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## LETTER TO THE EDITOR

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

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### Abstract

The structures of the liquid surface of sodium have been characterized with extensive first-principles molecular dynamics simulations based on ensemble density functional theory. Friedel oscillations in the electronic charge density at the free surface were found to persist across the solid-to-liquid melting transition, and remain decoupled from the atomic positions. Strong atomic layering was observed both at the liquid surface and at an artificial 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.

Intensive theoretical [1–5] and experimental [6, 7] work has focused on liquid metal surfaces, showing the existence of *surface induced layering*, where liquid atoms near the surface arrange into distinct layers. Such behaviour is not usually present at free surfaces of dielectric or ionic liquids [8], while it is observed for metallic and dielectric liquids confined by hard walls [9]. These differences in surface structure mirror fundamental differences in bonding and screening. The interplay of comparable energetic and entropic effects can lead to a varied thermodynamical phenomenology for the structure of liquid surfaces and interface boundaries, including in-plane and out-of-plane ordering transitions, reminiscent of the complex stability and phase diagrams of crystalline surfaces.

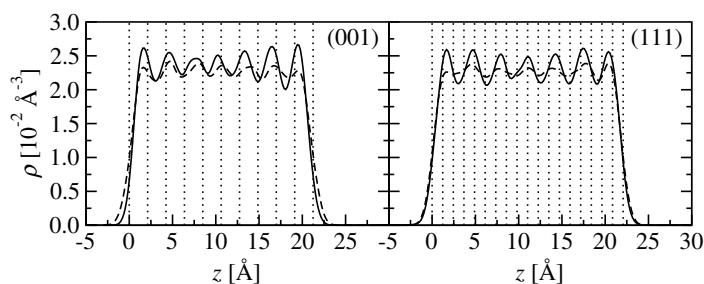
Computer simulations have played a pivotal role in investigating the nature and mechanisms of layering at liquid metal surfaces. Effective-Hamiltonian simulations [1] suggested the rapid decay of the valence electron density acts as a wall against which the atoms pack, in analogy with layer formation at a solid–liquid interface [9]. Glue-model simulations of liquid Au, Al and Pb [2] led to the complementary suggestion that under-coordinated surface

atoms attempt to regain the favourable 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 that covalent bond induced correlations were responsible for the layering of the density [3]. It has also been 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 pre-empted by solidification) [4]; this seems to be supported by very recent experimental data for a molecular liquid [10]. Lastly, it was proposed on the basis of DFT calculations for Mg that electronic Friedel oscillations drive the inter-layer relaxations at solid metal surfaces [11].

Prompted by these studies, we have characterized the structure of liquid surfaces and interfaces of sodium with extensive first-principles calculations (over 250 ps in total, on cells of  $\sim 160$  atoms). Sodium was chosen as a paradigmatic 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 experimental results have appeared for Na:K alloys and pure K [7], 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 the other metals for which layering was conclusively observed (Ga, In, Hg, Sn) [6]. The liquid surfaces of Na, Li, Na:K alloys, Al, Mg and Si [5] were also studied recently from first principles—albeit using approximate orbital-free versions of DFT based on kinetic energy functionals [12]—with atomic surface layering observed.

We used state-of-the-art approaches [13] to first-principles molecular dynamics (MD) to examine the microscopic structure and dynamics at the free surface or interface. More importantly, we devised a series of *gedanken* computer experiments to elucidate the role and nature of the electronic and atomic responses to a surface or interface. Firstly, we performed extensive simulations of the Na liquid surface at two temperatures (400 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 intra-layer atomic ordering. These systems were melted and equilibrated at high temperature; then a vacuum layer of thickness of  $\sim 11$  Å was added at the outer [001] or [111] faces of the bulk samples to create liquid slabs. MD simulations for each of these slabs were performed for 50 ps (20 ps of equilibration, 30 ps of data collection) at 400 and 500 K [14]. Careful consideration was given to finite-size effects, by (a) analysing the density–density autocorrelation function [3], which demonstrated independence of the oscillations propagating from the two opposite surfaces of each slab, and (b) running a series of classical MD simulations (with the Chacón *et al* Na pair potential [4]) on larger systems (e.g. for liquid slabs twice as thick, or with cell cross-sections up to 16 times as large), which established that the systems were large enough to avoid any effect of one surface on the local structure of the other, and small enough not to have layering washed out by capillary waves [14]. All simulations used ensemble density functional theory and a 0.5 eV cold-smearing generalized entropy, a formulation particularly efficient for metals [13]. We used Troullier–Martins pseudopotentials, the PW91 generalized-gradient approximation exchange–correlation functional, non-linear core corrections, and the Baldereschi point for Brillouin zone integrations [15].

Figure 1 shows the density profiles normal to the liquid slab; clear oscillations in the atomic densities are visible, indicating layer formation. Layering is clearly evident in the simulations at 400 K; above that temperature, entropy starts to overcome the ordering in the liquid, and at



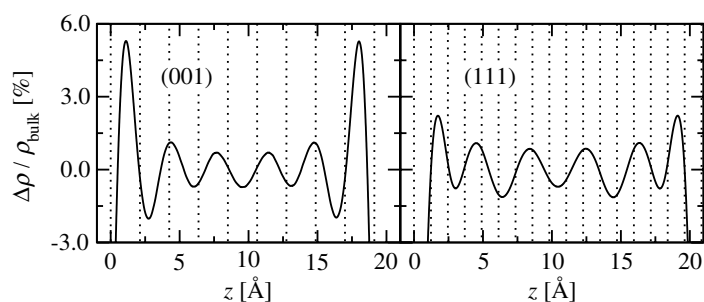
**Figure 1.** Atomic density profiles for the different (001) (left) and (111) (right) liquid slabs, plotted normal to the liquid surfaces for simulations performed at 400 K (solid line) and 500 K (dashed line); the vertical lines indicate the layer positions in the crystalline surfaces.

500 K the atomic peaks are already significantly reduced. The atomic density profiles indicate formation of seven liquid 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. The seven layers formed in the liquid slabs are unrelated to the atomic layers in the original crystals from which they were obtained by melting. The heights of the surface peaks are roughly the same as for the second peaks in from the surface, a situation closer to that seen in the analysis of the experiments, and quite different from that found in the orbital-free simulations [5], and in our classical simulations. The average atomic layer spacings are  $2.98 \pm 0.23$  and  $3.02 \pm 0.25$  Å at 400 and 500 K respectively; these are quite close to the expected Friedel wavelength for sodium  $\lambda_{\text{Fr}} = 3.4$  Å [16], making differentiation between Friedel and confinement effects difficult in Na, the case under consideration.

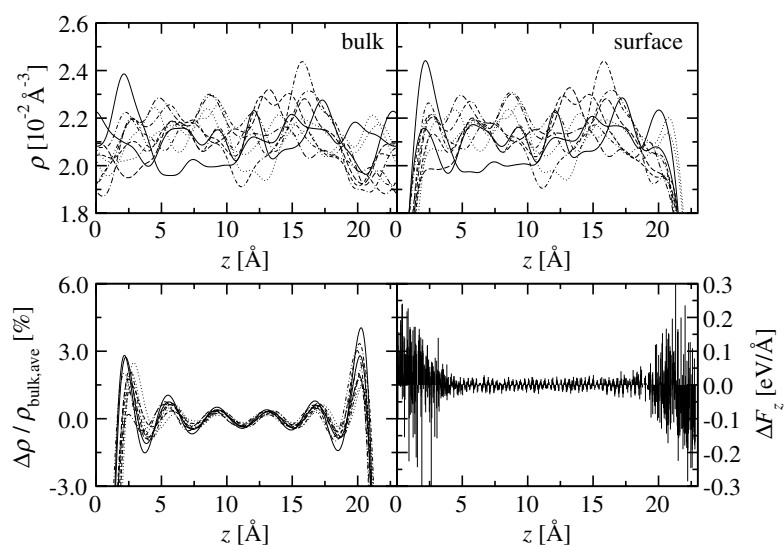
In order to establish whether layering is driven by electronic screening, confinement, or densification following decreased coordination at the surface, we examined—in a computational proof of principle—two different case studies for which these effects can be decoupled.

Firstly we found the electronic responses of a perfect solid and 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 screening was due to 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 determined individually, and then subtracted to obtain direct information on the electronic screening [11]. In figure 2 we show results for 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 [11], and highlight the remarkable appearance of Friedel oscillations due to the response of the valence electrons to the perturbation created by the surface boundary [16].

Next, we performed the same analysis for thermally equilibrated bulk liquid samples. We took atomic configurations from a number of uncorrelated time steps of a 500 K bulk liquid MD simulation, and inserted a thick vacuum layer in each. Again, the atomic positions were kept frozen, so no relaxation or thermalization of the atoms was allowed and thus no atomic layers were present. The valence electronic densities appear in the top panels of figure 3 for a set of bulk configurations and their cleaved counterparts. Remarkably, when charge density

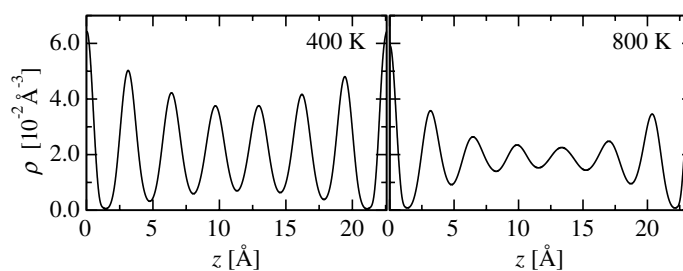


**Figure 2.** Valence electronic charge density response to the creation of surfaces in perfect crystalline Na, cleaved to expose either the (001) or (111) surfaces. The vertical lines indicate the positions of the atomic layers.



**Figure 3.** Top panel: valence electronic charge densities for uncorrelated configurations from a bulk liquid MD simulation: periodic bulk system (left) and cleaved systems (right). Bottom panel: charge density differences between the bulk and cleaved systems, clearly showing Friedel oscillations (left) and Hellmann–Feynman atomic force differences between the bulk and cleaved systems in the direction perpendicular to the cleaved surfaces (right).

differences are taken, clean Friedel patterns are recovered (figure 3, middle panel) even for such disordered, ‘bulk liquid’-like surfaces, in close analogy with the cleaving of perfectly ordered solids. This 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 differences in the Hellmann–Feynman forces (in the direction perpendicular to the surfaces) for atoms in the bulk liquid and cleaved configurations. These differences are shown in the bottom panel of figure 3. The absence of observable Friedel-like patterns means the modulation of the atomic forces corresponding to the Friedel oscillations in the charge densities is below the level of thermal noise. While atomic force differences are visible in the regions where surfaces were created, these decay rapidly, and the dynamics of atoms more than 2–3 Å from the surface would not be significantly affected or modulated by the electronic response.



**Figure 4.** Atomic density profiles for the confined liquid at 400 K (left) and 800 K (right). The (001) fixed monolayers are at  $z = 0$  Å.

In the second part of our proof of principle we considered a confined liquid. We created in a bulk liquid simulation (with the (001) supercell geometry containing 160 atoms described earlier) a fixed layer of sodium atoms: as periodic boundary conditions were in place, the bulk liquid metal was confined between two infinite two-dimensional hard walls. Since the 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 (001) simulation cell cross-section). MD simulations were then performed at 400 and 800 K (with cell sizes scaled linearly). We show in figure 4 the atomic densities obtained. Again, distinctive layer formation is observed, even at 800 K (over twice the melting point of Na). In perfect analogy with the free surface liquid slabs, the atoms here rearranged themselves into seven distinct layers. Thus, we have again obtained layering of sodium atoms close to a boundary, notwithstanding the absence of Friedel oscillations. This consideration and the previously observed lack of modulation in the atomic forces attributable to the electronic response together rule out Friedel oscillations as driving atomic 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 initiate the formation of a distinct surface layer. Thus, a liquid analogue of the densification observed at free solid surfaces and the associated inter-layer contraction [17] also needs to be ruled out, pointing finally at geometric confinement effects as the foremost and common cause of layering oscillations at both the liquid surface and the liquid–solid interface of simple metals. These basic geometrical considerations are reinforced by the study of the pair distribution functions in the surface plane, that show a nearest-neighbour distance of  $\sim 3.8$  Å, which corresponds to 24–25 atoms in a quasi-hexagonal arrangement (the layers are not perfectly packed, with average in-plane coordination numbers between 4.5 and 5.3). Thus, for systems containing 160–162 atoms, we expect a number of close-packed layers between 6 and 7, consistent with what was found for the free and confined liquid systems. Close-packed layers at this density would be spaced by  $\sqrt{2/3} \times 3.8$  Å = 3.1 Å, which compares favourably with the free surface inter-layer spacings given earlier, and the values  $3.23 \pm 0.10$  and  $3.36 \pm 0.23$  Å for the liquid–solid interface at 400 and 800 K.

In summary, we have characterized with extensive first-principles MD simulations, at temperatures close to and well above the melting point, the free liquid surface and the interface between the liquid and a thin solid layer 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 forces on the atoms in the system. Very clear atomic 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.

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