Layering at liquid metal surfaces and interfaces: Friedel oscillations and confinement effects

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The structures of the liquid surface and the liquid-solid interface of sodium have been characterized with extensive first-principles molecular dynamics simulations. Friedel oscillations in the electronic charge density at the free surface were found to persist across the solid-to-liquid melting transition, with a small but distinctive electronic layering that remains decoupled from the atomic positions. Strong ionic layering was observed both at the liquid surface and at the liquid-solid interface, notwithstanding the absence of Friedel oscillations or under-coordinated atoms in the latter case. Confinement effects at these soft or hard boundaries drive the atoms into quasi-close-packed layers; even for this prototypical free-electron metal Friedel oscillations are not relevant to ordering.

PACS numbers: 61.25Mv, 68.03.Hj, 71.15.Mb, 71.15.Pd

Intensive theoretical and experimental work has focused on liquid metal surfaces, showing the existence of surface-induced layering, where liquid atoms near the surface arrange themselves into distinct layers. Such behavior is not present at the free surfaces of dielectric or ionic liquids, while it is observed for metallic and dielectric liquids confined by hard walls. These differences in the surface structure mirror fundamental differences in bonding and screening. The interplay of comparable energetic and entropic effects can then lead to a varied thermodynamical phenomenology for the structure of liquid surfaces and interface boundaries, including in-plane and out-of-plane ordering transitions, and reminiscent of the complex stability and phase diagrams of crystalline surfaces.

Computer simulations have played a pivotal role in investigating the nature and mechanisms of layering transitions at liquid metal surfaces. Effective-Hamiltonian simulations suggested that the rapid decay of the valence electronic density acts as a wall against which atoms pack, in close analogy with the layer formation at a solid-liquid interface. Glue-model simulations of liquid Au, Al and Pb led to the complementary suggestion that under-coordinated atoms at the surface attempt to regain the favorable coordination of the bulk liquid by moving inwards, increasing the density in the outermost layer and causing a density oscillation to propagate into the bulk. Density-functional theory (DFT) simulations of silicon (metallic in its liquid phase) found instead that covalent-bond induced correlations were responsible for the layering of the density. Recently it was suggested that metallic bonding does not play an important role per se, and a layered density profile should appear at the free liquid surface of any substance with a low ratio of melting and critical temperatures (with the caveat that the observation of layering is then usually preempted by solidification). Last, it was proposed on the basis of first-principles calculations for magnesium that electronic Friedel oscillations drive the interlayer relaxations at solid metal surfaces.

Prompted by these studies, we have decided to characterize the structure of liquid surfaces and interfaces of sodium by means of extensive first-principles calculations (over 250 ps in total, on cells containing ~160 atoms), using DFT paired with an accurate generalized-gradient approximation to the exchange-correlation potential. Sodium was chosen for its paradigmatic behaviour as a nearly-free-electron metal, and for the challenges it poses to experiments due to its low surface tension that leads to thermally-excited capillary waves. While recent results have appeared for Na:K alloys and pure K, layer formation was extrapolated from the lead-up to a peak in the x-ray reflectivity, rather than the direct observation of a full peak, as was the case for all other metals for which layering was conclusively observed (Ga, In, Hg). The liquid surfaces of Na, Li, and Na:K alloys have also been recently studied from first-principles – albeit using approximate orbital-free versions of DFT based on kinetic energy functionals – and ionic layering at the surface was observed.

In our calculations, we used state-of-the-art approaches to first-principles molecular dynamics (MD) to examine the microscopic structure and dynamics at the free surface or interface. More importantly, we de-
vised a series of gedanken computer experiments to elucidate the role and nature of the electronic and ionic responses to a surface or interface.

First, we performed extensive simulations of the Na liquid surface at two temperatures (400 K and 500 K) above the melting point (371 K). We started with two bulk structures corresponding to a bcc crystal containing either 160 atoms arranged in 10 layers along the [001] direction or 162 atoms in 18 layers along the [111] direction. We chose two different geometries to rule out any influence of the supercell cross-section on the intra-layer atomic ordering. These systems were melted and equilibrated at high temperature; then, a vacuum layer of thickness \( \sim 11 \, \text{Å} \) was inserted along the the [001] or [111] direction to create two liquid slabs from the bulk samples. MD simulations for each of these two slabs were performed for 50 ps (20 ps of equilibration and 30 ps of data collection) at 400 K and 500 K. Careful consideration was given to finite-size effects, by (a) analyzing the density-density autocorrelation function \( \mathcal{C} \), which demonstrated independence of the oscillations propagating from the two opposite surfaces in each slab, and (b) running a series of classical MD simulations on increasingly larger systems, which established that the systems chosen were large enough to avoid any effect of one surface on the local structure of the other surface, and small enough not to have layering washed away by capillary waves. All simulations used ensemble-density functional theory (EDFT) and a 0.5 eV cold-smearing generalized entropy, a formulation particularly efficient for metals. We used Troullier-Martins pseudopotentials, the PW91 generalized-gradient approximation for the exchange and correlation functional, non-linear core-corrections and the Baldereschi point for Brillouin zone integrations.

Fig. 1 shows the density profiles normal to the liquid slab; clear oscillations in the atomic densities are visible, indicating layer formation. Oscillations in the valence electronic densities are also seen, corresponding roughly to the interlayer regions. Layering is clearly evident in the simulations at 400 K; above that temperature, entropy starts to overcome the ordering in the liquid, and at 500 K the atomic peaks are already significantly reduced. The atomic density profiles indicate formation of 7 layers parallel to the surface; while the finite thickness of our slabs meant that layers appeared throughout the systems, we stress again that classical simulations showed that the structure and layering at the surface would not change if more layers were introduced.

Second, in order to establish whether layering is driven by electronic screening, confinement, or densification following decreased coordination at the surface, we examined – in a computational proof of principle – two different case studies for which these effects can be decoupled.

We first monitored the electronic response of a perfect solid and of a disordered bulk liquid to the creation of surfaces. These surfaces were obtained, for any given atomic configuration, by cleaving a sample in half and rigidly separating the two fragments with the insertion of a large amount of vacuum. The atoms were not allowed to relax, and thus all the screening comes from the reorganization of the electronic charge density in response to the appearance of surface boundaries. We calculated the charge redistribution induced by such perturbations: electronic densities for the bulk and the cleaved systems were first individually determined, and then subtracted to obtain direct information on the electronic screening. In Fig. 2 we show the results for the case of an ordered solid, where, starting from a bcc Na crystal, characteristic Friedel oscillations appear following the creation of ideal (001) or (111) surfaces. These results are in close agreement with the findings for Mg of Ref. [13], and highlight the remarkable appearance of Friedel oscillations due to the response of the valence electrons to the perturbation created by the surface boundary.

Next, we performed the same analysis for thermally-equilibrated bulk liquid samples. We took atomic configurations from a number of uncorrelated timesteps of a 500 K MD simulation of the bulk liquid, and for each configuration inserted a thick vacuum layer. Again, the atomic positions were kept frozen, so that no relaxation or thermalization of the atoms was allowed and thus no atomic layers were present. The valence electronic densities for these configurations are shown in the top panels of Fig. 3 for a set of bulk configurations and their cleaved counterparts. Remarkably, when charge-density differences are taken, very clean and distinct Friedel patterns are recovered (Fig. 3, middle panel) even for such disordered, “bulk liquid”-like surfaces, in close analogy
with the cleaving of perfectly-ordered solids. This result proves the persistence of electronic Friedel oscillations through the melting and disordering of the solid. It also underlines how, for this simple metal, the effect of the atomic positions on the electronic response is minimal.

To confirm this last point we examined the differences in the Hellmann-Feynman forces (in the direction perpendicular to the surfaces) for Na atoms in the bulk-liquid and cleaved configurations. These differences are shown in the bottom panel of Fig. 3 and highlight the absence of Friedel-like patterns in the atomic forces. While differences in the atomic forces in the region where surfaces were created are clearly visible, these effects decay rapidly, and the atoms away from the surface by more than 2-3 Å would not be significantly affected or modulated in their dynamics by the electronic response.

In the second part of our proof of principle we considered instead a confined bulk liquid. We created in our bulk simulations (using the (001) supercell geometry of 160 atoms described earlier) a fixed layer of sodium atoms: given that periodic boundary conditions were in place, the bulk liquid metal was then confined between two infinite 2-dimensional hard walls. Since these walls were only one-layer thick, and composed of metallic sodium at a density practically identical to that of the liquid, they would not give rise to any charge density discontinuity and associated Friedel oscillations. Also, no loss of coordination was experienced by the atoms in the liquid close to the interface, and thus there was no driving force towards densification at the liquid boundary. The fixed layers were created by rearranging 24 of the 160 atoms in the bulk liquid supercell into an hexagonal planar structure (slightly strained in one direction, to accommodate the square cross-section of the (001) simulation cell). MD simulations were then performed at 400 K and 800 K. We show in Fig. 4 the atomic and valence electronic densities obtained. Again, the distinctive formation of layers is observed, persistent now even at the high temperature of 800 K. In perfect analogy with the case of the liquid slabs, the atoms here rearranged themselves into 7 distinct layers. Thus, we have again obtained layering for the sodium atoms close to a boundary, notwithstanding the absence of Friedel oscillations. This consideration, together with the previously observed lack
of modulation in the ionic forces attributable to the electronic response, rules out Friedel oscillations in driving ionic layering. In addition, in the confined liquid sample – as opposed to the free surface – there were no under-coordinated atoms and no driving force to increase the density of the surface and to initiate the formation of a distinctive surface layer. Thus, a liquid analogue of the densification observed at the surface of open solid surfaces and the associated interlayer contraction also needs to be ruled out, pointing finally at geometric confinement effects as the foremost and common cause of layering oscillations both at the liquid surface and at the liquid-solid interface of simple metals. These simple geometric considerations are reinforced by the study of the pair distribution functions in the surface plane, that show remarkably persist through the transition to a liquid surface.

In summary, we have characterized with extensive first-principles MD simulations the free liquid surface and the liquid-solid interface of sodium, chosen as a paradigmatic example of a free-electron metal. We found clear signatures of Friedel oscillations at the solid surfaces that remarkably persist through the transition to a liquid surface. These oscillations are decoupled from the underlying atomic positions, and do not appreciably affect the ionic forces on the system. Very clear ionic layering was observed for the liquid surfaces, and an even stronger layering was found for the liquid confined by its own solid. Given that Friedel oscillations are absent in the latter case, and that a homogeneous valence charge density rules out any driving force for densification at the boundary, we conclude that geometric confinement is the foremost cause of layering. The confinement induced by the presence of a solid boundary is stronger than in the case of a vacuum boundary, and layering is correspondingly stronger for the liquid bound by its own solid.

B. G. W. thanks the New Zealand Foundation for Research Science and Technology and the Cambridge Overseas Trust for research studentships.

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