Realistic simulations of Au(100): Grand Canonical Monte Carlo and Molecular Dynamics

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Abstract

The large surface density changes associated with the (100) noble metals surface hex-reconstruction suggest the use of non-particle conserving simulation methods. We present an example of a surface Grand Canonical Monte Carlo applied to the transformation of a square non reconstructed surface to the hexagonally covered low temperature stable Au(100). On the other hand, classical Molecular Dynamics allows to investigate microscopic details of the reconstruction dynamics, and we show, as an example, retraction of a step and its interplay with the surface reconstruction/deconstruction mechanism.
The (100) surface of noble metals (Au, Pt, Ir) shows a quasi-hexagonal reconstruction, which has been deeply investigated both experimentally [1,2] and theoretically [3]. The reconstruction is characterized by an approximate (in Au and Pt, where a slight incommensurability is observed) or exact (in Ir) $(1 \times 5)$ unit cell, arising from the interplay of a slightly contracted and distorted triangular surface layer with the (square) second layer. This result can be interpreted in terms of a simple model (the glue model) incorporating the tendency of surface atoms to increase their coordinations [3]. As the result of a strong packing tendency, the density of the top layer at low temperature is about 24% larger than that of a regular (100) layer, and it tends to increase with temperature [4]. Moreover, the angular orientation of the top layer undergoes phase transitions well characterised by X-ray measurements [5].

At a temperature of $0.81T_m$, a deconstruction transition occurs, and the long-range hexagonal order parameter vanishes. A surprisingly exact coincidence of (rescaled) transition temperatures for the three noble metals is observed. In spite of this large amount of theoretical and experimental work, a detailed insight into the consequences of the strong density difference between a square, unreconstructed (100) layer and the reconstructed triangular surface is still lacking, particularly concerning the interplay between defects such as steps, and the reconstruction/deconstruction mechanism. To this end, Molecular Dynamics (MD) is a valid tool, especially for noble metals such as gold, where glue potentials have revealed to be predictive. Classical MD makes it possible to simulate a large number of atoms for a time scale of several nanoseconds, allowing for instance to follow the movement of a step on a surface. On the other side, a deep theoretical understanding of the deconstruction transition at high temperatures has not been achieved until now, and MD simulations have a difficulty in reproducing this aspect due to the atom number conservation constraint: strong density changes at the surface are involved, and crater/islands appear as a consequence of these changes and of the impossibility to create/delete atoms as needed. A more natural method in this case should be Grand Canonical Monte Carlo (GCMC). Recently, we have successfully applied this method to the preroughening of rare gas crystal surfaces [6] and to rare gas adsorption on an attractive substrate [7]. In the case of metals the low vapor pres-
sure and equilibration problems hinder in some way the success of the method. Preliminary results are however encouraging.

In this paper we present two examples of simulation on the Au(100) surface. The first is a calculation which reveals the possibilities of GCMC even in the case of metals: starting from a square surface, the system spontaneously formed a hexagonally reconstructed overlayer; the second example is a high-T MD simulation of a step on this surface, and its interplay with the reconstruction. In both studies we have adopted a slab geometry with Periodic Boundary Conditions along the $x-y$ directions. The potential we used is the glue potential \[8\] which consists of a two-body term and of a density dependent term, mimicking the valence electrons effects in metals.

First, we will report on our GCMC study. Our Monte Carlo procedure involves small displacement moves (m), creations (c), and destructions (d) with relative probabilities $\alpha^{(m)} = 1 - 2\alpha$ and $\alpha^{(c)} = \alpha^{(d)} = \alpha$, with $\alpha \simeq 0.25$. Small moves apply to all particles, whereas creation/destruction is restricted to a fixed surface region, about four layers wide. We have simulated two different systems at low temperature: a non-reconstructed surface (A) and a reconstructed quasi-hexagonal surface (B) In both cases the slab had 225 atoms per layer, and was 16 layer thick. We found the following results:

1. upon adsorption of atoms on the square top layer [system (A)], the adatoms are included and the equilibrium state of the surface is, correctly, the $(5 \times 1)$ reconstructed quasi-hexagonal state;

2. upon adsorption of atoms on the reconstructed layer [system (B)], another reconstructed layer forms, and the former first layer, now covered, deconstructs immediately into a nearly regular, square (100) layer.

The surface density $\rho_{(s)}$ for system (A) continuously changes from the bulk value to the hexagonal value. The chemical potential is $\mu = -3.92\text{eV}$ and the averaged density $\langle \rho_{(s)} \rangle$ levels up at a nearly correct value of 1.30. All simulations are performed at $T = 800\text{ K}$. 

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Figure 1 shows the initial unreconstructed state (A), two intermediate states with hexagonal zones which begin to form, and the equilibrium final state, triangularly ordered.

For system (B) the evolution of the number of atoms of the ad-layer and the population of the first two adsorbed layers is shown in Figure 2. The density of the first layer decreases nearly to the bulk value when the ad-layer has completed its growth, and completes its square ordering when another adlayer has adsorbed on it.

These results show that the GCMC simulation method is efficient also on the microscopic scale: structural phase transitions involving strong density changes and rearrangement of atoms are correctly driven by the grand canonical Markovian chain we used in order to sample this particular statistical ensemble. Not only the correct density is achieved, but also an almost perfect short-range order is obtained both in the reconstructed top layer and in the square bulk layers. This fact is remarkable, if one takes into account the fact that an off-lattice model was used and no constraints on the lattice structure were given.

Let us now present the other study concerning Molecular Dynamics simulation of a step on a flat Au(100) surface. We adopted the same glue potential as before in the slab geometry (16 layer slab, with a maximum of 2500 atoms per layer), numerically integrating Newton’s equations for simulation times of the order of nanoseconds.

Upon increase of temperature, the lateral density of a flat reconstructed Au(100) surface shows a tendency to increase (enhancement of lateral coordination is compensated by an anomalous outwards relaxation of the first layer). We find in our simulations an increase of the T = 0 lateral density of 1.24 with respect to the bulk, to 1.35 for T = 1000K. This behavior is in close agreement with experiment for both Au and Pt.

When a step is added to the flat surface, it becomes a free source of atoms for a layer which needs to increase its density. Heating can therefore trigger step retraction on a hex-reconstructed surface. We have studied the mechanism of this retraction in Au(100) in a ‘one step geometry’. Usual periodic boundary condition in the x – y plane of the slab are not suitable to simulate a surface with a single step: only an even number of steps allows matching at the boundaries, due to the ABABAB... stacking of (100) layers in a fcc crystal.
In order to allow modelling a single step, we have adopted special boundary conditions: if an atom of a layer $A$ crosses the slab boundary which is parallel to the step, it appears on the other side displaced vertically by one layer, with the proper horizontal mismatch between layer $A$ and layer $B$. In this way, a single step separates an $A$ terrace from a $B$ terrace.

When the step retracts, it uncovers by doing so a portion of terrace which in turn must also become reconstructed. This must occur most naturally by incorporation into the lower terrace of atoms formerly belonging to the upper retracting terrace, whose retraction must in turn be accelerated by this loss. Conversely, when a step advances, it covers a portion of terrace which must at the same time deconstruct. This must liberate excess atoms, which must in their turn be incorporated in the advancing upper terrace, causing it to advance even more. While this “positive feedback” is obvious, the mechanisms of its actual occurrence have not been described before, and their consequences seem worth studying in some detail.

The starting point of our simulations was an equilibrated step at $T=800K$ (Figure 3) then suddenly brought to a higher temperature of $950K$. The equilibrium lateral density of the upper surface suddenly jumps upwards by 5%, whence the step begins to retract. We show in Figure 4 some stages of the simulation. To clarify the process we have marked in yellow the top layer atoms, labelled the atoms which participate in the process, marked with a number the initially top-layer atoms, and with a letter the atoms initially belonging to the second layer. After 70 ps (Figure 5), retraction has occurred and the uncovered zone has become reconstructed: atoms which were formerly on the step edge (atoms 1-7 and 11-15), have been incorporated into the lower terrace and form with the atoms of the formerly quadratic substrate a hexagonal pattern. The positive feedback which we had anticipated does exist, and appears also to play a dynamical role in rendering the retracting step particularly wiggly.

In conclusion, we have presented two examples of simulation on the Au(100) surface. Concerning the GCMC exemplification, we must give, of course, credit to the glue potential we have used [8], but we are confident that the interplay between efficient phenomenological potentials and particle-non-conserving algorithms such as the one just described will lead to interesting predictions in the field of structural transitions at surfaces, in particular because
no assumptions on the final structure need to be made in advance. Summarizing, this simple test indicates the feasibility of a surface GCMC simulation, applied in particular to metals modeled by classical many-body (glue) forces.

The single step simulation shows an example of non-standard Periodic Boundary Conditions, and the power of classical MD for the investigation of microscopic details of physical phenomena. Single atoms can be ‘followed’ during the simulation; in this case, an interesting interplay between step movement, density change and reconstruction has been exploited.

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I. FIGURE CAPTIONS

Fig. 1:(a) The initial state of Au(100): the top layer is perfectly square and unreconstructed; (b) the Monte Carlo creation of new particles starts modifying the structure; (c) the correct lateral density is achieved; (d) quasihexagonal order (equilibrium state) is obtained at surface after the Monte Carlo simulation. Color of atoms reflects their height, atoms in (d) are brighter due to vertical expansion (about 20%) connected to the reconstruction of the first layer.

Fig. 2: Evolution of the particle occupancy of the initially first layer and of two layers growing on it (system (B)). Layer densities are normalised to bulk (100) lateral density. The first layer decreases its density and becomes square with defects, and eventually perfectly square when two complete layers are adsorbed on it. The deconstruction of the underlying layer increases the growth rate of an adlayer.

Fig. 3 (color): Top view of a detail of the simulated slab. Equilibrated step at 800 K, suddenly brought to a higher temperature of 950 K. Yellow atoms are top layer atoms, blue atoms belong to the second layer.

Fig. 4 (color): Intermediate snapshots of the simulation (frames are separated by 1.4 ps). The step has retracted and a whole line of atoms (1-7) passed from the step rim to the
second layer. Atoms 13, 14, 5, 6 and 7 are part of the reconstruction of the uncovered zone of the second layer.

Fig. 5 (color): The final situation, with evident shrinking of the step (70 ps of simulation have been completed). The uncovered zone has become reconstructed, and atoms 1−7, formerly at the step edge, as well as 11−15, formerly second line, have been incorporated into the lower terrace. Also note the new large wiggliness of the retracted step.
REFERENCES

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[1] M. A. Van Hove, R. J. Koestner, P. C. Stair, J. P. Biberian, L. L. Kesmodel, I. Bartoš and G. A. Somorjai, Surf. Sci. 103 (1981) 189; 218; G. Binnig, H. Rohrer, Ch. Gerber and E. Stoll, Surf. Sci. 144 (1984) 321; K. Yamazaki, K. Takayanagi, Y. Tanishiro and K. Yagi, Surf. Sci. 199 (1988) 595.

[2] S. G. J. Mochrie, D. M. Zehner, B. M. Ocko, and D. Gibbs, Phys. Rev. Lett. 64 (1990) 2925; D. Gibbs, B. M. Ocko, D. M. Zehner, and S. G. J. Mochrie, Phys. Rev. B 42 (1990) 7330; B. M. Ocko, D. Gibbs, K. G. Huang, D. M. Zehner, and S. G. J. Mochrie, Phys. Rev. B 44 (1991) 6429.

[3] F. Ercolessi, E. Tosatti, and M. Parrinello, Phys. Rev. Lett 57 (1986) 719; F. Ercolessi, M. Parrinello, and E. Tosatti, Surf. Sci. 177 (1986) 314.

[4] A. R. Sandy, S. G. J. Mochrie, D. M. Zehner, G. Grubel, K. G. Huang and Doon Gibbs, Phys. Rev. Lett. 68 (1992) 2192.

[5] D. L. Abernathy, D. Gibbs, G. Grubel, K. G. Huang, S. G. J. Mochrie, A. R. Sandy, and D. M. Zehner, Surf. Sci. 283 (1993) 260.

[6] F. Celestini, D. Passerone, F. Ercolessi and E. Tosatti, Surf. Sci. 402-404 (1998) 886

[7] F. Celestini, D. Passerone, F. Ercolessi and E. Tosatti, submitted to Phys. Rev. Lett.

[8] F. Ercolessi, M. Parrinello and E. Tosatti, Philos. Mag. A, 58 (1988) 213.
[9] D. Passerone, F. Ercolessi and E. Tosatti, Surf. Sci. 377-379 (1997) 27.
