Modeling atomic force microscopy at LiNbO$_3$ surfaces from first-principles

S. Sanna $^*$, C. Dues, W.G. Schmidt
Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany

ABSTRACT

Atomic force microscopy (AFM) at LiNbO$_3$ surfaces is simulated from first-principles. The forces acting on different atomic tip models interacting with $x$-cut and $z$-cut LiNbO$_3$ surfaces are calculated within density functional theory. The AFM simulations are compared with atomic resolved AFM measurements. The species-dependent tip-surface interaction found in the simulation allows for the verification of microscopic models for different surfaces. In particular, it is shown that the atomic force microscopy contrast is governed by the charge accumulation at the oxygen ions. Van der Waals forces cloud the scans, without qualitatively modifying the AFM pattern. The microscopic surface models proposed here explain both the origin of the measured AFM patterns and the observed spatial resolution difference corresponding to different surface orientations.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Ferroelectric surfaces are of great technological relevance due to manifold applications in the field of electro-optics and acousto-electronics [1–4]. Among ferroelectric surfaces, LiNbO$_3$ surfaces are widely employed, although, the knowledge of their stoichiometry and morphology is still limited. Atomic force microscopy (AFM) is one of the few experimental techniques which allows for the investigation of insulating surfaces at the atomic scale. Indeed, in the last 30 years AFM has become a major tool for imaging and manipulating matter at the atomic scale [5]. Due to its high resolution, AFM is best suited to map surfaces and reveal their atomic structure [6–8]. Theoretical calculations have proven to be of great importance in the interpretation of AFM measurements [9–11]. Ferroelectric surfaces are generally investigated by the AFM variant usually referred to as piezoresponse force microscopy (PFM), which allows to manipulate ferroelectric domains. PFM takes advantage of the converse piezoelectric effect to excite deformations of the sample with a metal-coated tip under alternating bias [12]. Yet, true atomic resolution at ferroelectric LiNbO$_3$ surfaces is extremely challenging due to unscreened surface charges, and has only been recently achieved by Rode et al. [13] with frequency-modulated AFM. Thereby the strongly polar LiNbO$_3$(0001) surface was measured in liquid environment, in order to screen the AFM tip from the surface charges. Different spatial resolution was achieved at surfaces of different polarization, which was explained with the different electronic charge distribution at the LiNbO$_3$(0001) surfaces. Subsequently, the LiNbO$_3$(2 $\bar{T}$0) surface, commonly referred to as $x$-cut, was investigated with a similar approach [14]. Comparing their results with structural models derived from high-energy calculations within density-functional theory (DFT), the authors were able to propose atomic geometries for the LiNbO$_3$ surfaces. However, the comparison between theory and experiment was only indirect, as the electronic charge distribution is not necessarily identical with the atomic force at the surface. Thus, further simulations are necessary for the conclusive interpretation of the AFM data. For this reason, we have simulated AFM scans from first-principles, in which the forces acting on a model silicon tip are calculated within DFT. AFM scans of several stable terminations of the LiNbO$_3$(0001) and LiNbO$_3$(2 $\bar{T}$T0) surfaces have been modeled. The resulting AFM patterns are in very good agreement with the measurements. It is shown that the force-distance characteristic of differently polarized faces of the LiNbO$_3$(0001) surface differs strongly and leads to a different force contrast. Moreover, it is shown that the atomic force microscopy contrast is governed by the charge accumulation at the oxygen ions.

* Corresponding author. Tel.: +49 (0)5251 60 2333; fax: +49 (0)5251 60 3435. E-mail address: simone.sanna@uni-paderborn.de (S. Sanna).

http://dx.doi.org/10.1016/j.commatsci.2015.03.025
0927-0256/© 2015 Elsevier B.V. All rights reserved.
2. Methodology

First-principles total-energy calculations have been performed within the DFT as implemented in the Vienna ab initio simulation package VASP [15]. Thirteen valence electrons per atom have been considered for niobium (4s² 4p⁶ 4d⁴ 5s¹), one for lithium (2s¹) and hydrogen (1s¹), six for oxygen (2s² 2p⁴) and four for silicon (3s² 3p²). Nuclei and remaining core electrons were treated within the pseudopotential approach using the projector-augmented wave method (PAW) [16]. Due to the overall satisfactory agreement with the experimental results and for consistency with our previous works, the exchange and correlation functional is modeled within the generalized gradient approximation (GGA), in the semi-local form proposed by Perdew and Wang (PW91 [17]). Electronic wave functions were expanded in a plane wave basis containing waves up to a kinetic energy of 400 eV. As there is no experimental evidence of LN surfaces with net spin moment, our approach does not consider spin-polarization.

The stability of surface terminations of different stoichiometry and morphology is not investigated in this work. We rely on the stable surface models proposed in Refs. [18,14], instead. According to these models the LiNbO₃ surfaces are modeled by hexagonal slabs 

\[
\text{LiNbO}_3(2\overline{2}T\overline{0}) \quad \text{surface (x-cut)}
\]

enriched in lithium with respect to the material bulk and is –Li₁₂ terminated. The (0001) surface (z-cut) is strongly polar, and characterized by polarization dependent stoichiometry and morphology. The positive side is –Nb₂O₂–Li₂ terminated, while the negative side is –Li–O terminated. x-cut surfaces are modeled by orthogonal slabs consisting of 132 atoms and separated by a vacuum layer of about 10 Å. z-cut surfaces are modeled by hexagonal slabs containing 68 atoms and separated by a vacuum layer of about 10 Å. Gamma centered \(2 \times 2 \times 1\) k-point meshes [19] were used to carry out the integration in the Brillouin zone. Both the plane wave cutoff and the k-point meshes have been proven to yield converged results. To correct for the spurious forces introduced by the artificial field caused by neighboring slab images, dipole corrections were applied [20]. The correction consists of an external dipole perpendicular to the surface in the vacuum region of the supercell [21].

The atomic positions were relaxed until the Hellmann–Feynman forces acting on each atom were lower than 0.01 eV/Å and then kept frozen during the AFM simulation. The van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions are known to heavily affect the AFM measurements and have to be included in our models. Unfortunately, semilocal density functionals such as the GGA employed in this work do not account for dispersion forces. A pragmatic method to work around this problem is to add a correction term that is derived from the London dispersion formula, i.e. to use the so called DFT-D approach. Specifically, we use the parameters proposed by Grimme [22].

In order to properly model AFM and understand the different spatial resolution achieved e.g. at the LiNbO₃(0001) [13], both the constitutions of the tip and the operating mode must be correctly reproduced. AFM consists in measuring the forces acting on a sharp tip which is brought close to the surface to be scanned. The quality of the AFM records typically depends on the surface being measured. The atoms at the end of the tip experience different forces when they form incipient chemical bonds with distinct substrate atoms. Also, highly corrugated surfaces typically result in stronger AFM contrast than flat surfaces, due to the strong decay of the forces with distance. The AFM tip employed in the experiments depends on the system to be investigated. Several special modifications of the standard AFM setup have been proposed to enhance the force contrast and thus increase the spatial resolution. In particular, the experimental equipment is modified in order to improve the sensitivity to the forces dominating the investigated system. Thus, the AFM tip can be coated with magnetic materials to map magnetic surfaces, or with gold for covalent bonding of biological molecules at surfaces. With the exception of custom products such as the mentioned gold or diamond coated tips, most AFM tips are made from silicon or silicon compounds (e.g. borosilicate glass and silicon nitride). In particular, the AFM tips used in Refs. [14,13] were made from monolithic silicon. Typically, the tips are about one µm long and have curvature radii on the order of nanometers, i.e. well beyond DFT simulations. In order to model an AFM tip, one could properly cut silicon bulk, as shown in Fig. 1(a). However, the interaction of the lowest Si atomic layers with the surface is most dominant. Therefore, the model tip can be reduced to a few Si atoms as represented in Fig. 1(b), which also results in a great saving of computational power. More refined tip models [Fig. 1(c)], may include other atomic species than silicon, though.

While the simplest possible silicon tip is modeled by a single silicon atom [Fig. 2(a)], real silicon tips will instantly oxidize as soon as they are not operated in UHV-conditions. Thus, it might be appropriate to consider oxidized tips as in Fig. 2(b). Moreover, real tips are made chemically inert by different treatments, so that the dangling bonds might be saturated by hydrogen atoms to further refine the model. In the configuration illustrated in Fig. 2(c) the Si atom retains the tetrahedral coordination as in Si bulk. All the models represented in Fig. 2 are tested in this work.

The AFM setup can be operated in different modes, depending on the samples to be investigated. Possible imaging modes are divided into static (also called contact) modes and dynamic (non-contact) modes. Non-contact mode AFM suffer less from tip or sample degradation and is thus preferable for a variety of applications. All available AFM measurements of LiNbO₃ surfaces were performed in dynamic mode [13,23,14]. In our models the AFM tip is kept at the calculated equilibrium distance above the highest surface atom. This is about 2 Å for all investigated surfaces, with the exception of the positive LN(0001). The equilibrium distance in this case is above 3 Å. The energy vs. tip-surface distance is shown as an example for the LN(0001) in Fig. 3. Our simulations model constant height record mode and are comparable with the FM-AFM measurements of Ref. [13].

The site-specific short-range forces in AFM, are often superimposed by other contributions [24] such as electrostatic or magnetic forces. In addition, dispersion forces play a major role in the interaction between tip and substrate. In particular, the interaction of the tip with the positive LN(0001) surface would be purely repulsive without considering the vdW forces (see Fig. 3, right hand side).

In order to model AFM records, the magnitude of the force acting on the tip has been evaluated at equidistant points on the surface. Thereby the force acting on the Si atom of the tip in Fig. 2(a) or on the O atom of the tips in Fig. 2(b) and (c) has been considered. The number of mesh points amounts to 126 and 90 per surface unit cell for the x-cut and z-cut, respectively. This corresponds to a sampling point each 1 Å at the x-cut and each 0.5 Å at the z-cut. The forces between two raster points are evaluated by bicubic interpolation of the calculated points. Our approach does not require prior calibration and, in contrast to special experimental setups, is applicable to systems characterized by ionic type bonds as well as to systems characterized by covalent bonds. Several alternatives to our method are available in the literature. Indeed, different ab initio approaches for the modeling of AFM images have been proposed recently, each with peculiar features. Sasaki and Tsukada developed an analytical theory to understand the physics of the cantilever-forced vibration in noncontact AFM, and simulated the records of the Si(111) 7 × 7 surface [25]. Caciu and co-workers dedicated a great attention to the possible structural changes of clean silicon tips during the AFM imaging.
process and their implications on the contrast of the recorded images. Thereby they studied the interaction between silicon tips with [111] and [001] terminations [26,27]. Chelikowsky et al. proposed a computational scheme to simulate non-contact atomic force microscopy images without explicit modeling of the AFM tip. The latter is represented, in their approach, by an analytic orbital. Jelinek and co-workers elaborated a refined approach that allows to discriminate the substrate chemistry by accurate analysis of the short-range forces occurring between tip and sample [9–11]. Recently Foster et al. developed a calculation scheme combining atomistic static and molecular-dynamics techniques at different level of approximation in order to model non-contact scanning force microscopy (SFM) operation by a perturbed oscillator [30,31].

3. Results

3.1. The (2TT0) surface

The LiNbO3 (2TT0) surface is a prominent system in the fields of electro-acoustics and electro-optics, as it is largely employed for the realization of surface acoustic wave devices [3] and x-cut optical waveguides [4]. Microscopic models of the thermodynamically stable (1 × 1) surface terminations are available [18]. According to the proposed models, x-cut surfaces are Li-enriched with respect to the LN bulk. Indeed a –Li12 termination has been found to be formed under most growth conditions. Nevertheless, other stable terminations, such as a relaxed truncated bulk –Li9Nb6–O9 and –Li9 may also occur for very O-rich conditions. AFM measurements at the same surface had assigned the –Li12 model to the measured samples [14]. Thereby a oblique pattern with lattice parameters of \( a = 0.75 \pm 0.02 \) nm, \( b = 0.54 \pm 0.02 \) nm and \( \alpha = 94.85^\circ \) was measured and assigned to the outmost oxygen layer.

Based on the x-cut models of Ref. [18] we have simulated the AFM data, which are then compared with the measurements of Ref. [14]. Fig. 4 shows the results of our AFM simulations of the –Li9 [panels (a)–(c)] and of the –Li12 terminated [panels (e)–(g)] surfaces using the three tips shown in Fig. 2. The AFM simulations reveal qualitatively the same pattern for each surface termination, irrespective of the tip model. However the SiOH4 tip leads to clean and detailed records, while AFM images taken with the Si–O tip are less defined and to some extent noisy. Therefore, we will only use the SiOH4 [Fig. 2(c)] tip for the following investigations. The bright spots in the images correspond to oxygen ions. The electronegative oxygen ions tend to accumulate electronic charge in their neighborhood, causing a major interaction with the AFM tip. This is in agreement with the interpretation of the AFM pictures on the basis of the electronic charge distribution proposed in Ref. [14]. While the –Li12 terminated (2TT0) surface yields an AFM map that is in agreement with the experiment, this is not the case for the other thermodynamically stable terminations. As an example, we show the AFM models corresponding to the –Li9 termination in Fig. 4. The bright spots still correspond to the topmost oxygen layer, however, the calculated AFM pattern is not compatible with the measurements. The oxygen ion corresponding to the bright spot lies 0.5 Å above the other oxygen ions, which are therefore less noticeable.

In order to show that the –Li12 terminated (2TT0) surface yields to an AFM map that is in agreement with the measurements we have replicated the simulated records of Fig. 4(g) according to the surface periodicity. The resulting pattern is shown in Fig. 5(a) and perfectly matches the corresponding measurements, shown in Fig. 5(a). The extrapolated oblique pattern has dimensions of 0.76 nm \( \times \) 0.55 nm, and \( \alpha = 95.12^\circ \) and is therefore in excellent agreement with the experimental results. We want to remark, though, that it represents the periodicity of the oxygen sublattice and not the surface unit cell. Indeed, the surface unit cell is orthogonal with dimensions of 1.390 nm and 1.788 nm, as explained in Ref. [18]. The underlying cations are not distinguishable, neither in the measured nor in the simulated AFM images. Fig. 5(b) shows the AFM picture which results from the not occurring –Li9 termination. It clearly does not match the experimental findings.
3.2. The LiNbO₃(0001) surface

The LiNbO₃(0001) is a prototypical strongly polar surface, largely exploited for the realization of technological devices. Substrate assisted molecular deposition, acousto-electronic and electro-optical devices are examples of today’s applications [1,2]. Several experimental [32–37] and theoretical studies [38,39,18] have been dedicated to the investigation of the electronic and morphological properties of this surface. The picture resulting from these studies shows a striking dependence of the physical and chemical properties on the polarization direction. Only the 1/C₂ surface periodicity at ambient temperature, is common to both orientations. While reconstructions at the weakly polar SrTiO₃(001) and BaTiO₃(001) surfaces have been recently demonstrated by scanning tunneling [40,41] and transmission electron [42] microscopy, LiNbO₃(0001) is the first strongly polar surface which has been investigated by AFM with atomic resolution. In particular, AFM studies showing the non reconstructed (0001) morphology [13], as well as AFM studies demonstrating surface reconstructions at high-temperatures [23] and explaining the relationships between temperature, surface charge and surface reconstructions [43] are available. Interestingly, AFM images with true atomic resolution are only available for the negative surface (0001). Even if quite unusual, this must not be surprising, as the resolution limit of AFM is given by the structural properties of the atomic wavefunctions of tip and sample, which is in general polarization dependent. For this reason, the different resolution was addressed as an intrinsic surface property in Ref. [13], and traced back to the different roughness and bond strength at oppositely polarized surfaces. Our AFM models corroborate this interpretation.

Fig. 6 shows the simulation of AFM scans at the LiNbO₃(0001) (a) and LiNbO₃(0001)(b) surfaces, respectively. The scans were performed with the tip in Fig. 2(c). Both pictures show a 1 x 1 surface periodicity, corresponding to the hexagonal (0001) surface unit cell with a₁ = 5.147 Å and x = 60°, in very good agreement with the experimental observations. However, while the AFM simulation at the negative side is more structured and rich in contrast, the positive side appears flat, resulting in a weaker AFM contrast. Indeed, the forces acting on the tip at the positive surface only vary in the range between 0.05 and 0.10 eV/Å, while at the negative surface the forces vary within the more than twice larger interval between 0.05 and 0.28 eV/Å.

The force contrast observed at the two surfaces are at one side the consequence of the different surface roughness (Rq = 1.644 and 2.216 at the positive and negative surface, respectively [44]), and at the other side the consequence of the lack of strong charge accumulation centers such as oxygen ions at the positive side. While the bright spots at the negative side are close to the topmost oxygen layer, the bright spots at the positive side can be assigned to the topmost Li-atom. Indeed, no oxygen at the topmost layer which can act as charge accumulation center is present at the positive surface. The force contrast at the positive side is therefore much

![Image](https://via.placeholder.com/150)

**Fig. 3.** Energy vs. distance curves calculated for the positive and negative Li(0001) with the tips shown in Fig. 2(c). Straight and dashed lines show the values calculated with and without vDW corrections. The energy minimum calculated with vDW is chosen as the origin of the energy scale.

![Image](https://via.placeholder.com/150)

**Fig. 4.** Simulation of AFM records of the –Li₆ terminated (upper part) and –Li₁₂ terminated (lower part) LiNbO₃(2TT0) surface and atomic structure of the corresponding region. AFM images (a), (e) are achieved with the tip shown in Fig. 2(a), images (b), (f) with the tip shown in Fig. 2(b), and images (c), (g) with the tip shown in Fig. 2(c). The bright spots in the pictures correspond to oxygen ions.
weaker than at the positive side, explaining the different resolution achieved in AFM experiments. The spatial resolution might be increased drawing the AFM tip closer to the surface. This region is characterized by a steep repulsive potential for the tip. Thus, if measurements are performed in the region, the tip experiences stronger force differences between neighboring surface points.

In order to verify this assumption and at the same time estimate the effect of vdW forces, we perform AFM scan simulations pushing the tip a distance of 2 Å from the surface, both at the positive and at the negative LN(0001) side. Thereby the calculation of the vdW forces is switched off, in order to see the influence of dispersion forces more clearly. The results of the simulations are shown in Fig. 7 (b) and (d) as well as in Fig. 6 (c) and (d). The bright spots in the pictures are assigned to oxygen ions.

**Fig. 5.** FM-AFM image of the LN x-cut from Ref. [14] (a) and theoretically modeled AFM records for the –Li9 (b) and –Li12 terminated x-cut model (c) and (d). In panel (d) some noise is applied by post processing to the calculated image. The bright spots in the pictures are assigned to oxygen ions.

**Fig. 6.** Theoretically modeled AFM records for the (a) –Li–O terminated Li(0001) and (b) –Nb–Li–O terminated Li(0001). The forces are given in eV/Å.

In order to verify this assumption and at the same time estimate the effect of vdW forces, we perform AFM scan simulations pushing the tip a distance of 2 Å from the surface, both at the positive and at the negative LN(0001) side. Thereby the calculation of the vdW forces is switched off, in order to see the influence of dispersion forces more clearly. The results of the simulations are shown in Fig. 7 (b) and (d), while Fig. 7 (a) and (c) show the corresponding part of Fig. 6 on the same scale for a comparison. While the AFM images are qualitatively identical to the simulations shown in Fig. 6, they appear much sharper. The forces acting on the tip vary in a wider range between 0.05 and 0.55 eV/Å, while the force range is larger at the positive side, as the tip is much closer to the surface than in Fig. 6. Again, the bright spots at the positive side are easily identified as the topmost Li atoms, while the bright spots at the negative side correspond to the oxygen atoms. As the AFM pattern closely corresponds – even if much more distinct – to the scans calculated with vdW, it can be assumed that vdW forces at LiNbO3 surfaces affect the spatial resolution clouding the scans, without qualitatively modifying the AFM pattern.

**Fig. 5.** FM-AFM image of the LN x-cut from Ref. [14] (a) and theoretically modeled AFM records for the –Li9 (b) and –Li12 terminated x-cut model (c) and (d). In panel (d) some noise is applied by post processing to the calculated image. The bright spots in the pictures are assigned to oxygen ions.

**Fig. 6.** Theoretically modeled AFM records for the (a) –Li–O terminated Li(0001) and (b) –Nb–Li–O terminated Li(0001). The forces are given in eV/Å.

**Fig. 7.** Simulation of AFM records of the –Nb–O3–Li2 terminated LiNbO3(0001) surface calculated with vdW (a) and without vdW (b) as well as of the –Li–O terminated LiNbO3(0001) surfaces calculated with vdW (c) and without vdW (d). The atomic structure of the corresponding region is shown at the right hand side.

### 4. Conclusions

AFM measurements on different LiNbO3 surfaces have been simulated in the framework of the density functional theory. A tip model representing an oxidized silicon tip leads to the most clear AFM records. AFM simulations are in agreement with the corresponding measurements for all the investigated surfaces, and can thus be used to discriminate between surface terminations within the thermodynamic stability region. The AFM contrast mechanism is governed by oxygen ions, which act as charge accumulation centers. Other atomic species are, on the contrary, less visible. For this reason, some care is needed in extrapolating the surface periodicity from AFM images. As an example, the AFM pattern measured and calculated at x-cut mirrors the oxygen sublattice, which has a shorter periodicity than the true surface unit cell. The sensitivity of the AFM method to oxygen atoms also explains the different resolution achieved in measurements at the positive and negative z-surface. The negative surface is strongly corrugated and presents oxygen ions at the topmost layer, which ensure a strong AFM contrast. The positive surface is atomically flat and has no oxygen ions at the topmost layer, instead. For this reason the AFM contrast is limited and true atomic resolution difficult to achieve. Due to their pronounced electronegativity and the consequent capability to accumulate electronic charge in their neighborhood, oxygen ions are expected to dominate the AFM patterns also in other materials than LiNbO3. Van der Waals forces affect the AFM spatial resolution clouding the scans, without qualitatively modifying the AFM images.

### Acknowledgments

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged financial support (projects TRR142 and SCHM1361/21). All the calculations were performed at the Paderborn Center for Parallel Computing (PC²) and at High Performance Computing Center in Stuttgart (HLRS).
References