Surface molecular dynamics simulation with two orthogonal surface steps: how to beat the particle conservation problem

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Abstract

Due to particle conservation, Canonical Molecular Dynamics (MD) simulations fail in the description of surface phase transitions involving coverage or lateral density changes. However, a step on the surface can act effectively as a source or a sink of atoms, in the simulation as well as in real life. A single surface step can be introduced by suitably modifying planar Periodic Boundary Conditions (PBC), to accommodate the generally inequivalent stacking of two adjacent layers. We discuss here how, through the introduction of two orthogonal surface steps, particle number conservation may no longer represent a fatal constraint for the study of these surface transitions. As an example, we apply the method for estimating temperature-induced lateral density increase of the reconstructed Au (001) surface; the resulting anisotropic cell change is consistent with experimental observations. Moreover, we implement this kind of scheme in conjunction with the variable curvature MD method, recently introduced by our group.

Keywords: Molecular dynamics; Gold; Surface structure, morphology, roughness, and topography; Low index single crystal surfaces; Vicinal single crystal
I. INTRODUCTION

Classical Molecular Dynamics (MD) simulation of crystal surfaces is generally inadequate for the description of physical situations involving large density and structure changes including some surface reconstructions, incomplete melting, thermal preroughening and roughening, etc. due to the constraint of particle conservation. A single monatomic step can act as a source or sink of atoms: given a request for lateral density variation the step can move normally to its direction, to accommodate to it. Pairs of steps of opposite sign are generally easy to implement in a slab simulation: but this is not optimal, for it leads to a very limited size terrace, with non-negligible step-step interactions (≃ 1/L^2, if L is the terrace size), and general hindering of the step movement. To minimize this problem, one can introduce a single step per unit cell, which will weakly interact only with its own replicas (L being in this case the entire lateral size of the simulation cell) through periodic boundary conditions (PBC). To this end, the PBC must be modified so that a layer n on the cell right hand side is joined at the left hand side not with itself, but with layer n + 1. In this manner the single step is introduced topologically. That scheme was applied with success to the simulation of the lateral density increase of the reconstructed hexagonal overlayer of Au(001) \[1\]. The movement of the step was indeed observed, with an enhanced mobility connected in that case with the incommensurability between first and second layer \[2\].

However, a lateral density adjustment will in general take place in both directions on the surface and not just along one. The impossibility for the density to re-adjust in both directions (as implied by the unidirectional single step construction, and by rigid overall PBC parallel to the step) can also hinder interplanar sliding which might in real life require simultaneous sliding in both planar directions. The natural solution to this problem is to allow the same freedom in both orthogonal surface directions. A practical realization of this task is presented here through the implementation of two orthogonal steps. We will first
of all examine the practical implementation and the applicability to surfaces of unbent as well as of bent crystals, in the light of the recently introduced variable curvature molecular dynamics method [3]. We will then present direct examples of application, exploiting as done previously [2,3] gold surfaces as a test case.

II. THE DOUBLE STEP

A surface with regularly repeated steps separated by large terraces is a vicinal surface. A method for generating a vicinal surface for simulation is to rotate a slab by an angle $\theta = \arctan(L/h)$ with a flat surface and dimensions $L_x \times L_y \times L_z$ around the step axis (called $x$) (with $L$ the distance between the steps and $h$ the interplanar separation) and to “cleave” the crystal surface accordingly, generating a sequence of monatomic steps. If $L$ is chosen equal to $L_y$, a single step is produced. In a typical high symmetry direction of an fcc crystal, such as (111) or (001), the stacking of the layers is $ABCABC\ldots$ or $ABABAB\ldots$. If a single step is produced, the portion of terrace above the step and the one below will belong to layers of different sublattices, thus causing a mismatch in the periodic boundary conditions (PBC). This problem is solved through the introduction of an additional translation vector in the PBC, absorbing the mismatch between the two different layers [3]. An equivalent solution is to modify the dimensions and orientation of the simulation cell, which will no longer be built with an integer number of unit cells nor with walls parallel to high-symmetry planes of the crystal [4]. We prefer here the former approach.

If we now wish to add a single step along the orthogonal $y$ direction as well, a problem in the PBC will obviously appear also in the $x$ direction, and we will need two rotations of the slab. The first, through an angle $\theta \simeq L_y/h$ about the $x$ axis brings the $y$ axis into $y'$. The second, through an angle $\phi \simeq L_x/h$, about $y'$. The dimension of the cell is chosen so that a particle and its image lie at the same height $z$. 

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III. APPLICATION TO A FLAT SURFACE

As an example, we consider a Au(001) surface, whose hexagonal reconstructed layer is incommensurate, with a cell approximately \((n \times 5)\) with \(n \simeq 30\). In the \([110]\) (henceforth \(y\)) direction, 6 surface rows, shifted alternatingly so as to form a quasi triangular layer, are stacked on 5 rows of the underlying square second layer. In the \([1\bar{1}0]\) (henceforth \(x\)) direction, one soliton-like extra atomic row is present every \(n\) second layer rows. The surface finally appears as in Fig. 1, where a reconstructed Au(001) surface, 20 layer thick, is shown. Although there is in reality a single large terrace, that appears in the form of four sub-terraces of height 1,0,0,-1. The corrugation given by the \((5 \times 1)\) reconstruction periodicity is clearly visible.

To demonstrate how the two orthogonal steps are going to act as grand-canonical sources of surface atoms, we will exploit one well established but rather peculiar property of this surface: Au(001) increases its lateral density upon heating \([6,7,2]\). Physically this is due to the competing role of the \(d\)- and \(s\)-orbitals of gold: the consequence of this competition is a giant outwards relaxation, resulting in a consequent planar contraction of the first layer.

Since the \((6 \over 5)\) commensurability pinning in the \(y\) direction is much stronger than the \((n + 1 \over n)\) pinning in the \(x\) direction, the lateral contractions upon heating will generally be different between \(x\) and \(y\). Our goal here will be to discover what our approach predicts for them using the two-steps geometry, different between \(x\) and \(y\). Our goal here will be to discover by simulation what should happen in reality by using the two-step geometry. We modeled the surface with a slab with 20 layers of 1800 atoms each. The two surfaces were reconstructed with 31 rows over 30 in the \(x\) direction and 6 rows over 5 in the \(y\) direction. Our interatomic potential was the glue model of Ercolessi \textit{et al.} \([8]\) with a many body term mimicking the metallic cohesion of valence \(s\) and \(d\) electrons. Newton’s equations were numerically integrated with standard algorithms, and velocity rescaling is used to control temperature. After an initial quench to relax the slab atomic positions, we heated slowly (rate 100 Kelvin/nsec) up to 1000\(K\). Fig. 2 shows a top view of the surface of Fig. 1 before
and after it was heated in this way.

At the beginning ($T = 0$) the four sub-terraces had equal dimensions (left panel). At $T = 900K$ (right panel) the situation has now changed, with a visible withdrawal (even if superposed with meandering) of the x-step along the positive y direction, but no visible shift of the y-step along the x direction. As a result, the two lower subterraces 0, -1 have expanded at the expense of the two upper ones 1, 0. The relative x-step withdrawal is about 4%. Since that happens in one direction only, this measures exactly the relative lateral density increase in the top layer of our Au(001) on heating model between zero and 900 K. This value equals very closely the magnitude of the known surface lateral density increase of real Au(001) from room temperature to 900 K. Not surprisingly it is mostly the weakly pinned x-step that acted as a source of atoms for the terrace density increase, while hardly anything happened to the strongly pinned y-step. The reconstruction periodicity drift with temperature from $(5 \times 30)$ to roughly $(5 \times 28.5)$, which is precisely the trend seen experimentally.

IV. DOUBLE STEP AND VARIABLE CURVATURE

A second interesting application of the double step geometry is in conjunction with the Variable Curvature Molecular Dynamics (VCMD) method. That method allows the simulation of a bent slab, the radius of bending curvature treated as an additional degree of freedom. In the force-free case, the slab will adopt a spontaneous curvature in response to the surface stress difference of its two faces. Alternatively, a bending force or constraint can be applied to the slab, to force a given curvature. The associated fields of strain and stress in the slab will change its overall free energy and in particular that of its surfaces. In response, the equilibrium surface lateral density may also generally change, and we can gauge that change with our double step method. Special care must be taken in this case concerning PBC: if the slab is bent, a particle with velocity parallel to the bending direction which crosses the boundary of the simulation cell, must remain on the same ‘orbit’, thus
the translation vector added to the usual PBC refolding vectors should be also parallel to
the bending direction. With this in mind, we have considered two important cases under
bending: Au(001) \((1 \times 5)\) and the Au(111) with its \((\sqrt{3} \times n)\) reconstruction. Details of both
calculations will be reported in a forthcoming paper \([11]\). Here we just give some preliminary
results concerning Au(111). Under compressive strain, the density mismatch between the
substrate and the overlayer decreases, and the \(\sqrt{3} \times n\) periodicity should change, in particular
\(n\) should increase.

We started with a single \((\sqrt{3} \times 11)\) reconstructed domain \((n = 11\) is the equilibrium
value in the glue model \([12]\)) with 6 solitons which are parallel to the \([11\bar{2}]\) (henceforth \(x\)
direction and two orthogonal steps, a total of about 1200 surface atoms, for a slab thickness
of 40 layers. We applied a finite curvature in the \([1\bar{1}0]\) (henceforth \(y\) direction, and focused
on the face under compression (see Fig. 3).

Fig. 4 shows the phase difference of the overlayer over the second layer with and without
bending strain. The flat surface shows 6 solitons along the \(x\) direction (the peak of one of the
steps is visible), whereas under a compressive strain of about 4% the period of reconstruction
has doubled to \((\sqrt{3} \times 22)\) and there are only 3 solitons. The step parallel to the soliton
advances in this case, accepting atoms from the terrace. On the other hand, the other step
(orthogonal to the solitons) remains pinned, most likely due to strong commensurability.
Hence in comparison with the Au(001) studied in the previous chapter, we have step motion
parallel rather than orthogonal to the soliton, and we also demonstrate step advancing rather
than withdrawing.

V. CONCLUSIONS AND PERSPECTIVES

Two orthogonal single steps can be built topologically on a simulated crystal surface
through periodic boundary conditions. This device is shown to permit, under favorable
conditions, an effectively grand canonical study of the surface with molecular dynamics
(MD) simulation, otherwise strictly canonical. Any change of surface coverage will reflect
in an advancement or retraction of the two steps, that can be naturally quite anisotropic. The method is shown to work by means of two case studies: the thermal increase of lateral surface density of Au(001), and the strain-induced decrease of that of Au(111).

In both cases only one step eventually moved, but the presence of two orthogonal steps allowed to separate the lateral expansion in two directions. The conclusion that the contraction is dominant in one direction with respect to the other, although physically plausible, could not have been drawn with a single step geometry.

In the case of surfaces under strain, we are presently applying the same method to the curved Au (100), and the results will appear in a future paper [11].

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**FIGURE CAPTIONS**

- Figure 1: The 20-layers slab of the reconstructed Au (100) surface with two orthogonal steps; the corrugations given by the $5 \times 1$ periodicity is clearly visible.

- Figure 2: Top view of the Au (100) surface before and after heating at $900K$ (brighter atoms are higher, thus the top left terrace is the highest one). Before heating, the four subterraces have the same size (left); after heating, the horizontal step has retracted, signalling a lateral density increase (right). The numbers (0,-1,1) indicate the relative height of the four subterraces.

- Figure 3: First few layers of the simulated Au (111) slab under compressive strain along the $\bar{1}10$ ($y$) direction. Both the two orthogonal steps and the externally imposed curvature can be observed ($T = 800K$).

- Figure 4: Change in periodicity (phase difference of the overlayer over the second layer) of the Au (111) surface reconstruction under compressive strain: the flat surface shows 6 solitons along the $y$ direction (lower curve), whereas under a compressive strain of about 4% the period of reconstruction has doubled (upper curve).
Misfit of layer with substrate

No strain

4 % strain