Temperature dependent surface relaxation for Al(110) and Mg(1010) studied by orbital free ab initio molecular dynamics.

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We have performed orbital free ab initio molecular dynamics simulations in order to study the thermal behaviour of two open surfaces of solid metallic systems, namely the (110) face of fcc Al and the (1010) face of hcp Mg. Our results reproduce qualitatively both the experimental measurements and previous ab initio calculations performed with the more costly Kohn-Sham approach of Density Functional Theory. These calculations can be viewed as a validation test of the orbital free method for semiinfinite surfaces, and the results underpin its reliability.

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I. INTRODUCTION

If a bulk metallic crystal at zero temperature is instantaneously separated into two halves, exposing two pristine surfaces, then the electrons and the ions redistribute themselves, responding to the new environment, in order to lower the total energy. In the simplest cases this results in surface relaxation, where the spacing between layers near the surface varies with respect to its bulk values\(^1\). Screening of the surface and smoothing of the charge usually leads to an expansion of the first interlayer distance for close-packed faces. Inner interlayer distances usually change very little for this type of surfaces. For open surfaces, in addition, there is a possibility of diminishing the undercoordination felt by the outermost atoms by moving closer to the second layer, resulting usually in a contraction of the first interlayer distance. Inner interlayer relaxations also occur, in general leading to a damped oscillatory pattern of expansion, contraction, expansion and so on.

When the temperature is raised additional dynamic effects take place and it is possible to find experimentally a widely varying thermal behaviour. While general theoretical considerations conclude that thermal expansion is expected\(^2\), some surfaces exhibit an anomalously large effect for its first interlayer distance (Pb(110), Ni(100), Ag(111), Cu(110), Be(0001))\(^3\) and some others show a negative thermal expansion coefficient for this first interlayer distance, followed by positive coefficients for inner interlayer distances (Al(110)\(^4\), or even by an alternating sign behavior (Mg(1010)\(^5\), Be(1010)\(^6\)).

In this work we will focus on two of these “anomalous” systems, namely Al(110) and Mg(1010). Both are simple sp bonded metals, amenable to study within a pseudopotential formalism. Moreover, both of them have been studied by ab initio methods, namely using the Kohn-Sham (KS)\(^7\) version of Density Functional Theory (DFT)\(^8\). For Al(110) ab initio molecular dynamics (AIMD) simulations were performed\(^9\), which were able to reproduce both the oscillatory relaxations and the thermal behaviour observed experimentally. In the case of Mg(1010) theoretical calculations based on the quasiharmonic approximation (QHA) and static KS-DFT computations\(^1\), reproduced also the oscillatory pattern both in relaxations and in thermal expansion coefficients. It should be noted, however, that no AIMD simulations have yet been performed for this system.

KS-AIMD simulations represent a very powerful tool to study metallic surfaces, because, due to the use of DFT, the response of the ions to the rapid decrease of the electron density near the surface is calculated self-consistently. However its application has been very scarce in the literature because of practical difficulties, namely they are extremely expensive computationally. Some of this cost can be alleviated if one returns to the original formulation of DFT\(^8\), which uses the electron density as the only variable in the theory, without any resort to KS orbitals. In such an orbital free (OF) theory\(^10\), the electronic kinetic energy must be computed approximately (instead of exactly in the KS version), and local pseudopotentials are needed (in the KS version also nonlocal pseudopotentials can be used). However, the computing time and memory saved by disposing of the orbitals can then be invested in studying larger systems for longer times. This, while important in solid metallic surfaces, shows its full potential in the study of liquid metallic surfaces\(^11\), where the absence of long range order requires the use of large samples in order to obtain realistic results. Note that OF-AIMD still use DFT, and therefore the main power of the AIMD is preserved, i.e. the electrons and the ions near the surface respond selfconsistently to the rearrangement of one another.

While OF-AIMD simulations have been successful in the study of static and dynamic properties of bulk liquid metals\(^10\)\(^12\)\(^13\)\(^14\), as well as in the understanding of the thermal properties of some metallic clusters\(^15\) (including an anomalous variation of the melting temperature in Na clusters with size\(^16\)), its more approximate character (as compared to KS-AIMD ones) might induce someone to wonder if the theory is at all applicable to metallic surfaces, or at least to question how accurate it is. In this work we perform OF-AIMD simulations for the two solid systems mentioned previously, Al(110) and Mg(1010), for which the KS calculations can be taken as a benchmark. The case of Al will permit a direct
II. METHOD

A simple \textit{sp} bonded metal is treated as a set of \( N \) bare ions with valence \( Z \), enclosed in a volume \( V \), and interacting with \( N_e = NZ \) valence electrons through an electron-ion potential \( v(r) \). The total potential energy of the system can be written, within the Born-Oppenheimer approximation, as the sum of the direct ion-ion coulombic interaction energy and the ground state energy of the electronic system, \( E_g \), under the external potential created by the ions, \( V_{\text{ext}}(\vec{r}, \{\vec{R}_i\}) = \sum_{i=1}^{N} v(|\vec{r} - \vec{R}_i|) \),

\[
E(\{\vec{R}_i\}) = \sum_{i<j} \frac{Z^2}{|\vec{R}_i - \vec{R}_j|} + E_g[\rho_g(\vec{r}), V_{\text{ext}}(\vec{r}, \{\vec{R}_i\})],
\]

where \( \rho_g(\vec{r}) \) is the ground state electronic density and \( \vec{R}_i \) are the ionic positions.

According to DFT, the ground state electronic density, \( \rho_g(\vec{r}) \), can be obtained by minimizing the energy functional \( E[\rho] \), which can be written

\[
E[\rho(\vec{r})] = T_s[\rho] + E_H[\rho] + E_{\text{xc}}[\rho] + E_{\text{ext}}[\rho]
\]

where the terms represent, respectively, the electronic kinetic energy, \( T_s[\rho] \), of a non-interacting system of density \( \rho(\vec{r}) \), the classical electrostatic energy (Hartree term),

\[
E_H[\rho] = \frac{1}{2} \int d\vec{r} d\vec{s} \frac{\rho(\vec{r})\rho(\vec{s})}{|\vec{r} - \vec{s}|},
\]

the exchange-correlation energy, \( E_{\text{xc}}[\rho] \), for which we adopt the local density approximation, and finally the electron-ion interaction energy, \( E_{\text{ext}}[\rho] \), where the electron-ion potential has been characterized by a local ionic pseudopotential which has been constructed within DFT.

\[
E_{\text{ext}}[\rho] = \int d\vec{r} \rho(\vec{r}) V_{\text{ext}}(\vec{r}),
\]

In the KS approach to DFT \( T_s[\rho] \) is calculated exactly by using single particle orbitals. The huge computational effort involved in this approach for large systems is alleviated in the OF-AIMD approach by use of an explicit but approximate functional of the density for \( T_s[\rho] \). Proposed functionals consist of the von Weizsäcker term,

\[
T_W[\rho(\vec{r})] = \frac{1}{8} \int d\vec{r} |\nabla \rho(\vec{r})|^2 / \rho(\vec{r}),
\]

plus further terms chosen in order to reproduce correctly some exactly known limits. Here, we have used an average density model, where \( T_s = T_W + T_\beta \),

\[
T_\beta = \frac{3}{10} \int d\vec{r} \rho(\vec{r})^{5/3-2\beta} \tilde{k}(\vec{r})^2
\]

\[
\tilde{k}(\vec{r}) = (2k_F^0)^3 \int d\vec{s} k(\vec{s}) w_\beta(2k_F^0 |\vec{r} - \vec{s}|)
\]

\( k(\vec{r}) = (3\pi^2)^{1/3} \rho(\vec{r})^{1/3} \), \( k_F^0 \) is the Fermi wavevector for mean electron density \( \rho_e = N_e/V \), and \( w_\beta(x) \) is a weight function chosen so that both the linear response theory and Thomas-Fermi limits are correctly recovered. Further details are given in reference \[13\].

Another key ingredient of the energy functional is the local ion pseudopotential, \( v_{ps}(r) \), describing the electron-ion interaction. For each system, the \( v_{ps}(r) \) has been constructed from first principles by fitting, within the same \( T_s[\rho] \) functional, the displaced valence electronic density induced by an ion embedded in a metallic medium as obtained in a KS calculation. Further details on the construction of the pseudopotential are given in reference \[13\].

Given an ionic configuration, the electronic ground state is obtained, the potential energy for the ions is evaluated and the forces acting on them found using the Hellmann-Feynman theorem. These are then used to move the ions according to Newton equations of motion into a new configuration, after which the whole procedure is repeated.

III. RESULTS

In order to compare our OF-AIMD data with those obtained by KS calculations we have used in our simulations exactly the same setup as in the previous KS studies. As a result, in the case of Al(110) we have 8 layers of 9 atoms each plus a vacuum of 8.5 Å in our simulation cell, in which the in-plane lattice spacing is taken as the experimental one for each temperature considered. In the case of Mg(1010) we consider 16 layers of 4 atoms each and an 8.5 Å vacuum, with again the experimental in-plane lattice spacings.

A. Al(110)

The OF-AIMD simulations of Al(110) have been performed for two temperatures close to those where ex-
FIG. 1: Results for the interlayer relaxations in percent $100(d_{ij}(T) - d_{ij}^{\text{bulk}}(T))/d_{ij}^{\text{bulk}}(T)$, for Al(110). Full circles: OF-AIMD results. Line: best linear fit to them. Hatched squares: uncorrected KS-AIMD results. Lozenges with lines: experimental data.

Experimental data obtained through low energy electron diffraction (LEED) were reported, namely $T = 70$ and 310 K, and also at a higher temperature of 707 K, near one of the KS-AIMD simulations.

For comparison, the KS-AIMD simulation time was between 5 and 10 ps depending on the temperature (for $T = 700$ K it was 6 ps) with runs performed on a vector supercomputer (Hitachi S3600), and the OF-AIMD simulation times were between 8 and 16 ps after an initial equilibration time of 2-4 ps after an initial equilibration time of 2-4 ps (8 and 4 ps respectively for $T = 707$ K), with runs performed on an Intel Centrino laptop (with a Pentium M processor).

The interlayer distances obtained from our simulations are plotted in figure 1, together with the experimental data and the results of the KS-AIMD simulations. Note that the KS-AIMD results published in reference 9 were corrected rigidly by the difference between a KS calculation at $T = 0$ K using the same setup and another one using more layers, one atom per layer, and better Brillouin zone sampling. In figure 1 we have plotted the uncorrected results in order to make a fair direct comparison between the OF-AIMD and the KS-AIMD results for the simulation setup used.

B. Mg(10̅10)

The OF-AIMD simulations for this system have been performed near the temperatures at which the LEED study was performed, which also coincide with the temperatures of the KS-QHA calculations, namely $T = 106, 308$ and 399 K. The equilibration and production runs spanned a time of 4 and 8 ps respectively.

FIG. 2: Results for the interlayer relaxations in percent $100(d_{ij}(T) - d_{ij}^{\text{bulk}}(T))/d_{ij}^{\text{bulk}}(T)$, for Mg(10̅10). Full circles: OF-AIMD results. Thick continuous lines: best linear fit to them. Hatched squares: KS-QHA results. Dashed lines: best linear fit to them. Lozenges with error bars: experimental data. Thin continuous lines: best linear fit to them.

Figure 2 shows the results for this system. For the hcp structure in this orientation there are two types of interlayer distances, a short interlayer distance, between the first and second layers, between the third and fourth layers and so on, and a long interlayer distance (twice as large in the bulk solid) between the second and third layers, between the fourth and fifth layers and so on. We have separated figure 2 into two panels in order to appreciate more clearly the thermal variation of the interlayer distances of both types.

IV. DISCUSSION AND CONCLUSIONS

Starting with Al(110) we first remark that the OF-AIMD simulations recover the oscillatory pattern of interlayer relaxation observed experimentally, and also the thermal variation of these data, showing a negative first interlayer thermal expansion coefficient and a positive one for all the inner interlayer relaxations. The agreement with the experimental data at 70 and 310 K is excellent, but we would rather emphasize the reproduction of the trends rather than the numbers. One of the main reasons for stressing this is the lack of a detailed analysis of size effects in the simulations. According to recent all-electron first principles calculations of the properties of Al surfaces 17, it might be necessary to include as many as 23 layers in the simulation for the (110) orientation in order to obtain fully converged results. This of course needs to be tested for the OF-AIMD simulations before a comparison with experimental data can be made at a quantitative level.

Comparing with KS-AIMD results, we find a reason-
ably good agreement, taking into account the differences in the simulations (kinetic energy functional and pseudopotentials). In any case, again we think that the important point is the reproduction of the trends observed in the KS simulations.

Coming to Mg(1010), we again remark first that the OF-AIMD results reproduce the trends of relaxation and thermal variation in this system. The short interlayer distances both contract and show negative thermal expansion coefficient, while the long interlayer distances both expand and show positive thermal expansion coefficient. The magnitude of the contractions is reproduced with better accuracy than that of the expansions, but nevertheless the trend is the correct one.

When comparing with the KS-QHA data we outline three points. First, the magnitude of the relaxations obtained from the KS-QHA is closer to the experimental one than that of the OF-AIMD simulations. Second, the thermal variation of the KS-QHA and OF-AIMD results is very similar, as observed from the slope of the linear fit to both types of data. And third, both approaches underestimate largely the thermal variation found in the experimental measurements, which show a much larger slope for the first three interlayer distances.

Summarizing, the OF-AIMD results for the structure of the open surfaces considered and their thermal variation reproduce qualitatively the experimental trends. In many cases, the results are also very similar to those obtained through more expensive methods as KS-DFT, either used within AIMD simulations or within the QHA, with the only exception of the magnitude of the expansion of the long interlayer distances in the hcp structure. A quantitative comparison with experimental data is at present not sensible, since a detailed study of size effects in the simulations is necessary, most surely for Al(110) but probably also in the case of Mg(110). This analysis is under way and will be presented elsewhere.

In our opinion, the results shown in this work, added to those already published for bulk metallic liquids and for metallic clusters, further demonstrate that the OF-AIMD method is not only practical, but also reliable for the study of metallic systems, and in particular metallic surfaces.

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