuration. To sum up, the energy reductions by charge balancing and by glide dissociation are counteracting each other: both lead to a state of lower potential energy but a balanced charge reduces the stability of the glide dissociation. At the moment the origin of this effect is not yet clear.

For the type  $\mathcal{A}$  dislocations we found that this is exactly the point where interesting implications for the mechanical response may appear. Because glide dissociation does not occur for the charge-balanced case, the road to climb dissociation was opened. So the question appears if there is also a climb dissociated configuration that makes type  $\mathcal{C}$  dislocations sessile.

**Glide vs. Climb Splitting** In the case of type C dislocations, the glide stacking fault is identical to type A. However, a hypothetical climb stacking fault for type C would be located on a  $\{112\}$  plane. In Figure 22 the observed glide stacking fault ( $\{110\}$  stacking fault) and the hypothetical  $\{112\}$  stacking fault are shown next to each other.

For the  $\{1\overline{1}0\}$  stacking fault the basic stacking sequence is conserved and cation containing  $\{1\overline{1}0\}$  planes are still separated by oxygen ion  $\{1\overline{1}0\}$  planes. The  $\{11\overline{2}\}$  stacking fault, which would correspond to climb dissociation, is not feasible. There, the cations and anions are brought close to each other and electrostatic repulsion is strong. To the best of our knowledge this stacking fault has neither been observed in any experiment nor in simulations.

We, therefore, conclude that climb dissociation does not occur for type C dislocations. Consequently, the favored structure of this dislocation type is the glide dissociated configuration which we expect to be mobile under mechanical loading. The role of this dislocation type is, thus, more significant than that of type A dislocations.

**Re-association of Partials** The Peierls barrier is increased when going from the glide dissociated to the full dislocation. Re-association (constriction) of the partial dislocations into a full dislocation could, therefore, strongly affect the ability of this dislocation type to carry plastic deformation. Because the full and the glide dissociated variants are close in energy for type C dislocations, finite temperatures may supply sufficient activation energy to enable a re-association of the two partial dislocations. We test this hypothesis with annealing simulations at very high temperatures analog to Hirel et al. [155].

During annealing for more than 600 ps at 2500 K all tested dislocations transition from a glide dissociated configuration to a full dislocation configuration with an extended and disordered dislocation core, see Figure 37. The full dislocations are always higher in energy than the glide dissociated variants. For instance, in the case of the charge balanced dislocation the glide dissociated configuration was favored by  $0.52 \text{ eV} \text{Å}^{-1}$  over the full dislocation configuration before annealing. After the annealing procedure, the full dislocation configuration possesses a disordered dislocation core and carries  $0.78 \text{ eV} \text{Å}^{-1}$  more potential energy than the glide dissociated configuration. Why does the glide dissociated dislocation re-associate into a full dislocation at high temperatures if this requires additional energy?



Figure 37: (a) Glide dissociated type C dislocation after low temperature quasi-static relaxation. (b) The same dislocation after long high temperature annealing where the pair of partial dislocations has constricted to form a full dislocation with disordered core structure. Dislocation lines and Burgers vectors are indicated.

We suggest that the reason is twofold: a change in the shear modulus reduces the splitting distance and entropy stabilizes the disordered full dislocation core. Regarding the splitting distance, we have made a force-based estimate of the equilibrium splitting distance in Equations (30) and (31). Here, all material properties are temperature dependent. In fact, temperature will have the strongest effect on the shear modulus  $\mu$ , while lattice parameter a and stacking fault energy  $\gamma$  are expected to be less sensitive to temperature. Especially, as 2500 K is close to the experimental melting point of SrTiO<sub>3</sub> [183],  $\mu$  is decreased significantly. The shear modulus is in the enumerator of Equation (31) and, thus, the dislocation splitting distance in proportional to  $\mu$ . Consequently, a reduced splitting distance d at elevated temperatures is expected. At the same time effects of entropy S at the disordered full dislocation core become more pronounced with increasing temperature T. Put in other words, the contribution  $T\Delta S$  with  $\Delta S = S_{\text{disordered}} - S_{\text{split}}$  should in part compensate for excess energy of the full dislocation compared to the glide dissociated configuration. Because the ionic sub-lattices are ordered in the glide dissociated case (Figure 37 (a)) and disordered after annealing (Figure 37 (b)) we estimate the magnitude of the entropy contribution from the vibrational entropy of a more simple defect. Cazorla [302] has calculated a value of  $T \Delta S_{\text{vac}} \approx 20 \text{ meV}$  per formula unit for an oxygen vacancy in a perovskite at 400 K. We extrapolate this value linearly to 2500 K, multiply by two for the two oxygen positions within a dislocation line length of  $\vec{t} = a\langle 111 \rangle$  and normalize it to eVÅ<sup>-1</sup>. The resulting entropy contribution of 0.037 eV  $Å^{-1}$  is lower that the energy penalty of the full dislocation of  $0.52 \text{ eV} \text{\AA}^{-1}$ . However, this is only very rough estimate of the vibrational entropy contribution of a single defect on the oxygen lattice, while, in fact, all sub-lattices are disordered, see

Figure 37. Nevertheless, entropy certainly assists in the stabilization of the disordered core of the full dislocation.

As expected from the considerations about the stacking fault, climb dissociation could not be observed for type C dislocations. Nevertheless, we could confirm that the charge imbalance acts a driving force to diffusion. In the case of strongly charged dislocations, oxygen vacancies move from the dislocation into the crystal to reduce the charge at the positively charged dislocation cores. An example of such a diffusion path is shown for type D dislocations in Figure 41. The full C-type dislocation configuration is, therefore, stabilized by charge balancing and entropic contributions at the dislocation core. In summary, we can expect that partial dislocation re-association at high temperature leads to macroscopic embrittlement of SrTiO<sub>3</sub>.

**Outlook** We conclude that an efficient immobilization of type C dislocations by climb dissociation, like observed for type A, is unlikely. Thus, type B and C dislocations are carriers of plasticity while type A easily becomes sessile. Nevertheless, the low energy difference between the full and the glide dissociated variant renders type C prone to re-association at elevated temperatures and, thus, a decrease in mobility. Figure 38 shows a schematic landscape that summarizes the relation of the different dislocation configurations.

# 3.1.7 Dislocation Type $\boldsymbol{\mathcal{D}}$

**Literature** A  $\mathcal{D}$ -type dislocation possesses a Burgers vector  $\vec{b} = a\langle 110 \rangle$ , glide plane  $\vec{n} = \{1\bar{1}2\}$ , and the line vector  $\vec{t} = \langle 1\bar{1}1 \rangle$ , see Table 2. Therefore, it is a pure edge dislocation. The defining vectors are illustrated in Figure 39. This dislocation type was proposed to be the reaction product of two type  $\mathcal{C}$  dislocations [136] and, therefore, contributes to plasticity. Besides, type  $\mathcal{D}$  dislocations have the same  $\langle 110 \rangle$  Burgers vector like dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ ,  $\mathcal{C}$ , and  $\mathcal{E}$ .

**Inherent Dislocation Core Charge and Annealing** A dipole of dislocation type  $\mathcal{D}$  is composed of an oxygen terminated dislocation core carrying negative charge and one dislocation core that has a mixed termination carrying positive charged, see Figure 40. Again, the charge can be easily compensated by shifting half of the oxygen layer from the negative dislocation to the positive dislocation. This also lowers the potential energy because the electrostatic dipole between the two dislocations is cancelled.

When this dislocation type is relaxed, it stays a full dislocation and shows no signs of splitting. Even after the application of temperatures of 3000 K for several hundred picoseconds, the dislocation structure is stable. Analog to the charged variants of type C dislocations, the charged type D dislocations try to reduce there charge in the annealing simulations. We observe, that the positively charged dislocation emits oxygen vacancies reducing the inherent



configurational space

Figure 38: Schematic map for the relation of different configurations of type *C* dislocations. Dislocations with their symbolic elastic fields and possible charges are indicated as well as possible paths between the configurations. The vertical ordering is according to the potential energy as measured in simulation (not to scale). The horizontal ordering is somewhat arbitrary and only used to depict processes schematically. The configurational space may be either sampled by temperature or by time, especially if activated processes are necessary. Question marks indicate that the process for re-association is not certain, but we suspect a combination of lattice softening and entropic effects.

dislocation core charge. An example of oxygen vacancy diffusion is shown in Figure 41. If annealing is continued, we expect a full charge equilibration of the dislocation cores. Therefore, we continue the discussion with the charge balanced dislocation configuration, only.

**Glide vs. Climb Splitting**  $\mathcal{D}$ -type dislocations were found in TEM studies, and it has been proposed that climb dissociation occurs frequently [136, 156]. Although it has the same Burgers vector as the dislocation types discussed before, the glide plane of a type  $\mathcal{D}$  dislocation would be a  $\{1\overline{12}\}$  plane. Climb dissociation, however, would be along a  $\langle 1\overline{12} \rangle$  direction in a  $\{110\}$  plane.



Figure 39: Crystallographic orientation of defining vectors for dislocation type  $\mathcal{D}$ . Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). Reproduced from Figure 13 for convenience.

For the discussion of the glide plane refer to the section on dislocation type C. A stable stacking fault in the  $\{1\overline{12}\}$  plane is not possible and, thus, glide dissociation for type D dislocations is not expected. This is confirmed by our annealing simulations. However, a climb dissociation corresponds to a stacking fault in a  $\{110\}$  plane, which exhibits a local minimum, see Figure 20. Climb dissociation will, therefore, be investigated explicitly.

The energy of climb dissociated type  $\mathcal{D}$  dislocations is shown as a function of splitting distance in Figure 42. A stable splitting distance  $\frac{5a}{3}[1\overline{1}2]$  is found. This corresponds to a distance of 1.59 nm, which compares well to the splitting distances of the other dislocation types. Given that the stacking fault is crystallographically identical to the glide/climb stacking fault of the type  $\mathcal{A}$  to  $\mathcal{C}$  dislocations this does not come as a surprise. The equivalence of the stacking fault can be seen by the appearance of the same edge sharing oxygen octahedra (insets Figure 42) for these stacking faults.

**Dislocation Reaction** From the analysis of the splitting behavior and the annealing simulations we do not expect that type  $\mathcal{D}$  dislocations are particularly mobile. If they are not mobile but appear in samples that have been plastically deformed, then we need to answer the question of how this dislocation type is created. According to Jin et al. [136], type  $\mathcal{D}$  dislocations are the result of a dislocation reaction involving two type  $\mathcal{C}$  dislocations. We write the pseudo-reaction for these two dislocations explicitly. Consider a first dislocation of type  $\mathcal{C}$ ,

$$\vec{b}^{(1)} = \vec{b}^{(1)}_{edge} + \vec{b}^{(1)}_{screw},$$
 (34)

$$a\langle 1\,1\,0\rangle = \frac{a}{3}\langle 1\,1\,\overline{2}\rangle + \frac{2a}{3}\langle 1\,1\,1\rangle , \qquad (35)$$



Figure 40: Charge density in a simulation cell containing a type  $\mathcal{D}$  dislocation dipole. In order to obtain a smooth charge density that can be binned along the *x*-direction, the ionic point charges have been smeared out be a Gaussian distribution. Additionally, the integrated charges *q* for each dislocation and a representation of the terminal layer of the dislocation cut are given.

and a second dislocation of identical type but with opposite line direction:

$$\vec{b}^{(2)} = \vec{b}^{(2)}_{edge} + \vec{b}^{(2)}_{screw},$$
 (36)

$$a\langle \overline{1}\,0\,\overline{1}\rangle = \frac{a}{3}\langle \overline{1}\,2\,\overline{1}\rangle + \frac{2a}{3}\langle \overline{1}\,\overline{1}\,\overline{1}\rangle \,. \tag{37}$$

If these two dislocations interact a full edge dislocation of type  $\mathcal{D}$  results because the screw contributions cancel exactly:

$$\vec{b}_{edge}^{(new)} = \frac{a}{3} \langle 1 1 \overline{2} \rangle + \frac{a}{3} \langle \overline{1} 2 \overline{1} \rangle = a \langle 0 1 \overline{1} \rangle , \qquad (38)$$

$$\vec{b}_{\text{screw}}^{(\text{new})} = \frac{2a}{3} \langle 1\,1\,1 \rangle + \frac{2a}{3} \langle \overline{1}\,\overline{1}\,\overline{1}\,\overline{1} \rangle = \vec{0} \,. \tag{39}$$

Note, that this procedure, first, requires the presence of two type C dislocations. Therefore, we conclude that there must be a high density of dislocations, so such dislocations can accidentally meet. In addition, the two reacting dislocations must originate from opposite dislocation sources since they travel from opposite directions towards each other.



Figure 41: Type  $\mathcal{D}$  dislocation after long annealing at high temperature. Only oxygen ions are shown for clarity and color coding in red represents position where the oxygen vacancy has visited. One oxygen vacancy has been emitted from the dislocation core and diffused away which reduced the positive dislocation core charge. The dislocation is still localized as a full dislocation.

The reactions result in a full  $\mathcal{D}$ -type dislocation. The occurrence of climb dissociated dislocations of this type, as for type  $\mathcal{A}$ , requires sufficient thermal activation. Such thermal activation may be caused by the energy deposition of the TEM electron beam used for analyzing the dislocation structures. The fact that we do not observe climb dissociation in the annealing simulations at 3000 K can either hint to a significant activation barrier or to an entropic stabilization of the full dislocation core.

**Outlook** In summary, type  $\mathcal{D}$  dislocations are a product of the interaction of two type  $\mathcal{C}$  dislocations. High dislocation densities and multiple dislocation sources are required for it to form. As a product of two mobile dislocations, this dislocation type is rather immobile because of the large Burgers vector and the absence of glide dissociation. The energetically favorable climb dissociation renders it sessile. Consequently, the impact of type  $\mathcal{D}$  dislocations on macroscopic plasticity is expected to be negligible. We, therefore, do not investigate its behavior under applied load.



Figure 42: Energies of type  $\mathcal{D}$  dislocations for different climb splitting distances. Each point represents the average of at least three independent samples. Just the charge balanced results are shown which behave analog to the non-charge balanced case.

# 3.1.8 Dislocation Type $\mathcal{E}$

**Literature** An  $\mathcal{E}$ -type dislocation possesses also a Burgers vector of  $\vec{b} = a\langle 110 \rangle$  but is otherwise very different from the dislocation types discussed so far. With a line vector of  $\vec{t} = \langle 100 \rangle$  it is a mixed dislocation residing on an  $\vec{n} = \{001\}$  glide plane. The defining vectors are illustrated in Figure 43. Its special structure with the simple vectors can be expected to lead to a compact dislocation structure. Moreover, this dislocation type is the only one that is not related to some glide plane or climb plane of  $\{110\}$  orientation.

This dislocation type was found in nanoindentation experiments of polycrystalline SrTiO<sub>3</sub> [114]. Supplementary theoretical work was provided by Yang et al. [187]. It has been claimed that dislocations with  $\vec{b} = a\langle 110 \rangle$  and  $\vec{n} = \{001\}$  could be observed in several variants, ranging from pure edge to screw, just like the  $\langle 110 \rangle \{1\overline{1}0\}$  types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$ .



Figure 43: Crystallographic orientation of defining vectors for dislocation type  $\mathcal{E}$ . Unit cell of cubic SrTiO<sub>3</sub> with Burgers vector  $\vec{b}$  (orange), line vector  $\vec{t}$  (blue), and slip plane  $\vec{n}$  (purple). Reproduced from Figure 9 for convenience.

It is of significant interest to discuss this additional slip system due to its implications for arbitrary macroscopic ductility. If dislocations in this type  $\mathcal{E}$  configuration were mobile, there would be five slip systems (2 ×  $\langle 110 \rangle \{ 1\overline{1}0 \}$  and 3 ×  $\langle 110 \rangle \{ 001 \}$ ) available in SrTiO<sub>3</sub>. Therefore, the Taylor criterion is satisfied and "significant plasticity in polycrystalline SrTiO<sub>3</sub> ceramics can be expected" [187, 303].

However, in nanoindentation experiments complex stress states with very high applied stresses can lead to all kinds of dislocations, since fracture is inhibited at the nanoscale and the necessary Peierls stress can be overcome [198, 304–308]. Thus, the role of type  $\mathcal{E}$  dislocations needs to be revisited.

**Charge at Dislocation Core and Dislocation Splitting** Mixed type  $\mathcal{E}$  dislocations feature a screw component as well as an edge component. The edge component, is terminated by SrO or TiO<sub>2</sub> units, see insets in Figure 44. If the ions carried nominal charges, i.e., Sr<sup>2+</sup>, Ti<sup>4+</sup>, and O<sup>2-</sup>, these terminating layers would be charge neutral and charge between the two dislocations would be balanced. However, the interatomic potential by Thomas et al. [157] uses the ionic charges as a fit parameter. While the full SrTiO<sub>3</sub> formula unit is charge neutral, the fractional charges on the ions create charged SrO<sup>0.44+</sup> and TiO<sub>2</sub><sup>0.44-</sup> layers, see Figure 44. Note that this observation does not invalidate the results of the other dislocation types studied because there it is a true ionic imbalance that leads to charged dislocation cores. If nominal charges were assumed in the cases  $\mathcal{A}$ ,  $\mathcal{C}$ , and  $\mathcal{D}$ , the charge imbalance would be even more significant.

However, the electrostatic repulsion of equal sign charges being located opposite to each other is important for a possible climb dissociated configuration. In Figure 45 we show



Figure 44: Charge density map for type  $\mathcal{E}$  dislocations using the effective charges from the interatomic potential versus nominal charges. Insets show the unrelaxed dislocation structure where SrO and TiO<sub>2</sub> termination is visible. The charge imbalance comes from the use of effective charges in the interatomic potential.

the starting configuration for the study of climb dissociated  $\mathcal{E}$ -type dislocations. Evidently, there would be either  $\text{SrO}^{0.44+}$  or  $\text{TiO}_2^{0.44-}$  layers directly adjacent to each other in a climb stacking fault. This configuration cannot be stable due to its massive electrostatic repulsion. Thus, the study of this climb stacking fault is prohibited in the framework of fixed charge interatomic potentials. Such a stacking fault would require the use of a different potential or elaborate DFT calculations that allow for charge transfer to adapt the ionic charges at the climb stacking fault.

Although we cannot study this dislocation type atomistically with the desired accuracy, we can still make some very relevant analytic considerations. First, we note that even when charge balanced, the two differently terminated dislocation variants can be expected to show slightly different behavior. Such a difference has also been encountered in studies of dislocations with  $\vec{b} = \langle 100 \rangle$ ,  $\vec{t} = \langle 001 \rangle$ , and  $\vec{n} = \{010\}$  [137].

Second, the glide dissociation suggested by Mao and Knowles [114] would only be possible if the  $\gamma$ -surface in the glide plane had a metastable minimum in between full Burgers vector shifts. The corresponding  $\gamma$ -surface for the {100} plane has been presented in Figure 20.



Figure 45: Different hypothetical configurations of climb dissociated type  $\mathcal{E}$  dislocations. A climb stacking fault is either constituted by two adjacent SrO layers (a) or by two adjacent TiO<sub>2</sub> layers (b). Connecting lines between cations are shown as a guide to the eye.

While the local minimum in the  $\{1\,1\,0\}\,\gamma$ -surface has been related to the glide dissociation of dislocations with  $\{1\,\overline{1}\,0\}$  glide planes such a feature is absent in the  $\{1\,0\,0\}\,\gamma$ -surface. Glide dissociation of type  $\mathcal{E}$  dislocations is, thus, not feasible.

**Full Dislocation Structure** Despite the restrictions due to the nominal charges we try to model the full native dislocations with SrO and  $TiO_2$  termination. When relaxed in low temperature conditions dislocations of either termination show no rearrangement. As expected, spontaneous dissociation into partial dislocations does not occur.

Even with sufficient thermal activation of 2500 K over long time scales (analog to the annealing simulations in Section 3.1.6) the dislocation core structure is unchanged. Only slight disordering of individual ions at the dislocation core is observed. We conclude that type  $\mathcal{E}$  dislocations cannot lower their Peierls barrier by splitting which is consistent with the calculated  $\gamma$ -surfaces. This dislocation type, therefore, plays a minor role in the macroscopic plastic behavior of SrTiO<sub>3</sub>. It may still be relevant in nanoindentation experiments, where the loading scenario is very different.

### 3.1.9 Discussion

In this section we have carefully investigated the low temperature structure of dislocations in SrTiO<sub>3</sub> that were suggested in literature. A special focus is put on the dislocations that can be introduced mechanically at low temperature, i.e., below 1000 K. The different types of dislocations possess a Burgers vector of  $a\langle 110 \rangle$  but differ with respect to dislocation line vector and glide plane. A summary of the results is given in the overview of Figure 46. Throughout this part we also found good agreement between analytical approximation and

type	as-created	charge balanced	
$\mathcal{A}$	glide dissociated, mobile	e by agation	tendency to climb dissociate sessile
B	is charge balanced	rchangeable on and prop of kinks	glide dissociated mobile
С	glide dissociated mobile	inter formatic	glide dissociated but less stable can easily become sessile
D	tendency to climb dissociate sessile	ociation flide mobile	tendency to climb dissociate sessile
Е	is charge balanced	no dissc by g and im	no glide dissociation possible sessile

Figure 46: Summary of expected dislocation behavior based on quasi-static calculations.

simulations, e.g., for the splitting distance. We acknowledge, that our considerations only target stoichiometric  $SrTiO_3$  and the interaction of dislocations with point defects or doping is left to further studies.

**Glide Dissociation** Dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  belong to the subgroup of  $\langle 1 1 0 \rangle \{ 1 \overline{1} 0 \}$  dislocations. They glide dissociate spontaneously into two equal and collinear partial dislocations which reduces their elastic energy and potentially lowers their Peierls stress. The glide dissociation is in line with the rule of thumb that stable stacking faults in ionic crystals require that some basic stacking sequence is retained and atoms of equal sign charge do not come too close to each other [111]. Glide planes other than  $\{1 \overline{1} 0\}$  planes do not show metastable stacking faults in SrTiO<sub>3</sub>. From this we conclude that dislocation types  $\mathcal{D}$  and  $\mathcal{E}$  are not relevant for slip transfer, while types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  contribute to macroscopic plasticity.

**Inherent Dislocation Core Charge** Since dislocation type  $\mathcal{A}$ ,  $\mathcal{C}$ , and  $\mathcal{D}$  have a (partial) edge character, the terminating layers of their dislocation cores are inherently charged because they are either anion or cation dominated [112, 138]. This inherent charge is a decisive factor regarding the tendency of type  $\mathcal{A}$  and  $\mathcal{C}$  dislocations to glide dissociate. Moreover, these dislocation types and the state of their core are probably very sensitive to defect equilibria that involve charged defects. Because dislocation mobility is expected to strongly depend on the dislocation glide dissociation, the dislocation core charge has an indirect and possibly significant impact on the plastic behavior of SrTiO<sub>3</sub>. Note that this effect is qualitatively different from dislocation pinning by charged defect clouds that accumulate

around dislocations [103]. In turn, one also has to recognize that the dislocation charge influences the local defect equilibria in  $SrTiO_3$ , e.g., via the emission of oxygen vacancies as exemplarily shown for type  $\mathcal{D}$  dislocations.

**Climb Dissociation** An important result concerns the most intensively studied dislocation type  $\mathcal{A}$ . The full dislocation is unstable and spontaneously glide dissociates into two equal partials. However, by careful preparation of glide and climb dissociated dislocations of this type we could show that the climb dissociated variant is the most stable configuration. The reason is the destructive overlap of the mechanical stress fields in this configuration that reduces the elastic dislocation self-energy. Dislocation climb dissociation is commonly associated with sessile dislocations, as a motion in such a configuration would require massive diffusion. The fact that a climb mechanism could be the reason for SrTiO<sub>3</sub> becoming brittle at elevated temperature, however, also opens the route to dislocation multiplication mechanisms like the proposed multiple cross glide mechanism [106].

**Conclusion** In this section we have studied the (quasi-)static structure of dislocations in  $SrTiO_3$ . Next, we continue on the roadmap presented in Figure 47 and investigate the behavior of the relevant dislocation types under external load. Ultimately, the aim of this process is to gain a better understanding of the ingredients required for plasticity in  $SrTiO_3$  and possibly other materials of similar perovskite crystal structure.

	Section 3.1	Section 3.2	Section 3.3
	Equilibrium Dislocation Structure	Dislocation Motion	Dislocations in Experimental Settings
subject	low temperature configurations of dislocation types $\mathcal{A} - \mathcal{E}$ - $\langle 110 \rangle \{ 1\overline{1}0 \}$ disloca- tion types can glide	?	?
results	<ul> <li>dissociate</li> <li>types D &amp; E</li> <li>probably immobile</li> <li>configuration strongly</li> <li>dependent on charge</li> </ul>		

Figure 47: Summary of the main findings. In this section the equilibrium structure of dislocations at low temperatures has been covered. The next section proceeds with dislocation motion.

# 3.2 Dislocation Motion

In the previous part we have investigated the quasi-static structure of several dislocation types. This allowed identifying sessile and mobile dislocations. In this section we try to validate these considerations by actually applying load to the dislocations. To this end, we quasi-statically calculate the Peierls stress of various dislocations and observe their behavior during applied load and motion. Specifically, we address the following questions:

- 1. What is the Peierls stress of dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$ ?
- 2. How does kink formation and migration affect the stress level required to move dislocations?
- 3. What is the mode of motion of the dislocations, and how do they interact with point defects?

# 3.2.1 Lessons From a Quasi-static Analysis

In our discussion of static equilibrium structures in the athermal regime we focused on dislocations that have been proposed in literature. These dislocations were found in  $SrTiO_3$  after mechanical load has been applied in temperature regimes that are not too far from room temperature. Importantly, it is known that the plastic behavior of  $SrTiO_3$  single crystals changes around 1000 K, so we have restricted the discussion to temperatures well below this threshold [127].

A dislocation contributing to plastic deformation also needs to be mobile. First, the dislocation itself must have a structure that allows a facile motion. Second, the loading conditions must be appropriate to exert a force on the dislocation. Third, the motion of the dislocation should not be impeded by defects in the material. Let us discuss the first point here, the second point in the following paragraphs and lift the simplification of unhindered dislocation motion in Section 3.3.

It was found that all dislocation types  $\mathcal{A}$  to  $\mathcal{E}$  are stable in single crystals of SrTiO<sub>3</sub>. All of them possess the identical  $a\langle 110 \rangle$  Burgers vector. However, only dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  feature configurations that exhibit glide dissociation.

We have noted that the presence of glide dissociation enables a dislocation to glide more easily. The reason is the connection of the Peierls stress to the length of the Burgers vector. In Equation (21) we used the classical Peierls-Nabarro formula and exploited its relation between Peierls stress and ratio of Burgers vector and slip plane spacing [309]. This gave a first approximation for the relative mobility of the different dislocation types. However, this model was developed and mostly used for simple metals such as Al or Ag. Indeed, the problem

is not as simple in a structure like a perovskite and when two connected partial dislocations are considered. The following paragraphs point to the difficulties in the calculation of the Peierls stress using some well-known concepts of elasticity theory.

#### 3.2.2 Analytic Peierls Stress Calculation

It was shown by Huntington [211] and comprehensively discussed in Refs. [179, 297] that the Peierls stress in a mono-atomic metal depends on the stacking in the slip plane. Two solutions have been derived for an alternating stacking and a facing stacking, see Figure 48. Alternating stacking describes the situation where the atoms on two sides of the slip plane are shifted by half of a Burgers vector. In a two-dimensional picture this is the situation between two close packed planes in a close packed hexagonal lattice, see Figure 48 top left. Here, the atoms are not on top of each other but the atoms in one row reside in the valleys formed by the atoms of the row below it. That is the situation for the cation sub-lattice of the perfect perovskite lattice. The Peierls stress of an isotropic and linear elastic material in this Peierls-Nabarro approach is [297]:

$$\tau_m^{\rm PN} = \frac{\mu}{1-\nu} \exp\left(\frac{-\pi h}{b(1-\nu)}\right),\tag{40}$$

where  $\mu$  is the shear modulus,  $\nu$  is the Poisson's ratio, h is the distance between equivalent lattice planes perpendicular to the glide plane, and b is the magnitude of the Burgers vector. On the contrary, imagine the situation where the atoms across the slip plane face each other, see Figure 48 bottom left. This situation appears, provided a 2-dimensional representation, in a close packed slip plane of a simple square lattice. The Peierls stress for this situation (Huntington approach) is estimated to be [297]

$$\tau_m^{\rm H} = \frac{\left(0.15 + 0.06(1 - \nu)\frac{b}{h}\right)\mu}{1 - \nu} \exp\left(\frac{-\pi h}{b(1 - \nu)}\right). \tag{41}$$

These values are valid for edge dislocations, screw dislocations can be treated by omitting the factor  $(1 - \nu)$ . Note, that there are actually older variants of the Peierls-Nabarro formula for  $\tau_m$  which have errors in the exponent as well as the prefactor [179, 211, 297]. Nabarro [179] discusses the historic evolution of these formulae noting that, generally, Equation (21) underestimates the Peierls stress. Here we use the more accurate formulae by Huntington [211] which are discussed in detail by Nabarro [297].

The problem with the perovskite structure is that the definition of facing versus alternating stacking depends on the choice of the sub-lattice as well as the configuration seen by the leading versus trailing partial, see Figure 48. Additionally, ionic bonding is very different from metallic bonding. Thus, it is unclear whether Equation (40) or Equation (41) holds true. In Figure 48, we illustrate the problem of stacking: in the ideal perovskite crystal Sr- and Ti-ions alternate while they face each other inside the  $\{1\ \overline{1}\ 0\}$  stacking fault that is relevant for dislocation types  $\mathcal{A}$  to  $\mathcal{C}$ . What remains certain, however, is that the glide dissociated dislocation has a reduced Peierls stress compared to the full dislocation.



alternating sequence in ideal crystal  $\rightarrow$  leading partial

facing sequence in stacking fault  $\rightarrow$  trailing partial

Figure 48: The stacking sequence inside the slip plane impacts the Peierls stress. While the oxygen sub-lattice (red) is conserved inside and outside of the stacking fault, the cation stacking sequence looks different to the leading and the trailing partial. In the ideal crystal strontium (green) and titanium (blue) have an alternating stacking; inside the stacking fault the species face themselves across the slip plane.

As an example we explicitly evaluate  $\tau_m$  for a type  $\mathcal{A}$  dislocation using as input the values shown in Table 5, shear modulus  $\mu = 107$  GPa, Poisson's ratio  $\nu = 0.26$ , and the assumption of isotropic elasticity. Using the Peierls-Nabarro approach from Equation (40) we obtain 17.3 GPa for the full dislocation and 2.07 GPa with half the Burgers vector. Instead, the modified Huntington model from Equation (41) gives 4.13 GPa and 403 MPa, respectively. Note, that the difference in  $\tau_m$  between the full and the glide dissociated dislocations is much smaller compared to the old Peierls-Nabarro formula Equation (21) which is presented in standard textbooks like Ref. [164]. For reference, it gives 4.14 GPa and 59 MPa for the full and glide dissociated dislocations, respectively. Thus, we expect that, e.g., Porz [132] significantly underestimates the Peierls stress for the glide dissociated dislocations.

Based on this discussion we expect that only glide dissociated dislocations are mobile due to their low Peierls stress compared to full dislocations. Additionally, because the partial dislocations are tied together by a stacking fault, the Peierls stress could be reduced further [179, 310] and be below our analytical predictions. Also, because dislocation types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  have different dislocation core arrangements, we suggest that their Peierls barrier will differ. Before turning to a fully atomistic calculation of the Peierls barrier a few considerations on the setup and the mode of dislocation motion are in order.

# 3.2.3 Expectations Regarding Dislocation Motion and Limitations in Simulations

Dislocation motion can occur in different modes. So far, our estimates on the Peierls stress have been regarding individual edge or screw dislocations [179]. However, for pairs of partial dislocations the relative position of the two partials is of importance since they are tied together by a stacking fault. As pointed out by Benoit et al. [310] the connection of two partial dislocations alters the stress needed to move dislocations. And more generally, the



Figure 49: Different models of dislocation propagation. Left: Kink formation and propagation due to applied stress can lead to an interchange of dislocation segments with edge, screw, and mixed character. Top right: Two partial dislocations connected by a stacking fault can possess a spacing which is an integer (commensurate) or non-integer value (incommensurate) of the Burgers vector. Bottom right: If connected partials move consecutively the motion can be driven by the leading or the trailing partial. This increases or decreases the area *A* of the stacking fault, respectively.

motion of dislocations by kink formation and migration is an important mechanism for them to incrementally overcome the Peierls barrier instead of rigidly jumping from one Peierls valley to another [181]. The two aspects are displayed in Figure 49.

**Connected Partials** For simplicity, we first assume dislocations that are straight parallel partials and need to overcome the hill between two stable locations as a whole. If the two connected partial dislocations move simultaneously their distance is constant and both surmount the Peierls hill at the same time. The Peierls stress for this motion corresponds to the case of an individual partial moving [311].

However, the two partial dislocations are not independent. They are connected by an attractive force resulting from the stacking fault and a repulsive force resulting from their stress fields, see Equation (22). The combination of these forces can be imagined like a spring tieing the partial dislocations together. The higher the stacking fault energy and the stronger the dislocation stress fields (i.e., the larger the Burgers vector), the stiffer the spring becomes. It is quite probable that the equilibrium distance of the spring is not commensurate with the periodicity of the Peierls landscape ("non-integer spacing" in Figure 49). For instance, if the coupling between the partial dislocations pulls them closer together than dictated by

the minima on the Peierls energy landscape, the stacking fault assists the dislocations in climbing the Peierls hill. Therefore, the apparent Peierls stress is reduced [310]. Note, that this argument is purely based on the forces between the partial dislocations and does not entail activation energy transferred between the dislocations. While the coupling can lower the apparent Peierls stress, a reduction of the lattice friction to zero as suggested by Benoit et al. [310] seems unlikely. First, energy will still be dissipated when a dislocation moves from a Peierls hill into an adjacent Peierls valley. Second, the equilibrium distance of the repulsive and attractive forces between the partial dislocations (excluding the Peierls energy landscape) would have to equal exactly  $\frac{2n+1}{2}b_{full}$  with integer *n*. And third, the absence of Peierls stress would require that the connection between the partial dislocations is rigid and not spring-like. This requires very high stacking fault energies. High stacking fault energies, in turn, prevent glide dissociation altogether making the scenario of zero lattice friction suggested by Benoit et al. [310] impossible.

A related scenario appears if the dislocations do not move at the same time or at the same speed. The distance between the partials and, therefore, the area of the stacking fault can either increase or decrease [150]. If the stacking fault area increases, the stress to initially overcome the Peierls hill will be slightly increased since additional stacking fault area must be created and vice versa if the trailing partial moves alone. It is a very plausible scenario that the leading partial moves first, because the leading partial sees a shallower energy landscape than the trailing partial, see Figure 20. Then the increased stacking fault area could drag the trailing partial behind reducing its Peierls stress.

Which influence these effects have is not a priori obvious. MD simulations by Hirel et al. [150] have shown that type  $\mathcal{A}$  dislocations move by almost simultaneous motion of both partials. Type  $\mathcal{B}$  dislocations, however, first drastically increase the stacking fault area by motion of the leading partial before the trailing partial follows. However, this study used simulation cells with only 1 u.c. thickness, dislocation monopoles, and estimated the Peierls stress based on shear strain (instead of direct calculation by material response).

**Kinks** In addition to the different modes of motion for straight partial dislocations, it is known that dislocations usually bend under applied load and do not jump to their adjacent Peierls valley as a whole. The process by which a dislocation surmounts its next Peierls hill segment-wise is referred to as kink pair formation and consecutive migration of these kinks [310, 312]. It is schematically shown in Figure 49 how the kinking process can avoid the large energy cost that is required for a complete dislocation line to surmount the Peierls hill. Instead, the dislocation only overcomes this barrier locally and assisted by thermal fluctuations. The expansion of the kinked region ultimately leads to a situation where the dislocation as a whole has moved into its adjacent Peierls valley [312].

To observe dislocation kinking or bow-out of dislocation lines a short simulation cell along the dislocation line is inappropriate. Because periodic boundary conditions are in place the dislocation is only quasi-infinitely long. The periodic boundaries restrict the dislocation line to be connected across the boundary of the simulation cell. In fact, there are image



Figure 50: The self-interaction of the dislocation line across the periodic *z*-boundaries creates image forces. They prevent large bow-outs in short simulation cells (small  $L_z$ ) or prevent kinking altogether. To investigate these processes large simulation cells are required.

forces inversely proportional to the periodic dislocation line length  $L_z$  that tend to pull the dislocation straight and counteract the bow-out [164, 294]. Any kink or bow-out of the dislocation line immediately sees its periodic image across the boundary. Thus, a single pair of kinks cannot nucleate independently. In effect, for very short dislocation lines, especially the single u.c. length used in many studies [138, 150, 155], dislocation lines surmount the Peierls barrier as a straight line. While this leads to the correct Peierls barrier of a dislocation segment it does not give insights into the true motion of the dislocation in crystal. Therefore, we extend the simulation of short dislocation lines (Section 3.2.4) with the simulation of longer dislocation lines (Section 3.2.5), so we can observe kinking, see Figure 50. It is expected that simulation cells with different lengths along *z* give different values for the resolved shear stress. We also note that image forces due to the periodic dislocation array should be negligible due to the large sizes along the *x*- and *y*-axis and the ratio of the simulation cell sides [294].

The force that an externally applied shear stress exerts on a dislocation line can be calculated using the Peach-Koehler formula (Equation (8)). We apply the shear stress by adjusting the target values of the barostat while the temperature is fixed at 10 K (athermal regime). By holding each stress value for 40 ps we avoid dynamic effects of increasing the applied load too quickly. For dislocation types  $\mathcal{A}$  and  $\mathcal{B}$  the shear stress is chosen such that the dislocation experiences the full applied stress. The critical resolved shear stress when a dislocation starts to move is, thus, equal to the outer applied shear stress at that moment. In the case of type  $\mathcal{C}$  dislocations, we choose the two extreme scenarios: an applied stress that either loads the screw component ( $\tau_{xz}$ ) or the edge component ( $\tau_{xy}$ ) of the dislocation.

### 3.2.4 Dislocation Motion under the Influence of Periodic Images

In this section, we turn to the actual atomistic simulation of dislocations under mechanical load. First, we will discuss all three  $(110)\{1\overline{1}0\}$  dislocation types in thin simulation cells, where image forces are significant. Relaxed constraints due to image forces are discussed in Section 3.2.5.

**Type**  $\mathcal{A}$  Type  $\mathcal{A}$  dislocations exist in one of three different configurations: as-created glide dissociated, charge balanced full, and charge balanced climb dissociated. For the case of charged dislocations we further distinguish between as-created dislocations with positive charge (oxygen deficient) and negative charge (oxygen surplus). All types are loaded by a shear stress  $\tau_{xy}$  at 10 K. Note that the alignment of the crystallographic axes with the simulation cell axes has been defined in Table 3 and the orientation of the shear loading is shown in Figure 51. We expect only the glide dissociated variant to be mobile.

Indeed, we confirm that the charge balanced full dislocation cannot glide, see Figure 52 (a) – (c). Instead, we observe that this dislocation acts as point for crack nucleation. Consequently, the material ruptures around 6 GPa, see Figure 52 (c). Likewise, the climb dissociated dislocations, charged as well as neutral, do not exhibit dislocation glide (not shown).

The as-created simulation cell with the dislocation dipole features one positively charged (oxygen deficient) and one negatively charged dislocation (oxygen surplus) maintaining overall charge neutrality. Upon loading, the positive glide dissociated dislocation starts



Figure 51: Schematic drawing of the simulation cell setup with shear stress for type  $\mathcal{A}$  dislocations. Analog loading scenarios apply to dislocation types  $\mathcal{B}$  and  $\mathcal{C}$ . For details on the crystallographic orientations see Table 3.



Figure 52: (a) Change of dislocation position during load simulations of different type  $\mathcal{A}$  dislocation variants. For the snapshots only the oxygen ions are displayed and color coded by their coordination (blue = coordination too low, red = coordination too high). (b) & (c) Dislocations with charge neutral dislocation core is sessile and acts as nucleus for cracks at very high loads. (d) & (e) Dislocations with negatively charged dislocation core (oxygen rich) are sessile until they show some nano-cracks and dislocation emission above 4 GPa. (f) – (i) Positively charged dislocations (oxygen deficient) glide easily (f) until they emit oxygen vacancies balancing their charge (g). Charge balanced dislocations are sessile and only when nano-cracks are formed at increased load they can act as nuclei for new dislocations (h). When the load is removed from the sessile dislocation, the partial dislocations re-associate into a full dislocation as long as they stay charge neutral.

moving between 1.20 GPa and 1.25 GPa, see Figure 52 (a) & (f), in line with published MD simulations [150]. During motion the positive dislocation's glide dissociation distance increases slightly from 1.56 nm – 2.05 nm to around 2.3 nm – 2.5 nm. The motion of this oxygen deficient dislocation is not perfect, see Figure 52 (g). As it is gliding, the positive dislocation emits oxygen vacancies and becomes charge neutral. Once it has achieved charge neutrality, the dislocation remains in its glide dissociated configuration but stops moving. So after travelling only about 25 nm this dislocation and new neutral dislocations may be emitted, see Figure 52 (h). Instead, if we remove the stress, the neutral glide dissociated dislocation re-associates into a full dislocation with slightly widened core, see Figure 52 (i). It only dissociates again into its partial dislocations if a vacancy is provided and the dislocation becomes charged. This is exactly the behavior that was expected from the static simulations in Section 3.1.4: The neutral dislocation is more stable in the full configuration and immobile.

In order to see if the negatively charged dislocation could also move, we turned to charged simulation cell, where both dislocations are either positively charged or negatively charged. For the positively charged dislocation, we again observe easy glide confirming that their mobility is not sensitive to the dislocation dipole configuration. The negatively charged dislocations, however, do not glide easily, see Figure 52 (a) & (d). Only when  $\tau_{xy}$  is raised significantly beyond 4 GPa nano-cracks form at the sessile dislocation and new dislocations can be emitted, see Figure 52 (e).

We shortly summarize the intermediate results:

- Climb dissociated configurations of type A dislocations cannot contribute to plasticity.
- Full dislocations, as they appear for the charge balanced configurations, likewise, cannot glide.
- Negatively charged and neutral glide dissociated dislocations are virtually immobile.
- Positively charged dislocations have a Peierls barrier on the order of 1.20 GPa 1.25 GPa and are mobile as long as they are charged. However, the emission of oxygen vacancies occurs frequently and renders these dislocations sessile.

Why can only the oxygen deficient and positively charged dislocation glide easily? To investigate this matter we test a couple of hypotheses.

First, we expected that there is simply an energy difference of an oxygen vacancy at the dislocation and an oxygen vacancy positioned on a regular lattice site. If the latter energy was lower, the dislocation would see a driving force to move through the crystal and bring the oxygen vacancy which is initially located at its core to a more favorable position. Effectively such a driving force would add to the external applied load and ease the glide of oxygen deficient dislocations. In the dimensions chosen here there are two vacant sites at the

positively charged dislocation. However, comparing the energy when the oxygen vacancies are at the dislocation core and the energy of one or both of the vacancies manually placed somewhere else on the glide plane, i.e., far from the dislocation core, we could falsify this hypothesis, see Figure 53 (a). In fact, placing the vacancies at the dislocation is energetically favorable albeit a very small energy difference on the magnitude of approx.  $0.1 \text{ eV }\text{\AA}^{-1}$  per vacancy.

Second, we checked the stress tensor of the simulation cell. To this end, we measured the average stress on each simulation cell side during an *NVT* simulation at 10 K with Nosé-Hoover thermostat. Indeed, especially the stress tensor along the dislocation line, i.e., the component related to the dislocation line tension varies with positioning of the oxygen vacancies. Line tension is the energy change from a change in dislocation line length  $\frac{dE^{\text{pot}}}{dl}$  [159]. There is a clear trend of increased line tension when the two vacancies are not right next to each other, see Figure 53 (b). Therefore, also this hypothesis can be negated, as it is preferable to have the vacancies at the dislocation line from a line tension point of view.

In summary, there is no viable thermodynamic explanation why the positively charged and oxygen deficient dislocation glides more easily and why it emits oxygen vacancies during glide. Rather it seems that the emission of vacancies from the dislocation core requires energy input that is supplied by the dislocation motion and the resulting dissipated energy. Clarifying the origin of the peculiar difference between oppositely charged cores definitely requires further investigations.



Figure 53: (a) Potential energy  $E^{\text{pot}}$  for different positioning of oxygen vacancies  $V_0^{\bullet\bullet}$  with respect to an oxygen deficient type  $\mathcal{A}$  dislocation core. Values are referenced to the as-created configuration where both vacancies are at the dislocation core. (b) Absolute of normal stress  $\sigma_{zz}$  on the boundary of the simulation cell along the direction of the dislocation line z. Values are referenced to the lowest absolute value.
**Type**  $\mathcal{B}$  The scenarios of moving  $\mathcal{B}$ -type dislocations have been discussed in depth by Hirel et al. [150] who found that the screw splitting distance increases during glide and reported that the first partial starts gliding at 2.64 GPa. Since we are using the same interatomic potential, we can essentially reproduce the published results. Our type  $\mathcal{B}$  dislocations are loaded with  $\tau_{yz}$  and the Peierls stress is in the range of 2.50 GPa to 2.75 GPa at low temperature. Note that the difference in the Peierls barrier between type  $\mathcal{A}$  and  $\mathcal{B}$  dislocations is due to the stacking fault energy hypersurface. Because the edge dislocation type moves along another  $\langle 110 \rangle$  direction it only has to overcome the relatively small energy barrier with a limited slope and the intermediate minimum along that direction. The screw dislocation, however, glides along a  $\langle 100 \rangle$  direction. From Figure 20 it is apparent that the energy barrier is much higher and steeper along this direction. The presence of a greatly increased Peierls barrier is, thus, in line with our expectations.

However, Hirel et al. [150] did not give a conclusive explanation why the distance between the leading and the trailing partial increases under applied load from an average of 1.9 nm to as much as 3.7 nm - 5.6 nm, see Figure 54. At first glance, an increase in splitting distance seems contradictory because both partial dislocations experience the same Peach-Koehler force and should commence glide simultaneously. Yet, as we found in Section 3.1.5 there are multiple meta-stable positions corresponding to different splitting distances where the forces on the partial dislocations are balanced. From the equilibrium position of the smallest observed splitting distance, the partial dislocations see an asymmetric landscape that differs if they are the leading or the trailing partial. To move in glide direction the leading partial sees a relatively low barrier which is a combination of repulsive force from dislocation interaction, the Peierls stress, and the effect of the stacking fault. The trailing partial, however, sees a



Figure 54: Type *B* dislocation without applied load (top) and while moving under applied load (bottom). The distance between the partials, i.e., the stacking fault area, is increased during motion because the leading partial starts moving first.

relatively steep landscape because bringing the dislocations closer together results in more repulsive force proportional to 1/d. Thus, the leading partial can already move at much lower loads. Only when the leading partial has increased its distance to the trailing partial, the trailing partial sits in a shallower landscape because there is less back-stress from the leading partial. Thus, when the splitting distance has reached about 5 nm the trailing partials gets virtually dragged along. Put in other words, the leading partial has moved out of the way allowing the trailing partial to follow.

**Type** C We have shown in Section 3.1.6 that the glide dissociated configuration of type C dislocations is favored in the charged as well as the uncharged state. Because of the mixed character of this dislocation  $\tau_{xy}$  can be applied to move the dislocation via its edge component, and  $\tau_{xz}$  can be applied to drive it via its screw component. The two scenarios of loading with  $\tau_{xy}$  and  $\tau_{xz}$  are considered separately.

For the charge balanced dislocation at low temperature the Peierls stress for  $\tau_{xy}$  is in the range of 5.00 GPa – 5.25 GPa, and for  $\tau_{xz}$  it is in the range of 2.75 GPa – 3.00 GPa. This is surprisingly high, especially compared to type  $\mathcal{A}$  dislocations. A closer look reveals that the dislocations that glide actually possess a negative charge and leave behind a positive charge at their initial position, see Figure 55. This positive charge is due to oxygen vacancies that are left behind. Put in other words, we suspect that the negatively charged dislocation is actually pinned by the oxygen vacancies at its core that were created to balance the dislocation core charge. Thus, the high observed Peierls barrier is a result of a pinning by point defects at the dislocation core. Interestingly, this is analog to type  $\mathcal{A}$  dislocations that are also only mobile in their charged state.

In order to confirm that the charge balancing pins the dislocation to its position and to compare to the effect of charge in type  $\mathcal{A}$  dislocations, we next apply shear stress to type C dislocations with charged cores. The simulation setups with the charged cores feature one negatively charged and one positively charged dislocation core. The negatively charged and glide dissociated dislocation starts gliding at  $\tau_{xy} \approx 750$  MPa and  $\tau_{xz} \approx 400$  MPa – 450 MPa, respectively. During glide, the distance between the partial dislocations remains rather constant at approximately 1.9 nm – 2.0 nm and the dislocations are, in fact, strongly pinned by the additional or removed oxygen ions at their dislocation cores. The results are summarized in Figure 56.

Moreover, we note that the Peierls barrier here is even lower than for dislocations of type  $\mathcal{A}$  or  $\mathcal{B}$ . Additionally, it is intriguing that for type  $\mathcal{A}$  dislocations the positively charged dislocation was mobile while for type  $\mathcal{C}$  dislocations only the negatively charged dislocations are mobile. We confirmed this finding by studying simulation cells with only positively charged dislocations and only negatively charged dislocations (simulation cells are charged in that case). Again the  $\mathcal{C}$ -type dislocations with negative core move easily while dislocations with positive core require either very high loads (around  $\tau_{xy} \approx 4.55$  GPa) or initiate fracture



Figure 55: Static and moving configurations of type C dislocations. Only atoms of the oxygen sub-lattice is displayed and color coded when falsely coordinated. Neutral as well as negatively charged dislocations look similar in their static configuration. However, the charge neutral dislocation requires the emission of positive oxygen vacancies at high stresses to commence glide. In contrast, the negatively charged dislocation glides easily without the contribution of point defects.

(around  $\tau_{xy} \approx 7$  GPa). This behavior is basically inverse to the observation of type A dislocations, see Figure 52.

For the edge type  $\mathcal{A}$ , the positive charge on the dislocation line quickly balanced during glide by emission of oxygen vacancies during motion. Once the dislocations were charge neutral, they stopped moving. The situation is different for the mixed type  $\mathcal{C}$  dislocation. A balancing of the negative charge on the mobile dislocation would require the emission of oxygen interstitials or the creation of vacancies on a cation site. Apparently, the energies for the creation of such defects are large, such that they are not observed here [26, 27]. Consequently, the negatively charged glide dissociated dislocations of type  $\mathcal{C}$  are more mobile than their type  $\mathcal{A}$  analog and can sustain their mobility over a longer distance. In a real crystal, of course, the moving dislocation could also intercept and sweep-up other point defects already present in the material, e.g., from a natural oxygen vacancy concentration or dopants. Note, that this is in agreement with experimental findings from nanoindentation of SrTiO<sub>3</sub> under reducing conditions. Reduction increases the concentration of mobile oxygen vacancies and lowers the dislocation mobility [207].



Figure 56: Summary of the different responses of variants of type C dislocations.

Nevertheless, the reasons for the peculiar charge dependence and for the strong reduction of the Peierls barrier is not clear at this point. While glide occurred along the  $\langle 1 1 0 \rangle$  and  $\langle 0 0 1 \rangle$  direction for the type A and B dislocations, respectively, glide follows the  $\langle 1 1 \overline{2} \rangle$  direction for the type C dislocation, see Table 3. It requires the surmounting of a rather steep barrier, see Figure 20, but the energy landscape does feature intermediate minima. The relatively rigid spacing between the partial dislocations compared to types A and B suggests that the partials are tied together rather strongly. This could enable a reduction of the Peierls stress because a partial that moves down the local energy landscape can drag or push its corresponding partial moving upwards the energy landscape [310]. At this point the calculation of  $\gamma$ -surfaces with defects and charges could lead to further insights explaining the differences between the edge and the mixed dislocation types. We suggest accurate DFT calculations to solve this issue in the future.

# 3.2.5 Dislocation Motion in Large Simulation Cells

The short simulation cell dimension along the direction of the dislocation line (*z*-axis) effectively prevents any kinking of dislocations [164, 294]. To allow for kinking of dislocations the dislocation line between the periodic boundaries has to be longer. For all three dislocation types we, therefore, increase the length of the *z*-axis from 2 u.c. to 60 u.c.. Based on the TEM images by Yang et al. [199] we expect that this size is sufficient to observe nucleation and propagation of kinks. Apart from a replication of the simulation cell along *z* by a factor 30, these simulations are identical to the ones presented in Section 3.2.4.

**Type**  $\mathcal{A}$  For the larger dislocation line length (here 23.4 nm) we only study the glide dissociated charged configuration of the  $\mathcal{A}$ -type dislocation since it is the only mobile variant. The critical resolved shear stress is slightly reduced from about 1.25 GPa to the range of 1.05 GPa – 1.10 GPa. Again the positively charged dislocation glides easily, while the negatively charged dislocation is sessile. The formation and propagation via kinks can be clearly observed in Figure 57. In the simulation we start from the as-created partial dislocation which are straight parallel lines, see Figure 57 (a). Kinks on the dislocation line form despite the low temperature of only 10 K, see Figure 57 (b). We note that kinks on the leading and trailing partial preferentially occur at the same points which supports the statement that the partial

dislocations are tied together rigidly by the coupling of their stress fields and the stacking fault. Moreover, we notice that only in the initial stage of the dislocation motion, Figure 57 (c), kinks of double and triple height occur. Once the dislocation has started gliding, the dislocation lines become straight again and kinks of double height are rarely observed, see Figure 57 (d) & (e).

The reason for the strong waviness of the dislocation lines during the initial phase of dislocation glide is the frequent emission of oxygen vacancies from the dislocation. For the short dislocation segments we have observed that oxygen vacancies are emitted from the positively charged dislocations ultimately leading to charge neutral and sessile dislocations, see Section 3.2.4. The same process of oxygen vacancy creation is observed for long dislocations, see Figure 58. In fact, the very high charge density on the as-created dislocations results in an array of oxygen vacancies in the original position of the dislocation. Basically they are created as the dislocation commences moving. The vacancy emission events pin the dislocation such that it appears as if the dislocation line is forming kinks, see Figure 57 (c). But also during motion of the dislocation, individual vacancies are left behind in the wake of the dislocations. Nevertheless, because of the longer dislocation line with a larger number of oxygen deficient sites at the dislocation core, it takes longer for the dislocation to equilibrate its charge. Thus, the longer dislocation line can stay in its mobile configuration for longer distances. This observation also raises the question, if there is an optimal dislocation core



Figure 57: Propagation of a long type A dislocation and kink formation. Only the dislocation lines (orange) and oxygen octahedra (blue) are displayed for clarity. Kinks form on the initially straight dislocation lines (a) in similar locations for leading and trailing partial (b) – (e) indicating that the motion of the two partial dislocations is correlated. During the initial phase of dislocation glide the dislocation lines appear rough and have multiple kinks (c) while they are more straight once the dislocations have left their initial positions (e).



Figure 58: Oxygen vacancies emitted in the wake of a long type A dislocation. Dislocation lines (orange) and falsely coordinated oxygen ions are indicated. Blue clusters each enclose an oxygen vacancy. (a) Initial dislocation positions with the negatively charged dislocation on the orange glide plane and the positively charged dislocation on the green glide plane. (b) Only the latter moves leaving behind oxygen vacancies.

charge enabling sustained glide and even lower Peierls stresses. However, addressing the question is left to future investigations.

**Type**  $\mathcal{B}$  In the case of type  $\mathcal{B}$  dislocations the  $\tau_{yz}$  at which dislocations move is independent of the system size, i.e., around 2.50 GPa – 2.75 GPa. Moreover, dislocations remain straight and kinks of double height are never observed. Just like for type  $\mathcal{A}$ , we regard this as evidence that the kink nucleation is the limiting step during dislocation motion. For short  $\mathcal{B}$ -type dislocation lines no emission of defects from the moving dislocation was observed, and the dislocation moved smoothly. However, the long dislocation lines emit numerous point defects during glide, see Figure 59.

In Figure 59, defects have been traced by highlighting falsely coordinated oxygen ions in the oxygen sub-lattice. The defects are aligned on the glide plane of the dislocation, i.e., in the wake of the dislocations and are restricted to the oxygen sub-lattice. Evidently, there is a number of oxygen ions that are coordinated with too many other oxygen ions as well as oxygen ions whose coordination number is lowered. Additionally, we observe that many of the defects align in series along the *x*-direction, which is the direction the dislocation has moved through the lattice. This indicates that oxygen ions are kicked out of their ideal position as the dislocation passes. As a consequence associated oxygen Frenkel pairs are



Figure 59: Defects formed in the wake of a type *B* dislocation during glide from its initial position in (a). Dislocation lines (orange) and falsely coordinated oxygen ions are indicated. Green plane is the glide plane, particles in red are over-coordinated, particles in blue are under-coordinated. Thus, blue clusters enclose oxygen vacancies while red clusters enclose oxygen interstitials.

observed. Besides the aligned series of Frenkel pairs there are also individual vacancies and interstitials that are separated by some distance, suggesting that the dislocation actually picked up oxygen ions during glide and then left them behind at a later point creating first a vacancy and then an interstitial. Overall, the stoichiometry of the dislocation line does not change.

Frenkel pair formation in perovskite materials is known from high energy irradiation that displaces oxygen ions off their lattice position [45, 313]. Among the other possible Frenkel pairs it has the lowest energy, i.e., oxygen is more easily kicked out of its position than strontium or titanium [45]. Still, significant amounts of energy, i.e., several electronvolts, are required to form oxygen Frenkel pairs.

As we apply a constant shear stress of 2.75 GPa to the samples, the  $\mathcal{B}$ -type dislocations move at a velocity of approx. 3300 m s<sup>-1</sup>. At such high speeds dynamic effects can impede the dislocation motion [314]. Additionally, the energy landscape for type  $\mathcal{B}$  dislocations is much steeper than for type  $\mathcal{A}$  dislocations, see Figure 20. On the one hand, this results in higher Peierls stresses of  $\mathcal{B}$ -type dislocations compared to  $\mathcal{A}$ -type dislocations as discussed in Section 3.2.4. On the other hand, when the dislocation line has surmounted the Peierls hill (Figure 8) and falls into the next Peierls valley, a larger amount of energy is dissipated. Thus, we suspect that the large dislocation speed and the high energy dissipation rate are at the core of the defect formation by dislocation glide. Similar observations have been nicely illustrated by Marian et al. [314] for the case of screw dislocations in bcc iron. They note that dislocation motion at high stresses "becomes rough, resulting in spontaneous self-pinning and production of large quantities of debris." At low temperatures single vacancies and interstitials are formed during dislocation propagation. While they attribute the observation in bcc metals to frustrated kink formation, the process is not yet clear for the case of SrTiO<sub>3</sub>. Notably, however, the formation of "debris" in the wake of a screw dislocation in iron is likewise restricted to long dislocation lines and cannot be observed when the dislocation line length is shorter than the kink mean-free path. For short dislocation lines in our simulations of SrTiO<sub>3</sub> in Section 3.2.4 we, additionally, point out that point defects interact with themselves across periodic boundaries. In fact, it is very plausible that the elastic self-interaction of point defects [315] prevents the point defect formation altogether in the scenarios with short dislocation lines. Only in large simulation cells sufficient space is created for point defects to form.

When the stress on the simulation cell is relaxed after the deformation and the material is subsequently annealed, e.g., at 1000 K for more than 20 ps, all defects that are in agglomerates and that are connected as series are annihilated. This is, again, in line with literature on screw dislocations in iron [314]. Vacancies and interstitials that are isolated remain. Nonetheless, because the migration barrier for oxygen interstitials is much lower than for vacancies [45] they diffuse around easily into the bulk. On the original glide plane a surplus of the oxygen vacancies are left behind.

**Type** C For type C dislocations in the as-created configuration with charged dislocation cores and increased line length the stress level drops to 600 MPa – 650 MPa for  $\tau_{xy}$  and to 350 MPa – 400 MPa for  $\tau_{xz}$ . These dislocations move as straight lines without the creation of a single defect, see Figure 60 (a). This confirms, that the charged variant of this dislocation is indeed very mobile. In fact, it is again the negative dislocation that moves, while the positively charged dislocation core produces an immobile dislocation.

Analog to the situation with the short dislocation lines, the charge balanced dislocations can only move at very high loads. Here  $\tau_{xy} = 4.5$  GPa – 4.75 GPa and  $\tau_{xz} = 3.0$  GPa – 3.25 GPa are required. However, to start moving, the dislocations create arrays of defects at their original location and also a few point defects while they move. Overall, they attain a partial negative charge during this process, confirming that the mobile configuration should be charged. In fact, many more point defects are created under application of  $\tau_{xy}$  than  $\tau_{xz}$ and the dislocation line is very curvy and uneven in the former case. We attribute this to the very high stresses applied. Once the dislocations have freed themselves from their initial pinned position the load is actually much too high and the mode of motion changes from a slow propagation to an extremely out of equilibrium process with rough motion similar to the  $\mathcal{B}$ -type dislocation [314, 316, 317]. Examples of the situations with and without charge balancing are shown in Figure 60.

Again, the reason for the easy and smooth glide of only the negatively charged dislocation requires further research.



Figure 60: Defects formed at and behind a type C dislocations after the dislocations have moved some distance. (a) As-created negatively charged dislocation. (b) Charge balanced dislocation. The dislocations (orange lines) start in the left part of each figure and move to the right. Gray lines indicate the boundaries of the simulation cell, the green plane is the plane where the dislocation has glided, particles in red are over-coordinated, particles in blue are under-coordinated. Only oxygen ions are shown.

# 3.2.6 Discussion

In a series of simulations we have studied three  $\langle 110 \rangle \{1\overline{1}0\}$  dislocation types and their relevant configurations with respect to their ability to glide under applied load. We also varied the boundary conditions revealing the influence of finite size effects. The simulations were conducted quasi-statically at 10 K. In Figure 61 we summarize the response of the tested configurations.

Dislocations of types  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  possess configurations that are mobile. For the cases that could be compared to literature, results were in excellent agreement [150]. Our initial predictions, that only glide dissociated variants are mobile were confirmed. Thus, since dislocations of types  $\mathcal{D}$  and  $\mathcal{E}$  do not possess any configurations that suggest easy glide, they have not been explicitly tested.

Especially, charged type C dislocations are expected to contribute to macroscopic plasticity of SrTiO<sub>3</sub>. They have the lowest Peierls stress and glide without the creation of additional point defects. In fact, if a more complex loading state of a combination of  $\tau_{xy}$  and  $\tau_{xz}$  is used the Peierls stress might be even lower. In contrast, one should keep in mind that the charge at the dislocation cores is unfavorable from the viewpoint of electrostatic energy. Thus, when dislocations are not moving and the conditions for sufficient diffusion are given, the charge

at the dislocation core is likely to balance leading to more sessile dislocations. Experimental evidence for this process, however, is not yet available.

With our simulations we also addressed the influence of finite simulation cell sizes by comparing simulation cells with short and long dislocations line segments. The reason for the finite size effects seems to be the elastic self-interaction of defects across the periodic boundaries. This influences the dislocations themselves as well as point defect which interact via their strain fields (defect dipole tensor). On the one hand, the reduction of the finite size effects resulted in the possibility for dislocations to form kinks and propagate by kink formation and motion. Thus, the resolved shear stress was reduced in some of these cases. On the other hand, point defects were created much more extensively in the wake of moving dislocations when they were having more space to accommodate their strain fields as well as charges. In summary, we expect that the motion of dislocation types  $\mathcal{A}$  and  $\mathcal{B}$  is limited by kink formation at low temperatures, and that many of the studied dislocation type leave behind point defects, especially when moving swiftly.



Figure 61: Top: Behavior of dislocations under applied shear load for different dislocation types and configurations. Bottom: Lowest measured Peierls stresses calculated from short as well as long quasi-periodic dislocations.

Having confirmed which dislocation types interact most favorably with applied stress, we will next address the question if these are also the dislocation types that dominate in loading scenarios that are closer to experimental conditions. A single dislocation moving in a solid only carries the deformation of the magnitude of its Burgers vector. Thus, if macroscopic plasticity is observed, it is the consequence of the motion of a large number of dislocations. As macroscopic plasticity is indeed observed in  $SrTiO_3$  single crystals experimentally, the next section of this thesis will focus on this very topic. We thereby will address the last step of our roadmap formulated in Figure 62.

	Section 3.1	Section 3.2	Section 3.3
	Equilibrium Dislocation Structure	Dislocation Motion	Dislocations in Experimental Settings
subject	low temperature configurations of dislocation types $\mathcal{A} - \mathcal{E}$	application of mechanical load to relevant configurations	
results	<ul> <li>(110){110} dislocation types can glide dissociate</li> <li>types D &amp; E probably immobile</li> <li>configuration strongly dependent on charge</li> </ul>	<ul> <li>confirmed results from Section 3.1</li> <li>only glide dissociated dislocation move</li> <li>charge state strongly affects mobility</li> <li>type C is most mobile</li> </ul>	

Figure 62: Summary of the main findings. In this section the ability of individual dislocations to move under applied load has been covered. The next section proceeds with complex arrangements of dislocations.

# **3.3 Dislocations in Experimental Setups**

For the macroscopic plasticity observed in  $SrTiO_3$  single crystals, multiple dislocations are required which form a complex and interacting arrangement. These interactions as well as the processes during dislocation motion are essential for the macroscopic plasticity. They will be the focus of this section. To this end, we relate experimental observations to simulations of large arrangements of dislocations. The following scenarios are considered:

- In bulk deformation experiments dislocations were heterogeneously nucleated at a stress concentrator [156]. It was shown experimentally, however, that not all dislocations could originate from this single stress concentration and the surrounding defects [132]. Instead, there need to be alternative ways to nucleate and multiply dislocations. However, such dynamic processes at the atomistic level are almost impossible to observe experimentally. Here, MD simulations as presented in Section 3.3.2 are an indispensable tool for revealing these dislocation-mediated processes.
- 2. It has been shown [132, 198] that pre-existing dislocations strongly influence the plasticity of SrTiO<sub>3</sub> at a microscopic level. We, therefore, address the question if there needs to be a certain dislocation arrangement present in order to facilitate macroscopic plasticity up to high strain, see Sections 3.3.3 and 3.3.4.
- 3. The experimental testing of plasticity in  $SrTiO_3$  is almost exclusively done under compressive load. Yet, ceramics are generally very susceptible to brittle fracture under tensile load [318]. Thus, we are interested in the question if dislocations in  $SrTiO_3$  can also assist plastic deformation during tensile load, see Section 3.3.5.

We will first discuss, how our simulations connect experimental findings to atomistic observations and how we use experimental setups to guide the design of our simulations.

# 3.3.1 Correlation of Lab Results and Modeling

We extend the discussion about the type and configuration of individual dislocations from Sections 3.1 and 3.2 to networks of dislocations. In large scale MD simulations more realistic scenarios can be studied by allowing for a wide variety of dislocation interactions as they occur in physical samples, see Figure 63. The virtual samples discussed here were inspired by experimental work of our collaborators. Therefore, we will report experimental and modelling results in parallel. Experimental methods, however, will only be discussed shortly, but details can be found in the respective literature.

**Notch Experiment** In order to generate dislocations in  $SrTiO_3$  that can be accurately investigated experimentally, it is desired to stimulate dislocation activity only on very select



Figure 63: Dark-field x-ray image of a plastically deformed SrTiO<sub>3</sub> single crystal. Bright contrast indicates strain fields. Due to the high resolution with simultaneous large field of view (here on the order of hundred micrometers) several individual dislocations as well as the grouping of dislocation into slip bands are visible. Evidently, there are numerous dislocation in experimental samples that can have complicated interactions. Cross slip and jogs can be seen from bends of individual dislocation lines. Image is a courtesy of Lukas Porz, for details see Ref. [156].

glide planes. To this end, Dr. Lukas Porz [156] applied a notch to a single crystalline sample before compression experiments, see Figures 65 and 66. In single crystals the orientations of all glide planes with respect to the crystal geometry is known at all times. Therefore, applied stress can address an exclusive group of glide planes, namely those with the largest Schmid factor, and dislocation glide is restricted to these planes. Nevertheless, in SrTiO<sub>3</sub> there are four glide planes with equivalent Schmid factor for uniaxial compression along the [001] direction. Here, the notch assists by breaking this symmetry creating a stress concentration at its tip. At the same time, defects at the notch tip are created by the mechanical application of the notch inside an otherwise almost dislocation-free crystal of exceptional purity. Thus, this setup enforces that dislocations preferentially nucleate and start moving at the tip of the notch and follow two well-defined glide planes, see Figure 66. Such well-ordered dislocation structures, generally, ease the interpretation of experimental results.

**Micropillar Experiment** The experiments using the micropillar setup were conceived by Dr. Xufei Fang (unpublished work). Round pillars with diameters of few micrometers are milled from the surface of  $SrTiO_3$  using a focused ion beam (FIB), see Figure 64. With a flat punch indenter the pillars can be compressed. Because the micropillars are milled from regions close to the surface, treatments applied to the surface before milling of the pillars have a strong influence on the behavior of the material.



Figure 64: Uncompressed micropillar in three-dimensional view (left) and top view (right). This unpublished work is a courtesy of Xufei Fang [319].

The compression testing of the micropillars was assisted by Christian Minnert and Dr. Sebastian Bruns, both at TU Darmstadt. TEM images were taken by Prof. Wenjun Lu at Southern University of Science and Technology, China.

**Dislocations from Polishing and Ball-indenter** While the notched samples give a very well controlled geometry for creating dislocations, they are limited with respect to the attainable dislocation density. Using a rough and unfinished polishing it is also possible to introduce high dislocation densities in the surface-near regions of  $SrTiO_3$  single crystals [136].

An alternative method was designed by Xufei Fang. Here the gentle application of spherical diamond indenters or the repeated application of a steel ball-indenter to the crystal surface creates dislocations that emerge at the indenter position and extend from there into the material in a star-shaped fashion [154, 213, 320]. Cracking is prevented by choosing the correct indenter radius and limiting the load.

**Transfer to Computer Model** For the large scale MD models we seek to design scenarios that allow a certain comparison to the experimental loading scenarios of the notched sample and the micropillar compression. Both scenarios are shown in Figure 65.

In the former scenario a notched simulation sample at the nano-scale is used. It has a height of 720 u.c. (*z*-direction) and a cross-section of  $L_x \times L_y = 360 \times 5 \text{ u.c.}^2$ . The loading along the long axis resembles the experimental scenario and ensures that dislocations originate at the notch. We choose two-dimensional periodic boundary conditions while the side with the notch features open boundaries. Due to the short  $L_y$  this sample represents a quasi-two-dimensional setup.



Figure 65: Representation of experimental and modeled samples for the notched samples (left) and the micropillar scenario (right). All samples have been subjected to uniaxial compression and typical length scales are indicated. Additionally, the observed quantities reveal how experimental and theoretical investigations supplement each other. Reproduced from Figure 19 for convenience.

In the second scenario, simulating a full micro- or nanopillar exceeds the capabilities of our MD simulations. Moreover, a simple down-scaled version of a pillar would likely result in a lack of comparability because of the significantly increased influence of the surface. Rather, we simulate a slice through a pillar similar to the electron microscopy specimen from Figure 75. We compare two situations for two different sample geometries, a thin sample  $(L_x \times L_y \times L_z = 400 \times 16 \times 800 \text{ u.c.}^3)$  and a thick sample  $(200 \times 64 \times 400 \text{ u.c.}^3)$ . In the first situation the thin as well as the thick sample, both ideal single crystals, are compressed along the *z*-axis with boundary conditions identical to the notched scenario. In the second situation, the same samples are subjected to a similar loading with fully periodic boundary conditions. This forces homogeneous nucleation of dislocations once the stress level is sufficient. After stress removal, equilibration, and opening of the *y*-boundary these samples are also subjected to compression testing.

**Limitations** As we cannot capture the size of experimental samples in the atomistic simulations some limitations do apply. For the cases where the simulation cells are thin along

one periodic direction, i.e., the notched sample and the thin single crystal slab, the periodic boundaries tend to enforce straight dislocation lines along this direction, see discussion in Section 3.2.5. In the large and thick samples the range of interaction of dislocations is significantly expanded. Furthermore, the loading rates in the MD simulations (engineering strain rate  $\dot{\epsilon}_{eng} = 1.42 \times 10^8 \, \text{s}^{-1}$ ) are high compared to most real world compression experiments ( $\dot{\epsilon}_{eng} = 10^{-5} \, \text{s}^{-1}$  to  $10^{-1} \, \text{s}^{-1}$ ) [154, 205]. Nevertheless, the atomistic insights with extremely high spatial and temporal resolution are an important complement to experiment. All of these limitations will be discussed together with the results below.

# 3.3.2 Dislocations from a Stress Concentrator

#### **Experimental Findings**

Experimentally, a single crystal of SrTiO<sub>3</sub>, which was almost free of dislocations, was machined with a notch and compressed along its [001] direction. The results are published in Refs. [129, 132, 156]. In Figure 66 (a) the setup and the schematic slip planes are shown. In Figure 66 (b) the whole notched sample is shown as a visual light optical image. Here the dislocations have been made visible by etching with hydrofluoric acid. It can be seen that the dislocations are localized in slip bands that originate from the notch. From the main slip bands that are located 45° to the loading direction (plane of maximum shear stress) secondary slip bands originate; all are located on {011} slip planes. This is generally in line with the dislocations of types  $\mathcal{A}, \mathcal{B}$ , and  $\mathcal{C}$ . However, the fact that there are secondary slip bands connected to the primary slip bands implies that there are either incidents where dislocations from the primary slip band change glide direction or new dislocations form on a new slip plane. In fact, the dislocation density inside the slip band is on the order of  $2 \times 10^{13}$  m<sup>-2</sup> while it is  $< 10^7 \,\mathrm{m}^{-2}$  in the unaffected crystal [132]. Looking at the primary slip bands one is tempted to think that all the dislocations originated at the notch and were then driven into the more central regions of the specimen by applied stress. Because of the way the loading was performed and the fact that etch pits at the crystal surface are visible, we know that the dislocations must at least possess a partial edge character at the surface. If we assume for simplicity that all dislocations visible in Figure 66 are edge dislocations that originated from the notch, they must all possess identical Burgers and line directions. As a consequence of the overlapping displacement fields of these edge dislocations, see Table 1, there would be a significant rotation of the crystal lattice. This can be easily imagined if we think of edge dislocations as inserted or removed crystal half-planes: On one side of the slip band there would be significantly more crystal planes than on the opposite side. Such a configuration would entail unrealistic stresses. Additionally, it was confirmed by dark-field x-ray imaging, that there is negligible lattice rotation (mosaicity) in the slip bands [156].

Consequently, we conclude that there are basically negligible net strain fields created by the slip band as a whole. The reason must be that the strain fields of dislocations cancel each other. Thus, for any dislocation that originated at the notch there must be an equivalent dislocation of opposite Burgers vector or line direction such that overall strain fields cancel.



Figure 66: Left: Illustration of the experimental geometry for the compression testing of the notched sample. Right: Visual light image of the notched sample after compression showing the slip bands. Both images are adapted Ref. [132] with permission from Lukas Porz.

Such a dislocation must necessarily travel in the opposite direction. In essence, there are dislocations that originate at the notch and travel deeper into the crystal as well as dislocation originating inside the crystal and travelling towards the notch. It is, therefore, inevitable that dislocations are created inside the slip band. This could be the result of dislocation nucleation inside the bulk, which is, however, rather unlikely due to the high barriers for homogeneous dislocation nucleation. Rather, it is probable that the forward travelling dislocations multiply in a form that constructs dislocations with opposite orientation. A similar process could also explain the secondary slip planes that extend at a 90° angle to the original slip band [105].

#### **Explanation by Simulation**

To check this hypothesis we constructed the notched simulation sample as described before. Due to its one short dimension with the associated periodic boundaries, the dislocations are expected to be straight type A dislocations aligned along the *y*-axis. And due to the loading

condition along the *z*-axis they should travel at a 45° angle from the notch to the opposite side of the sample, i.e., the glide plane is either (101) or ( $\overline{1}01$ ).

In Figure 67 the material response as the result of the compression simulation is shown. Note, that the free surfaces of the  $SrTiO_3$  slab are inherently charged because we have cut the crystal along the {100} planes. We have checked that the general shape of the stress-strain curve as well as the microscopic processes are independent of the surface charges, see Section 2.4.4. However, the stress level, at which dislocation nucleation commences, very strongly depends on the charges at the surface. In the unmodified case the notched surface carries a strong negative charge and the opposite surface an equal amount of positive charge. Here, the first dislocations nucleate at around 2.5 GPa. For the case where surface charges have been compensated, this value is raised to 12.8 GPa. In fact, this could be a hint that dislocations in this setup are also generally charged, because they react to the electric field produced by the surface charges [103].

The dislocations that are gliding in the simulation are exclusively A-type in a glide dissociated configuration. Yet, there are dislocations of different charge states: positively charged, negatively charged, and even charge neutral dislocations are observed to glide. This is not surprising because the stress level in the simulations is extremely high compared to our earlier quasi-static loading of individual dislocations, see Section 3.2. The high stress level (much higher than  $\tau_m$ ) also reveals that nucleation of dislocations at a surface fault is much harder to achieve than simply moving an existing dislocation.



Figure 67: Overview of the notched simulation sample with uncharged surfaces at different levels of strain. Color coding shows regions of accumulated shear strain which indicate where a dislocation has sheared layers of atoms with respect to each other. Plots of stress and dislocation density during straining are shown on the right.

From the tracks of the dislocations during compression we find indications that the proposed dislocation multiplication does indeed occur. First, dislocations do initiate from the notch where a stress concentration is present. Second, they travel as type  $\mathcal{A}$  dislocations at a 45° angle away from the notch until they reach the opposite face of the crystal. Third, there are secondary slip planes that align at an angle of 90° to the glide direction of the initial dislocations. And fourth, multiplication inside the slip plane on parallel planes can be observed. The result are dislocations with opposite orientation that run in the opposite direction to the original dislocation. As deformation progresses, more and more artifacts appear such as the nucleation of dislocations at surface steps on the surface opposite of the notch. We will discuss the instances and features that lead to dislocation multiplication in detail in the following.

**Parallel Change of Glide Plane** In this instance of our simulation a dislocation changes its glide plane without an apparent reason, see Figure 68. Basically, this is a very small segment of dislocation climb. In Figure 68 we observe that the climb motion occurs in two steps. The leading partial dislocation first changes its glide plane by  $\frac{1}{2}\langle 110\rangle$ . When the trailing partial arrives at the spot where the leading partial has climbed it follows the leading partial onto the new glide plane. Because climb motion is non-conservative, there appear defects (agglomerates of vacancies) at the location where the climb has occurred. These defects can be non-stoichiometric and, thus, charged. By itself, this mechanism does neither lead to multiplication nor nucleation of further dislocations in the material [105], but it nicely illustrates the imperfection of dislocation glide. Note, that defects created by a dislocation will interact with consecutive dislocations or other defects.



Figure 68: Detailed view of climbing dislocation from the notched sample (charged surfaces). The coloring represents the shear strain that the atoms have experienced, which reveals where dislocations have traveled. Dislocation lines and Burgers vectors are also indicated. (a) Two partial type A dislocations move from top left to bottom right. (b) The leading partial dislocation has climbed one layer and the second partial is still on its original plane. (c) The trailing partial dislocation has also climbed leaving behind a step in their track and an agglomerate of vacancies (shaded in gray). Adapted from Ref. [156].

As there is negligible thermal activation in this simulation at 10 K this process is somewhat surprising. We suggest that the climb-instability discussed in Section 3.1.4, i.e., the fact that the climb configuration is favored over the glide configuration and the degeneracy of glide and climb stacking faults, are the reason for this effect. Marian et al. [314] showed in bcc iron that the frustrated formation of kinks on screw dislocations creates point defect clusters and leads to rugged dislocation motion. Replacing the cross glide of the screw dislocation kinks in iron with the climb of the edge dislocation in SrTiO<sub>3</sub> we have an analog scenario. In fact, the A-type dislocation is in an energetically frustrated position. It can glide to relieve the elastic energy of the crystal or climb to relieve the elastic energy of the dislocation itself. Additionally, the climb as well as the glide plane experience identical Schmid factors. Thus, the incremental climb and continued glide of type A dislocations is enabled by external load as well as the climb instability of the dissociated dislocation. The result is non-conservative motion of edge dislocations in SrTiO<sub>3</sub> very similar to the "kinetic roughening" observed in bcc metals [314].

Because the applied external load (Figure 67) is much higher here compared to the quasistatic loading in Sections 3.2.4 and 3.2.5, the dislocations move at about 1/4 of the speed of sound in SrTiO<sub>3</sub> [214]. Clearly the observed processes are far from equilibrium. The strong dynamic effects of the moving dislocations explain that we could not observe this process in the gentle loading used to obtain the Peierls stress [314, 316, 317, 321].

**Parallel Multiplication of Dislocations** This instance of imperfect dislocation glide extends the first scenario and an example is displayed in Figure 69. Like in the previous scenario, the leading partial changes to a parallel glide plane first, see Figure 69 (a). However, the trailing partial does not follow the leading partial but continuous glide on the original glide plane, see Figure 69 (b). Now, there are two partials on parallel glide planes. On the original glide plane a new trailing partial nucleates spontaneously, because any further motion of the old partial on this glide plane would create an extended stacking fault, see Figure 69 (c). Thus, there is again a complete set of leading and trailing partials on the original glide plane which can travel as a whole. On the new glide plane, the climbed partial entails the creation of an exactly opposite dislocation partial. Due to the continuously applied deformation the two partials move in opposite directions extending the stacking fault in between them. At some point the stacking fault becomes so large that two new partials spawn and complete the partials traveling in opposite directions, see Figure 69 (e). Finally, there is a complete set of partials on the original plane traveling in the original directions, and there are two sets of partials on the new glide plane traveling in opposite directions. Effectively, the dislocation has multiplied by a factor of three.

Now we have identified a possible mechanism for the nucleation of antiparallel dislocations via natural multiplication of moving dislocations in  $SrTiO_3$  [105]. Next we turn to explain how the slip bands 90° to the primary slip band can be formed.



Figure 69: Detailed view of dislocation multiplication on a parallel glide plane. The coloring represents the shear strain that the atoms have experienced, which reveals where dislocations have traveled. Dislocation lines and Burgers vectors are also indicated. (a) Moving pair of partial dislocations. (b) Leading partial has climbed, analog to Figure 68. However, the trailing partial does not follow. (c) One partial spawns completing the original leading trailing partial and a second partial forms as antagonist to the climbed partial. (d) The two antagonistic partials on the new plane are driven away from each other by applied stress and create an extended stacking fault. (e) New partials spawn in the stacking fault. (f) All pairs of partial dislocations are complete. Adapted from Ref. [156].

**Perpendicular Nucleation of Dislocations** In this instance a dislocation (heterogeneously) nucleates anew. Figure 70 (a) shows a region of the crystal where a small agglomerate of vacancies exists. This defect has been created by the cross glide/climb of a dislocation that had passed this spot earlier in the simulation. Now there is not only a strong applied stress to the sample from the outside, but also the dislocations moving inside the material create additional stress fields. In the case shown here, a dislocation travels past the defect just a few nanometers above, see Figure 70 (a). As the stress fields of the applied load and the dislocation overlap, a dislocation nucleates from the agglomerate of vacancies, see Figure 70 (b). In principle such a new dislocation could nucleate on any of the possible glide planes. Here, it is on a glide plane 90° to the original glide plane. After the first partial has nucleated, a second partial follows soon and both move together through the crystal, see Figure 70 (c). Note, that due to the loading condition and the crystal orientation, that were chosen as in



Figure 70: Detailed view of dislocation multiplication on an orthogonal glide plane. The coloring represents the shear strain that the atoms have experienced, which reveals where dislocations have traveled. Dislocation lines and Burgers vectors are also indicated. (a) A defect cluster (shaded in gray) has been left behind by another dislocation. (b) By the overlapping stresses of a passing dislocation and applied load a partial dislocation is created from the agglomerate of vacancies. Note that the stress intensity factor (Schmid factor) is identical on the diagonal planes. (c) As the first partial is driven away from its nucleation point by applied load a trailing partial spawns and follows in the same track. Adapted from Ref. [156].

experiment, the Schmid factor and the resolved shear stress is identical on this new plane. By many such processes, ultimately, a grid of dislocation tracks evolves. Of course, it can be easily imagined that any other type of defect could act as a similar point of nucleation for new dislocations.

**Some Side Remarks** In summary, we have seen how just very few dislocations gliding in  $SrTiO_3$  produce situations where defects and other dislocations can be generated. Consequently, even with few dislocations to start with, a cascade of multiplication and (heterogeneous) nucleation events enables macroscopic plasticity in a single crystal. The only prerequisite identified so far is that there needs to be at least one mobile dislocation that can facilitate the discussed processes. These initial dislocations were enabled by the stress concentration at the notch and the defects in its vicinity. However, nucleation at the surface required larger stresses compared to the Peierls stress.

Even with the limited size of the virtual samples used here (a dislocation can barely travel 200 nm before reaching the opposite surface) dislocations show a lot of interesting processes and interactions that produce further defects. However, we must be reminded that the dislocation type was restricted to type  $\mathcal{A}$  dislocations due to setup constraints. Also, the short dislocation line could ease the climb of the dislocation for the same reasons that have been discussed in the context of kink motion.

# 3.3.3 The Role of Pre-existing Dislocations

We have shown that dislocation cross-slip/climb and consecutive dislocation multiplication occur readily in the crystal from defects during the motion of A-type edge dislocations in SrTiO<sub>3</sub>. The presence of a few mobile dislocations alone seems to be sufficient to enable plasticity. Now, we elaborate on this point further by considering two scenarios where there is no stress concentrator in the form of a notch. In one scenario there is a perfect block of single crystalline SrTiO<sub>3</sub> with periodic boundaries along the *y*- and *z*-dimensions. It has a geometry of  $400 \times 16 \times 800$  u.c.<sup>3</sup>, so it again is very short along the *y*-direction forcing dislocations to be predominantly of type A, see Section 3.3.2. Put in other words, it is a quasi-two-dimensional setup. We compress the sample until failure along the *z*-direction. In the other scenario, dislocations are first introduced via homogeneous nucleation during the compression under three-dimensional periodic boundary conditions. Then this sample is relaxed at zero stress with open boundaries along the *x*-direction before compression testing analog to the pristine sample. The engineering strain rate is approx.  $1.3 \times 10^8$  s<sup>-1</sup> in simulation.

Based on these results we evaluate the role of pre-existing dislocations by comparing the behavior under compression of the pristine sample and the pre-compressed sample containing dislocations and defects. The obtained results are compared to the micropillar compression studies initiated by Xufei Fang. In these experiments micropillars with and without dislocations created by surface grinding and polishing were compared [136]. Note again, that there may be surface charges in the non-periodic setups of the SrTiO<sub>3</sub> simulations. As we confirmed in Section 3.3.2 they do not alter the microscopic processes but ease the nucleation of dislocations at surfaces. In fact, this shortens computation time and creates less overloading of the sample, so we will simply continue with samples where the surfaces are charged.

#### **Simulations With and Without Defects**

In Figure 71 (a) we see that the pristine quasi-two-dimensional sample is initially defect-free apart from the two open surfaces along the *x*-direction. In contrast, the sample with preexisting dislocations in Figure 71 (c) has been compressed to uniaxial strain of  $\epsilon_{zz} \approx 12\%$  under fully periodic boundary conditions. After dislocations of the  $\langle 110 \rangle \{110\}$  family have formed the sample is subsequently relaxed to zero stress with open surfaces along *x* achieving a dislocation density of around  $2 \times 10^{16} \text{ m}^{-2}$ . The resulting dislocations are almost exclusively of edge character (indicated in blue in Figure 71) and possess either a  $\langle 110 \rangle$  or  $\frac{1}{2} \langle 110 \rangle$  Burgers vector. This is in line with the expectation that the short distance along the periodic *y*-axis favors edge dislocations and the result that type  $\mathcal{A}$  dislocations are in their glide dissociated or undissociated state in the absence of thermal activation. For comparison note that the dislocation density is about  $10^{15} \text{ m}^{-2}$  in the surface regions probed by the micropillar experiments. This is significantly more than the  $2 \times 10^{13} \text{ m}^{-2}$  in the slip bands of the experimental notched samples [132, 136, 156]. In addition to a high dislocation density, the pre-compression has also created defects such as arrays of dislocations, small voids, short cracks, and a multitude of point defects, indicated as gray shading in Figure 71 (c).

The dislocation-free sample and the pre-compressed sample are shown in Figure 71 (a) and (c) before compression testing and in Figure 71 (b) and (d) after compression to 8% strain. The corresponding stress-strain curves and the course of dislocation density over strain are displayed in Figure 72.

For the pristine and defect-free crystal we initially observe an almost linear elastic behavior up to 7.7% strain at 6.9 GPa. Then a seemingly brittle failure occurs which is marked by a sudden drop in stress as observed in Figure 72 (a). However, a closer look reveals that  $\mathcal{A}$ -type dislocations in their glide dissociated variant are nucleated from multiple points at the surface. Therefore, we observe a non-zero dislocation density in Figure 72 (b). These dislocations travel at velocities up to 9750 m s<sup>-1</sup> which is higher than the longitudinal speed of sound  $v_{\text{long}} = 8022 \text{ m s}^{-1}$  [214], see Figure 73. As the dislocations travel through the material, their supersonic shock waves homogeneously create further dislocations in the pristine bulk regions of the crystal. It is known that supersonic dislocations can theoretically be created at very high strains but their relevance to the mechanics of a solid has seen little investigation [176, 321–323]. To the best of our knowledge supersonic dislocations have not been observed in any solid experimentally [164]. Rather they can be seen as the carrier of an inelastic shift between two lattice planes. This pathological behavior is, thus, evidence of a brittle failure, and we expect to see crack formation in an analog experimental investigation.

In contrast, the pre-compressed sample, see Figure 71 (c), has a significant dislocation density before the compression testing is performed. Even at low loads the first dislocations start moving, and we observe an extended plastic regime in Figure 72 (a) between 2.7% and approx. 10% strain. During this period the overall dislocation density in the sample decreases. For one, it is an indication that the options for dislocation multiplication are limited. For two, there was a very high dislocation density initially that was produced in the homogeneous nucleation setup where there was no sink for dislocations. As there are open boundaries during the compression testing and the dislocation can actually leave the crystal towards the open surface, it is natural that dislocation density decreases. We also tested straining the sample with doubled strain rate. The stress-strain curves are essentially identical confirming that the ductile behavior is not very sensitive to strain rate [205].

At strains around 10% the maximum of the stress-strain curve is reached. This is where one of the short cracks, which had formed as a result of the homogeneous dislocation nucleation, extends through the material, see Figure 78 (a).



Figure 71: Samples without (a) and with (c) pre-existing defects have been compressed to 8% strain in (b) & (d), respectively. Dislocations are displayed as colored lines which are all straight and appear as dots due to the quasi-two-dimensional setup of the simulation cell (*y*-dimension in only 16 u.c. long). Gray shading indicates defective crystal structure which may be surfaces, interfaces, grain boundaries, nano-cracks or point defects.



Figure 72: Comparison of compressive stress  $-\sigma_{zz}$  (a) and dislocation density  $\rho_d$  (b) during compression of the thin samples from Figure 71. The situations with and without pre-existing dislocations are shown. If dislocations are absent, the sample shows brittle failure and the only dislocation activity appears at the moment the fracture occurs. With pre-existing dislocation the sample yields plastically at the expense of dislocation density. At the maximum stress of the sample with pre-existing dislocations a crack has formed, see Figure 78 (a).

#### **Experimental Findings**

The experimental analog to these simulations are micro-pillars of 3 µm diameter that were machined by FIB. These pillars are created from a surface near region of single crystalline SrTiO<sub>3</sub>. Images of the whole samples taken by scanning electron microscopy (SEM) and thin slices from the pillars imaged by weak beam low angle annular dark field scanning transmission electron microscopy (WB-LAADF-STEM) are shown in Figure 74. The latter can resolve the local presence of dislocations.

In Figure 74 (a) we see that there are indeed no dislocations in the micro-pillars machined from pristine single crystalline  $SrTiO_3$ . In contrast, Figure 74 (b) shows a significant amount of dislocations in the surface near region which have been introduced by grinding/polishing prior to machining of the pillar [132, 136].



Figure 73: Groups of dislocations travelling at supersonic speed. Mach cones are visible through color coding by von Mises shear strain.

During compression, the dislocation-free pillar exhibits brittle fracture at strains in the range of 2.5% - 5.5% which corresponds to loads of 1.5 GPa – 5.5 GPa. However, the pillar with surface dislocations transitions from the elastic to the plastic regime at less than 0.5 GPa. In the plastic regime, the samples exhibit ductile behavior up to strains in the range of 20%. To confirm that this plasticity is indeed carried by dislocations, WB-LAADF-STEM pictures are taken again after 10% compression, see Figure 75.

We can observe that the dislocation density in the surface region has increased. The regions very close to the surface, i.e., the topmost micrometer, has a dense mesh of dislocations that reside on different  $\{110\}$  planes. Several micrometers below the surface, however, there appears to be a single dominant glide plane which also belongs to the  $\{110\}$  family and carries less dislocation density.



Figure 74: Micropillars without surface dislocations crack while micropillars having dislocations are ductile. (a) and (b) are WB-LAADF-STEM images of micropillars slices without and with dislocations from surface treatment, respectively. Bright contrast indicates the presence of dislocations. (c) and (d) show the micropillars after compression. While the pristine sample cracked in a brittle fashion, the pre-treated sample exhibits slip traces at the surface typical for ductile behavior. This unpublished work is a courtesy of Xufei Fang [319].



Figure 75: (a) Cross-section of the specimen from Figure 74 (d). After 10 % compressive strain a lot of dislocations are visible on {110} planes with a gradient of increasing dislocation density towards the surface. (b) Detailed view of the topmost layer showing that individual dislocations can be discerned. This unpublished work is a courtesy of Xufei Fang [319].

### **Relevance of Pre-existing Dislocations and Defects**

The brittle stress-strain curves from experiment and simulation for the dislocation-free samples are matching very well. Different levels of stress and strain are most likely due to the difference in loading rates as well as finite size effects in the atomistic simulations. Additionally, because the theoretical  $\gamma$ -surfaces do not exactly reproduce experimental values, the stress required for dislocation nucleation cannot be re-produced exactly [136, 149].

From the electron microscopy images it is clear that there are abundant dislocation sources after the surface treatment. During deformation dislocations could be created by heterogeneous nucleation, e.g., at microscopic stress concentrators such as agglomerates of vacancies, as well as dislocation multiplication processes like the ones identified in Section 3.3.2. In contrast, the absence of plasticity in the pristine samples confirms the hypothesis that the presence of dislocations and other imperfections enable the nucleation and multiplication of dislocations [104, 105].

With our MD simulations we could indeed verify that ideal  $SrTiO_3$  single crystals are brittle. Because of the controlled setup in simulation we can be absolutely sure that there are no pre-existing defects. Plasticity, thus, hinges on the restriction, that there need to be means of nucleating initial dislocations or multiplying pre-existing dislocations. We show, that having a large amount of all kinds of defects including dislocations inside a  $SrTiO_3$  crystal immediately leads to a much more compliant and ductile behavior. In simulation, plasticity is limited to approx. 10% strain because dislocation density decreased and cracks appeared during compression. Thus, nucleation and multiplication are not efficient enough to sustain larger amounts of plastic deformation in our simulations.

Regarding the brittleness of the pristine samples, the obvious question appears, why plasticity has also been observed in cases where there was no pre-treatment of  $SrTiO_3$  single crystals without obvious stress concentrator, e.g., Refs. [127, 128, 154, 184, 199, 205]. All these studies employed single crystals of millimeter size. While the micro-pillars are so small, that finding a dislocation or imperfection in the  $SrTiO_3$  pillar in unlikely, the volume subjected to load is much larger for macroscopic single crystals. Even at very low pristine dislocation densities and with very careful preparation, one can always expect to find a defect that can act as a suitable stress concentrator or a dislocation that can multiply/spawn new dislocations [132].

To this end, the experiments on the microscale and the connection from experiment to simulation are crucial. They unambiguously prove that there need to be imperfections initially to avoid brittle fracture at the microscale.

# 3.3.4 The Role of Dislocation Type and Dislocation Interaction

In the previous section we have identified the importance of pre-existing defects for the ductility of SrTiO<sub>3</sub>. Because of the short *y*-dimension of the virtual sample, the dislocation types were mainly restricted to variants of A-type dislocations. Since we expect that dislocations of types B and C are more important to plasticity than type A dislocations (see Sections 3.1 and 3.2) we now compare their behavior in a macroscopic setup. Therefore, we take the results from the previous Section 3.3.3 where we had thin slabs and were restricted to type A dislocations and perform the analog experiments with thick slabs, see Section 3.3.1. Our expectation is, that this allows for different dislocation types as well as more dislocation interactions.

#### **Differences in Initial Dislocation Structure**

We construct a perfect single crystal and a pre-compressed sample that features pre-existing dislocations. In the thin pre-compressed scenario, there is an initial dislocation density of about  $2 \times 10^{16} \text{ m}^{-2}$  (shown in Figure 71 (c)), while it is about  $4.4 \times 10^{16} \text{ m}^{-2}$  for the thick pre-compressed sample shown in Figure 76. Because the thin sample suffers from strong image interaction across the periodic boundaries only type  $\mathcal{A}$  dislocations are accessible limiting the maximum dislocation density. In the thick sample the volume is accessible to dislocations along all directions enabling also type  $\mathcal{B}$  and  $\mathcal{C}$  dislocations, thus, increasing the maximum dislocation density. Additionally, the fraction of mobile dislocations is very different. Again, the thin scenario featured almost exclusively (110){110} dislocations of type  $\mathcal{A}$ . Yet, only about 50% of the total dislocation line length has a  $\frac{1}{2}\langle 110 \rangle$  Burgers vector, i.e., they are partial dislocations expected to be mobile. The rest predominantly has a full (110) Burgers vector. In contrast, in the thick scenario 74% of the initial dislocation line length is attributed to dislocations with a  $\frac{1}{2}(110)$  Burgers vector. Consequently, there is a much larger fraction of possibly mobile dislocations for the thick sample. Figure 76 (a) shows the dislocation structure before the compression testing where the local character of the dislocation has been color coded, i.e., blue, red, and gray represent edge, screw, and mixed character, respectively. Apparently, there is a mix of type  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$  dislocations. The thin scenario exhibits almost exclusively edge dislocations, see Figure 71 for comparison. Figure 76 (b) identifies the full and partial Burgers vectors.

#### Plasticity in Thin and Thick Scenarios

In Figure 77 we show the stress-strain curves of the thin as well as the thick sample alongside the respective dislocation densities. Regarding the pristine samples that are initially free of dislocations, the thin and the thick samples behave essentially identical. They show a clear elastic regime up to several percent strain before brittle collapse occurs, see Figure 77 (a).



Figure 76: Initial dislocation configuration of the pre-compressed thick sample. (a) Dislocation lines are color coded by their local character, i.e., edge (blue), screw (red), and mixed (gray). (b) Same configuration as in (a) but color coding shows dislocations with  $\frac{1}{2}\langle 110 \rangle$  Burgers vector that can show easy glide in green and other dislocations in dark gray. Other defects such as vacancies (see gray shaded regions in Figure 71) are not shown for clarity.

This further confirms the hypothesis that pre-existing defects (notch, dislocations, etc.) are required to facilitate plasticity in  $SrTiO_3$  macroscopically.

The behavior of pre-compressed samples, however, shows differences. Again, there is an initial elastic regime up to 3.3 % strain before plastic deformation sets in. During the plastic deformation, the stress level in the thin sample continues to rise and the dislocation density decreases. On the one hand, this indicates, that plastic deformation is really carried by dislocations. On the other hand, it shows that the generation of new dislocations is insufficient to sustain plasticity. This, finally, leads to the fracture of the thin sample around 10 % strain where the stress level drops. In Figure 78 (a) this percolated crack is highlighted.

The thick sample with the more complex dislocation structure, however, exhibits a fairly constant stress level during its plastic deformation. In this scenario, the dislocation density stays on a high level and even slightly increases during the first few percent of plastic strain. In fact, we do not observe the formation of a crack at strains exceeding 30% strain. For



Figure 77: Comparison of compressive stress  $-\sigma_{zz}$  (a) and dislocation density  $\rho_d$  (b) during compression for four different scenarios. On the one side, samples without pre-existing dislocations show brittle failure and no dislocation activity. On the other side, the thin sample with pre-existing dislocations shows limited plasticity while the thick sample shows an extended regime of plastic yield. The thick sample also shows higher overall dislocation density compared to the thin quasitwo-dimensional sample because here the dislocation type is not restricted by the simulation cell geometry. For images of the samples with dislocations after compression see Figure 78.

comparison, strains of about 19% have been reported experimentally [199]. However, we note that due to the very high strain rate of the MD simulation, the crystal structure can become severely damaged at higher strains. This damage becomes significant beyond 35% strain. At higher values of strain the PTM structure identification is unable to classify 20% of the material as a crystal structure using an RMSD = 0.2. Thus, we stop the deformation here.

#### **Dislocations at a Microscopic Level**

The sustained high dislocation density of mobile dislocations in the thick sample (see Figure 77) suggests that there are mechanisms for dislocation nucleation or multiplication that



Figure 78: Samples with pre-existing dislocations from the thin (a) and thick scenario (b) after approx. the same compressive strain. Dislocations are displayed as colored lines and defective crystal structure is shaded in gray. A crack has formed during compression of the thin sample, which is highlighted in green.

are not available for the thin samples. However, it is very difficult to track individual events of dislocation multiplication. Here, we focus exemplarily on three situations where we see that (i) an individual dislocation gets pinned, (ii) two glide dissociated dislocations on the same plane react, and (iii) a dislocation bows out between two pinning points.

**Dislocation Pinning** The situation depicted in Figure 79 shows the reaction of two dislocations on different glide planes. While the first dislocation coming from the right side is moving in the paper plane, a second glide dissociated dislocation has its dislocation line parallel to the viewing direction and is highlighted in orange. In this particular instance the dislocation in the paper plane has a partial Burgers vector of  $\vec{b}^{(1)} = \frac{1}{2}[01\overline{1}]$  and glides on the (011) glide plane. The dislocation along the viewing direction marked in orange has a partial Burgers vector of  $\vec{b}^{(2)} = \frac{1}{2}[0\overline{11}]$  and is glide dissociated on the (011) plane. By reaction of the two partial Burgers vectors,

$$\vec{b}^{(1)} + \vec{b}^{(2)} = \vec{b}_{\text{lock}},$$
 (42)

$$\frac{1}{2}[01\overline{1}] + \frac{1}{2}[0\overline{1}\overline{1}] = [00\overline{1}], \qquad (43)$$



Figure 79: A dislocation moves (a) & (b) and gets pinned (c) at another dislocation with perpendicular line direction (highlighted in orange). After pinning, the dislocation bows out and rotates around the pinning point (d) as the sample is continuously compressed. The dislocation lines are color coded by their edge (blue) and screw character (red).

a new dislocation with a Burgers vector  $\vec{b}_{lock}$  preventing glide is formed. Thus, when these two dislocations meet each other in Figure 79 (c) they get pinned. The dislocation segment to the left of the pinning point then continues to bow-out under the continuously applied load.

Since there is a very high dislocation density in the pre-compressed samples, we observe many such events and products of dislocation pinning. We also note, that simply by the pinning and bowing of the dislocation around its pinning point, the total length of dislocation line increases, compare Figure 79 (a) with (d). Therefore, this process increases the dislocation density  $\rho_d$ . In the case of compressing the thin SrTiO<sub>3</sub> slab, two glide planes were activated, i.e., dislocations were allowed on the (101) and (101) planes only. On these planes only


Figure 80: Two dislocations with (110) Burgers vector (a) move towards each other (b) and react (c) & (d). The dislocation lines are color coded by their edge (blue) and screw character (red). Stacking fault area has been shaded magenta to indicate corresponding partial dislocations.

edge type dislocations (see Figure 78) are present. In contrast, the interaction of the two dislocations with orthogonal dislocation lines features a dislocation with edge character on a (011) plane and a dislocation with screw character on a (011) plane. Therefore, this process to increase  $\rho_d$  is not feasible in the scenario with the thin slab.

**Dislocation Reaction** The situation in Figure 80 features the reaction of dislocations on a common glide plane. Initially there are two dislocations in the same glide plane, Figure 80 (a), that move towards each other, Figure 80 (b). The moment the two oppositely oriented leading partial dislocations meet, they interact forming an extended stacking fault area Figure 80 (c). This area then constricts locally and is pinched off into two regions by the reaction of the trailing partials. Very quickly the trailing partials also meet and pinch off,

Figure 80 (d). Effectively the two dislocations have realized plastic deformation by mutual annihilation in a limited region.

**Dislocation Bow-out** The third situation in Figure 81 shows a very classic configuration where a dislocation is pinned in between two pinning points (highlighted in orange). Such a configuration has been studied intensively in literature and is, e.g., at the base of the well-known Frank-Read dislocation source [164, 324]. Here, the dislocation pinned between two obstacles bows-out under the applied stress. When it bows-out even further, one part of the dislocation reaches the surface, Figure 81 (c). The surface acts as a sink for the dislocation and the remaining segment continues to move by rotating around its pinning point Figure 81 (d).



Figure 81: A dislocation driven by external load (a) bows out between two pinning points, highlighted in (b). A segment of the dislocation reaches the surface (d) and the remaining segments continue to rotate around the pinning points (d). The dislocation lines are color coded by their edge (blue) and screw character (red).

We note again that this process realizes plastic deformation (dislocation reaches the surface), extends the dislocation line length (compare Figure 81 (a) with (d)), and would not be feasible in the simulation with the thin  $SrTiO_3$  slab. A full Frank-Read loop with multiplication cannot be observed because the dimensions of the MD sample are limited to rather small sized compared to experimental samples.

#### 3.3.5 Tensile Load

Up to now we were concerned with subjecting  $SrTiO_3$  to compressive strain. This procedure is in line with the testing that is commonly done in experimental setups. However, ceramics usually possess a very low  $K_{Ic}$ , i.e., they have a low resistance to crack propagation under tensile load [318]. This restricts their use and an engineer must take care to avoid tensile loads on ceramics. Therefore, it is highly desired to improve the tensile properties of ceramics as well [108].

Experimentally, the construction of samples for tensile testing can pose challenges [108]. In computer simulation the application of tensile load to our samples is trivial. Thus, we want to know if the sample geometry and the presence of dislocations also influence the mechanical behavior under tensile load. Apart from reversing the load direction we also introduce a small notch into one surface like in Section 3.3.2 in order to provide a stress concentrator. Additionally, we use samples with even higher initial dislocation density of around  $3 \times 10^{16} \text{ m}^{-2}$  and  $8 \times 10^{16} \text{ m}^{-2}$  for the thin and thick samples, respectively.

The stress-strain curves and dislocation density curves for tensile testing are displayed in Figure 82. For the samples without pre-existing dislocations we first observe an elastic regime in the stress-strain curve followed by brittle fracture, Figure 82 (a). The fracture is easy to identify, as there is not a single dislocation involved. Rather a crack perpendicular to the loading direction cleaves the crystal.

In the case of the thin sample with pre-existing dislocations, the stress-strain curve is very similar to the dislocation-free cases. There is little dislocation activity, which can also be seen from the insignificant change in dislocation density, Figure 82 (b). The small notch, that we introduced to see if dislocations could nucleate there, did not fulfil its purpose. No extra dislocation activity was observed around the notch. Instead, cracking started at defects that had been introduced by the pre-compressing procedure. Compared to the thin sample without dislocations, no significant change in strain to rupture was observed, and the yield stress even decreased slightly.

Just like the thin sample, the thick sample with pre-existing dislocations fails by cracking randomly at defects. In Figure 83 the sample before application of tensile load shows a high density of dislocations. Slightly above 6% strain a crack has formed, which is highlighted in green in Figure 83 (b).

Despite the brittle fracture, there appears to be a significant amount of dislocation activity during straining. The strong decrease in dislocation density before brittle fraction (see Figure 82 (b)) is evidence that some plastic deformation is carried by dislocations. At the same time, efficient means of dislocation generation are lacking, and new dislocations cannot be supplied. Going back to the compression stress-strain curve, Figure 77, we recognize that plastic deformation occurred at stress level exceeding 1.5 GPa. From the tension stress-strain curve, Figure 82 (a), it is obvious that the percolation of defects and formation of a crack occurs around 1.1 GPa. Thus, the stress level is sufficient to move dislocations, but it is not sufficient to generate new dislocations. Such a high stress level could only be reached under compression when crack opening is suppressed [325].



Figure 82: Comparison of stress (a) and dislocation density (b) during tension, analog to Figure 77. All samples show brittle fracture. Only in the thick sample with preexisting dislocations the fracture is delayed by dislocation activity.



initial state

at 7.2% tensile strain

Figure 83: Thick samples with pre-existing dislocations before (a) and after applying tensile load (b). Dislocations are displayed as colored lines and defective crystal structure is shaded in gray. A crack has formed and is highlighted in green.

#### 3.3.6 Discussion

In this section we discussed dislocation multiplication and the effect of brittle versus ductile micropillars that have been observed experimentally. Relating the results from simulation to experiment extends the picture from individual dislocations (see Sections 3.1 and 3.2) to complex and realistic arrangements of dislocations.

The first setup compared the nucleation of dislocations from a stress concentrator under compressive load. We could confirm that the plastic deformation is indeed carried by glide dissociated dislocations. They can possess different charge states but were restricted to be of  $\mathcal{A}$ -type by design of the simulation cell. Various interactions with defects and multiplication mechanisms were observed showing that multiplication occurs naturally as long as mobile dislocations exist.

Having established that moving dislocations are an essential ingredient for notable plasticity, we compared samples without artificial stress concentrators either with or without dislocations. These simulations supported experimental findings that SrTiO<sub>3</sub> single crystals are brittle if there are a priori no dislocation or defects in the material. However, even with pre-existing dislocations, the plasticity in our simulations was limited suggesting that dislocation nucleation and multiplication were inefficient. Because the initial simulations were restricting dislocations to be of predominantly type A, the possibilities of dislocation interactions were limited. With a different setup we allowed for a mix of dislocation types A, B, and C and also observed that a greater fraction of the dislocations were in glide dissociated configurations. This is in line with our quasi-static simulations which showed that dislocation of types B and C are most likely to stay glide dissociated. Additionally, we observed that allowing for all kinds of dislocations improved plasticity and allowed for sustainable high dislocation densities.

Finally, tensile load poses a significant problem to ceramics because the fracture toughness is typically low. We observed that plasticity under compression was enabled by dislocations. Meanwhile, plasticity under tension is still limited. Significant dislocation generation could not be achieved, rather brittle fracture occurred.

In Figure 84 we conclude the study of dislocations in  $SrTiO_3$  by completing the third part of our investigations. After the dislocation equilibrium structure and dislocation motion, the behavior of more complex dislocation arrangements has delivered valuable insights into the microscopic and dynamic processes at play.

	Section 3.1	Section 3.2	Section 3.3
	Equilibrium Dislocation Structure	Dislocation Motion	Dislocations in Experimental Settings
subject	low temperature configurations of dislocation types $\mathcal{A} - \mathcal{E}$	application of mechanical load to relevant configurations	micro- and macroscopic behavior of samples with many dislocations
results	<ul> <li>- ⟨110⟩{110} dislocation types can glide dissociate</li> <li>- types D &amp; E probably immobile</li> <li>- configuration strongly dependent on charge</li> </ul>	<ul> <li>confirmed results from Section 3.1</li> <li>only glide dissociated dislocation move</li> <li>charge state strongly affects mobility</li> <li>type C is most mobile</li> </ul>	<ul> <li>type A easily multiplies</li> <li>samples w/o defects are brittle</li> <li>ductility enabled by pre-existing dislocations</li> </ul>

Figure 84: Summary of the main findings. This last section concluded with the investigation of dislocation-based plasticity in samples featuring complex arrangements of dislocations.

# 4 Summary & Outlook

## 4.1 Equilibrium Dislocation Structure

In the first part of this thesis the equilibrium structures of various dislocations in  $SrTiO_3$  were investigated and classified into groups  $\mathcal{A}$  to  $\mathcal{E}$ . By comparing possible dislocation structures with analytic descriptions of dislocations [111, 112, 168, 176, 211, 297] we found that dislocation splitting and the order of magnitude of glide dissociation distance are correctly predicted, while analytic considerations regarding the Peierls stress remain ambiguous. We used DFT calculations to obtain the stacking fault energy hypersurfaces and evaluated that only the {110} plane features a stacking fault configuration that allows for glide dissociation. This is in line with geometric considerations using nominal ionic charges [112].

For dislocation types  $\mathcal{A}, \mathcal{B}$ , and  $\mathcal{C}$ , which all share a common Burgers vector  $a\langle 110 \rangle$  and glide plane  $\{110\}$ , we determined that they can all glide dissociate in similar ways. These glide dissociated configurations are expected to possess much lower Peierls barriers and be the enablers of plasticity in  $SrTiO_3$ . However, by careful design of the simulation setups we could show that the glide dissociation of dislocation types  $\mathcal{A}$  and  $\mathcal{C}$  is highly sensitive to the charge at the dislocation core. Changing of oxygen stoichiometry at the dislocation core, which could be enabled by diffusion at finite temperature, prevents glide dissociation in type  $\mathcal{A}$  dislocations and makes it less favorable for type C dislocations. Importantly, the glide dissociated form of the A-type dislocation is never stable. Due to the crystallographic orientation of Burgers vector and glide plane, the plane for dislocation climb is crystallographically identical to the glide plane. Thus, there is the opportunity for a climb analog to the glide dissociation. Because of the symmetry of edge dislocation stress fields, the elastic fields of A-type partial dislocations interact destructively in the climb dissociated configuration. Therefore, as our calculation show, the glide dissociated variant is metastable, while the climb dissociated configuration is the equilibrium state. However, climb dissociated dislocations cannot glide limiting the mobility of type  $\mathcal{A}$  dislocations.

In contrast, dislocations of type  $\mathcal{D}$  and  $\mathcal{E}$  cannot glide dissociate for crystallographic reasons. Thus, they cannot contribute to SrTiO<sub>3</sub> plasticity. However, for  $\mathcal{D}$ -type dislocations a climb dissociation is favored. Climb dissociation might also be possible for  $\mathcal{E}$ -type dislocations but could not be tested due to limitations with the interatomic potential in use. In summary, we found that dislocations of the  $\langle 1 1 0 \rangle \{ 1 \overline{1} 0 \}$  orientation with different line orientations are the only ones susceptible to dislocation glide at low to moderate temperatures. Thus, it is these dislocation types which should be targeted during dislocation engineering of SrTiO<sub>3</sub>. Depending on the conditions, especially the dislocation core dissociation and stoichiometry, different variants of these dislocations could dominate leading to different responses to external stress. To enable mechanical control over dislocations in SrTiO<sub>3</sub>, we addressed their response to external load in the next section.

#### 4.2 Dislocation Motion

Theory predicts that only the glide dissociated dislocations are mobile [179, 211, 297]. However, the applicability of classical theories for ionic crystal lattices such as the perovskite structure remains to be shown. Additionally, the motion of two partial dislocations connected by a high energy stacking fault may be significantly different from the motion of an isolated dislocation [150, 310].

Thus, we probed our molecular dynamics models for the stress required to move a dislocation of type  $\mathcal{A}$ ,  $\mathcal{B}$  or  $\mathcal{C}$  under conditions with and without strong image interaction created by periodic boundary conditions. In the simulations with short simulation cells and strong image interactions we found that the Peierls stress strongly depends on the charge at the dislocation core of the glide dissociated dislocations. The lowest Peierls stress was found for the negatively charged variant of dislocation type  $\mathcal{C}$ . These results underline that tailoring the charge state of dislocations, e.g., by doping or processing conditions, is a crucial ingredient to enable dislocation motion and, ultimately, mechanical control over the structure and arrangement of dislocations in a perovskite. Moreover, positively charged  $\mathcal{A}$ -type dislocations tend to relieve their high charge density at the dislocation core by emission of oxygen vacancies. We could show that this process reduces their mobility. The emission of vacancies holds true even for longer segments of  $\mathcal{A}$ -type dislocations.

In contrast,  $\mathcal{B}$ -type dislocations with screw character behave differently when they see strong image interactions compared to long dislocation segments. For short dislocation line length they glide smoothly. In contrast, when long dislocations lines are studied moving screw dislocations create oxygen Frenkel pairs in their wake without changing the overall stoichiometry at the dislocation core. The reasons for this rough dislocation motion most probably are the high dislocation velocities and the concurrent high energy dissipation rate during glide. We note that this behavior has resemblance with screw dislocations in bcc iron which also create defects in the crystal lattice when moving swiftly [314].

C-type mixed dislocations showed yet a different behavior. Their glide was ideal when negatively charged. When trying to move charge neutral dislocations, however, the dislocation is collecting negative charge by emission of oxygen vacancies during its glide and, thus, tends to change its core stoichiometry.

After all, the investigation of the gliding dislocations revealed that, generally, the stress required to move a dislocation as well as the smoothness of its motion are strongly influenced by the dislocation core charge. The negatively charged dislocation of type C glides most easily and ideally. In contrast, gliding A- and B-type dislocations can have a tendency to create point defects on the oxygen sub-lattice during glide.

Knowing that the various dislocation types react differently to dislocation core charge and that dislocation glide is often imperfect, the behavior and interaction of dislocations in larger arrangements is the next step in understanding how to mechanically engineer dislocations. This topic is addressed in the last section.

## 4.3 Dislocations in Experimental Setups

In the last section we compare experimental experiments of  $SrTiO_3$  compression with large scale MD simulations. The first scenario addresses the emission and multiplication of dislocations from a notched single crystal. The second scenario, micropillars with and without pre-existing dislocations were mechanically tested [319].

In the first case, the initial nucleation of dislocations was enabled by a stress concentrator in the form of surface notch. Our simulations exhibited very good qualitative agreement with the experimental observations. At high stresses and high dislocation velocities we observed a dynamic instability of the glide motion of type  $\mathcal{A}$  dislocations. Because the energy landscape for edge dislocation motion has one branch for glide motion and one branch for climb dissociation, the behavior of the dislocation is frustrated. Enabled by the high load and swift dislocation motion type  $\mathcal{A}$  dislocations switch their glide plane spontaneously similar to a cross glide mechanism. Again this process resembles the frustrated kink formation for screw dislocations in bcc iron that similarly results in crystal defects and "debris" created by the dislocation [314]. Ultimately, this instability with respect to dislocation climb enabled multiplication of type  $\mathcal{A}$  dislocations. In addition to climb and multiplication events, the nucleation of dislocations at agglomerates of vacancies by the superposition of external and internal stresses could be witnessed.

When no stress concentrators or inhomogeneities offer themselves as points of easy dislocation nucleation, a brittle failure of the single crystalline  $SrTiO_3$  samples was observed. In contrast, when samples contained a high density of pre-existing defects significant plasticity occurred. Taking the full bandwidth of interactions and dislocation types into account by choosing simulation cell volumes of sufficient size is crucial to reproduce this experimental behavior. Nevertheless, the existence of mobile defects did little to improve the response of the ceramic under tensile load where brittle fracture still dominated.

Concluding, note that our investigations have been limited with respect to the temperature range as well as the magnitude and speed with which external load was applied. It is left for

future work to verify the observed mechanism for further boundary conditions. Moreover, the energetic situation of the different defects created during dislocations motion warrants further studies.

## 4.4 Outlook

With this research we have contributed to the understanding of dislocations in the model perovskite ceramic  $SrTiO_3$ . In particular, we have revisited the structure of the low temperature dislocation types in cubic  $SrTiO_3$ . Using a systematic approach we classified the relevant dislocation types into five groups and subsequently calculated their structure, energetic hierarchy, Peierls stress, as well as interactions between dislocations.

Several unexpected observations have opened the view on unconventional mechanisms at play in dislocations and their glide motion. First, there is a static and dynamic instability of edge dislocations with respect to climb motion. This effect gives rise to rich and complex interactions with other defects during glide and could ultimately be an important ingredient in enabling macroscopic plasticity in SrTiO<sub>3</sub>. The sensitivity of the dislocation configuration and the Peierls barrier to the charge of the edge dislocation core, however, are puzzling and require further investigations. Second, screw dislocations exhibit a dynamic instability as well. During dislocation motion at high velocities, their glide is disturbed by the emission of defects. These observations bear striking resemblance to the glide of screw dislocations in bcc iron which show an instability creating significant amounts of debris in the crystal lattice. Since the cation sub-lattice of SrTiO<sub>3</sub> forms a bcc lattice this analogy is not too far-fetched but definitely warrants closer examination. Third, mixed dislocations also exhibit the glide dissociated configuration required for easy dislocation glide. They do not show a climb instability like their edge counterpart. Nevertheless, analog to the edge dislocation only charged dislocation cores enable easy glide. A closer look revealed, however, that the sensitivity to dislocation core stoichiometry is inverted, i.e., while the oxygen deficient edge dislocations glide easily, only the oxygen rich dislocations of the mixed dislocations glide. This yet to be explained peculiarity hints to a complex energy landscape that is sensitive to localized charges. Accurate nudged elastic band calculations of moving dislocations with varying stoichiometry and independent models taking into account charge transfers could reveal the multi-dimensional energy landscape at the heart of these dislocation glide processes. Fourth, the remaining two dislocation types did not exhibit configurations susceptible to easy dislocation glide. Despite being studied in literature, their relevance for macroscopic plastic deformation of SrTiO<sub>3</sub> is negligible.

Many of the observed mechanism are at least partly related to non-stoichiometry and charge localization. In this aspect, the use of rigid ion interatomic potentials is obviously limited. Supplementing and verifying our efforts with independent models including DFT calculation or other models that allow charge transfer as well as novel machine learning approaches are promising routes to an even better understanding of dislocations in  $SrTiO_3$  and improved predictive power.

Regarding the ultimate transformation of dislocations into an engineering framework, significant work has to be put into clarifying the behavior of dislocations with different external boundary conditions. In this study we have limited ourselves to ideal  $SrTiO_3$  at low temperature. It remains to be shown if our observations hold true in different temperature regimes, more gentle loading conditions and when extrinsic defects are considered.

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