Orbital-free ab-initio study of the structure of liquid Al on a model fcc metallic wall: the influence of surface orientation.

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Abstract. It is well known that liquids on a wall adopt layered structures, even for simple atom-atom and atom-wall interactions. Liquid metals, moreover, also stratify when a free surface is exposed. In this contribution we analyse the structure of 2000 atoms of liquid Al in contact with a metallic wall described atomistically (not in an integrated way), and modeled as an array of Al atoms fixed at the sites of an fcc lattice, somehow simulating a metallic material with a much higher melting temperature. We analyse how the liquid structure is affected by the orientation of the wall surface (100, 110 and 111), finding large differences in the liquid properties for the different surface setups. Specifically, for the 100 surface we find a “normal” solid-liquid interface, for the 110 orientation we observe a preferential positioning of the liquid atoms along the solid surface channels, whereas for the 111 setup an induced crystallisation of the liquid takes place.

1. Introduction.
Interfaces between solids and liquids play an important role in a number of technological and physical processes, like soldering, lubrication, wetting or crystal growth just to mention a few. Atomistic simulations for this type of systems can provide information not only on the density profile of the liquid perpendicular to the wall (as when an integrated z-dependent wall-liquid interaction is used), but also on the transverse in-plane order induced by the periodic surface potential, which depends on the crystal structure and the surface orientation. Such studies have been undertaken both for model systems (Lennard-Jones, hard spheres) and also for some metallic liquids (particularly, Al) in contact with metallic solids. The solid was routinely assumed to be in the FCC structure, whereas several orientations have been considered, mainly the (100) and (111) cases, although some studies also considered the (110) orientation. For a recent review, see [1].

The main caveat for the simulation of realistic liquids on realistic solids is the correct description of the forces between atoms. Even if the bulk liquid and bulk solid phases can be well described separately by given potentials, the presence of an interface brings forth the question of the cross interactions and the modifications in the potentials corresponding to one phase due to the proximity of the other (see ref. [2] for the case of liquid Al on solid Cu). One way to alleviate these problems is to study the liquid laying on a wall composed by the same type of atoms (e.g. liquid Al in contact with solid Al). This kind of simulations, however, are restricted to a temperature for which there is coexistence between solid and liquid, i.e., the
melting temperature, and several studies have indeed been performed this way [3, 4]. Higher temperatures are not feasible since the solid would melt. A last step to be taken in the modeling is to pin the solid atoms to their ideal crystallographic positions, not letting them move. In this way any temperature (of the liquid) is possible, and in fact one would be somehow simulating a solid with a much higher melting temperature. Hashibon et al [5] performed such an analysis for the case of liquid Al on ideal FCC Al at 1000 K, and analysed the properties of the liquid in terms of the solid surface orientation.

In most of the simulations of liquid metals on solids, the interactions were computed within the embedded atom model (EAM). Successful as it may be (for instance in the case of Al), nevertheless at the end one resorts to fitting parameters, and different parametrisations can lead to substantially different behaviours away from the fitting state. For instance in liquid Al the EAM parametrisation used by Hashibon et al leads to the appearance of a solid-like non-crystalline state at low temperatures [6] which is absent in other EAM parametrisations for Al, and also in real Al. Needless to say, many other interesting metallic liquids cannot be described within the EAM. There is therefore a call for a better description of the interactions, which can take consistently into account all the aspects present in solid-liquid interfaces, like mixing of atomic species, segregation or clustering. A clear candidate is Density Functional Theory (DFT) [7, 8], which would give rise to ab initio simulations. Standard ab initio simulations are however prohibitive for sizes that reasonably describe a solid-liquid interface. Orbital-free (OF) methods [9], which alleviate greatly the computational demands, open up such possibility. In this contribution we analyse the same system as Hashibon et al [5] through OF ab initio molecular dynamics (OF-AIMD), both as a check and as a seed for future studies on more realistic solid-liquid interfaces. We should mention that solid Al (100) in equilibrium with its melt has already been studied through OF-AIMD simulations [4], using however a different functional and pseudopotential than the ones used in this work; that study lead to a melting temperature around 300 K too low.

2. Theory and results.

Details on the approximate kinetic energy functional used in the OF-AIMD simulation and on the local pseudopotential can be found elsewhere [10]. The simulation cell is orthorhombic, and in the z-direction we have, consecutively, vacuum, several solid layers exposing a given orientation, 2000 liquid particles and further vacuum. All of this is repeated periodically along the three axes. Note that we are therefore studying simultaneously a free solid surface, the solid-liquid interface, and a free liquid surface; of these we focus here on the second one. Since solid atoms contribute to the forces on the liquid atoms but do not move, we do not need a large number of solid layers; we have taken 3, 6 and 3 layers for the (100), (110) and (111) orientations respectively, with a larger number for the (110) surface due to the smaller interlayer distance. This amounts to 294, 432 and 324 solid atoms respectively. The properties of the systems at 1000 K were obtained from OF-AIMD equilibrium runs 30-40 ps long. We analysed the density profiles corresponding to ions and to valence electrons (both of them layered), the transverse pair correlation functions (PCF), \( g_T(r) \), and the atomic motion (the mean squared displacement (MSD)) within the layers along the nearest neighbours lines of the solid surface (which conform channels in the (110) case) and in a perpendicular direction.

Results for the (100) orientation are shown in figure 1, and for the (110) orientation in figure 2. Although both orientations lead to layered profiles and gradual transition from solid-like to liquid-like transverse ordering, there are, however, important qualitative differences. The interlayer spacing in the (100) case is larger than the solid one, while in the (110) orientation, where it is much smaller, it is identical. The number of layers is similar, but in the (100) case they penetrate deeper into the liquid region. In the (100) case the transverse \( g_T(r) \) evolves from solid-like in the first layer to almost the bulk liquid one at the third layer, while for the (110)
orientation the influence of the solid surface extends quite longer: even at the sixth layer one can see clear differences with the bulk liquid $\rho_T(r)$. These results confirm those of Hashibon et al [5] for the same system. We provide additional information from the valence-electron profile and from dynamic properties. The electronic profile is in opposite phase to the ionic one inside the solid and also in the liquid part for the (110) orientation, while the phase shift decreases for the (100) orientation as a consequence of the larger interlayer spacing [11]. The analysis of the dynamic properties underpin the previous conclusions: while in the (100) case the atoms show for all layers a diffusive motion that is gradually hindered by approaching the solid, for

![Figure 1](image1.png)

**Figure 1.** Results for the (100) surface. (a) Ionic (full line and symbols) and electronic (dashed line) profiles. Vertical lines correspond to solid (100) interlayer spacing. (b) Transverse PCF in layers 1 to 3. Vertical lines correspond to the (100) solid surface, and dashed ones to the bulk liquid. (c) Mean squared displacements.

![Figure 2](image2.png)

**Figure 2.** Results for the (110) surface. (a) Ionic (full line and symbols) and electronic (dashed line) profiles. Vertical lines correspond to solid (110) interlayer spacing. (b) Transverse PCF in the labelled layers. Vertical lines correspond to the (110) solid surface, and dashed ones to the bulk liquid. (c) Mean squared displacements along (full lines) and across (dashed lines) the surface channels direction.
the (110) orientation we find two important differences, the first three layers are solid (atoms do not diffuse) and even as far as at the sixth layer (∼9 Å from the surface) there is a clear anisotropy, since the atoms diffuse better along the channels lines than across them.

The (111) surface orientation leads to quite different results: we find that as the simulation proceeds the liquid crystallises layer by layer. In the 32.25 ps simulated around 10 layers solidify (see figure 3). This suggests that at 1000 K the liquid is in fact somewhat undercooled and when faced with an appropriate seed undergoes crystallisation. While the (111) surface induces full solidification, the (110) surface is not as effective leading to 3 solid layers of decreasing ordering, and the (100) is especially ineffective, as only the first layer shows solid-like ordering but the atoms diffuse. In any case further checks of the thermodynamic melting temperature of our \textit{ab initio} model would be useful.

3. Conclusions.

Our results, besides confirming, extending and showing some differences with previous studies, show the ability of OF \textit{ab initio} method to describe solid metal - liquid metal interfaces in an atomistic way, using a large number of particles, which is especially important concerning the liquid part of the system. Moreover, our functional and pseudopotential [10] appear to give a better estimate for the melting temperature of Al than those used in ref. [4], although now it seems to be somewhat higher than the experimental one.

Further work along the lines of this work will include the study of free solid surfaces and of liquid metals on real metallic solids (with moving atoms); both kind of studies will however require the inclusion of more solid layers in the simulation than those used in this work.

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