A molecular dynamics study of density profiles at the free surface of liquid mercury

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Abstract. Molecular dynamics simulations have been performed to study the liquid/vapor interface of mercury as a function of temperature. Our calculations predict a biphasic equilibrium with non-monotonic density profiles not induced by the Friedel oscillations in the electronic density, but essentially due to atomic spacing in the liquid/vapor interface.

1. Introduction
Metallic liquids exhibit a complex surface structure in which the atoms are stratified parallel to the liquid/vapor interface in layers that persist into the bulk for a few atomic diameters. The existence of oscillations along the normal direction to the liquid/vapor interface for metals with low melting temperature (Hg and Ga) has been verified, by X-ray reflectivity measurements, only recently [1,2]. Since no oscillatory density profiles had been observed previously at the liquid/vapor (L/V) interface of dielectrics, layering was thought to be unique to metallic liquids. Despite different points of view, theoretical and simulations studies suggested that surface layering is due to the metallic character of binding interactions, that is to say to the account of the electron-gas whose signature is described by Friedel oscillations in the interionic potential. In addition, the many-body effects arising from the delocalized electrons emphasize to the appearance of surface oscillations. However, the previous statements have been called into question very recently. On the one hand, it has been pointed out that the many-body nature of metallic interactions does not necessarily play the leading role in the layering process [3], besides determining the shape of the interionic potential. On the other hand, a recent ab initio simulation study [4] shows that Friedel oscillations in the long-ranged part of the potential are not the driving force in atomic layering at the free liquid surface. In addition, the authors of a recent letter [5] have observed layers at the free surface of a nonmetallic liquid. This last finding supports that surface layering is a universal property of liquids at sufficiently low temperatures, as first suggested by Tarazona et al [3]. The authors demonstrated that fluids with isotropic pair interactions exhibit oscillatory interfacial structures for temperatures close to the melting temperature, provided that the ratio between the melting T_m and critical T_c temperatures is low. Cold liquids metals like Hg and Ga, which have low melting points leading to T_m/T_c = 0.13 and 0.15, respectively, support this result. We face the difficulty in reproducing the surface layering of cold liquids with an accurate interionic potential. In other words, an accurate theoretical study of cold liquids should require the knowledge of an effective interionic potential able to predict properly (i) the liquid branch of the

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coexistence L/V phase diagram in terms of temperature and density and (ii) the expected true liquid density when the solid melts. The surface layering of Hg is the main motivation of this work.

2. Interaction model and simulation details
Most of existing pair interaction models have been weakened by the fact that they over-estimate the melting temperature of real systems. Thus the observation of the oscillatory density profile at the free liquid surface is very often preempted by solidification, meaning that layering prediction is sensitive to the form of the interaction. It is difficult to guess the shape of an interionic potential that gives a realistic low $T_m/T_c$ together with an accurate incorporation of the subtle many-body effects in metals. In order to investigate the density profiles at the L/V interface, an interionic potential presenting low melting temperature is needed. In a previous work [6], we have developed an accurate interaction model to describe the structural and thermodynamic properties of liquid Hg, which reads

$$\Phi(r) = A_0 \exp(-\alpha r) - A_1 \exp[-\beta(r - R_0)^2].$$

The Born Mayer exponential term describes the repulsive part while the attractive part of the potential, whose minimum is located at $\tau = R_0$, is modelled by a Gaussian function. Here, $\Phi(\tau)$ presents a broad shape that is adapted to the study of Hg, since low melting point and high critical point are consequences of a broad and shallow pair potential [8]. Such form of interaction belongs to the class of the so-called ”Madrid liquids” [7]. The parameters are given in [6]. Contrary to pseudopotential theory [9–11], it should be noted that the model does not exhibit Friedel oscillations caused by the electron-gas, but, at a first stage, this is not a real drawback since, for Hg, these oscillations are strongly damped [9] as compared to other II B elements. Especially, this interaction model predicts the expected liquid density at the melting point ($T_m = 235 K$), namely $\rho_m = 13.69 \text{ g/cm}^3$, as well as the rest of the liquid branch of the pressure-temperature-density diagram. So, the predicted $T_m/T_c$ is sufficiently low so that this potential model can be considered as a good candidate to study the density profiles at the L/V interface in a wide range of temperatures. We carried out molecular dynamics simulations to determine the structure of the L/V interface at several temperatures. The equations of motion were integrated using a fourth order Gear predictor-corrector algorithm. The time step was chosen as 1 fs. Temperature control was achieved through the use of a Gaussian thermostat which fixes the total kinetic energy. In order to create an interface, we proceeded as follows. First, we equilibrated a liquid of 1000 Hg atoms at a temperature of 273 K and a density of 13.6 g/cm$^3$ (the density of liquid Hg at coexistence). The simulation cell had the following dimensions: $L_x = L_y = 24.56 \text{ Å}$ and $L_z = 40.61 \text{ Å}$. Periodic boundary conditions were applied in the three directions of space. We then used this equilibrated configuration as the starting point for the simulations of the interface. To simulate the interface, we simply performed a simulation without applying the periodic boundary conditions along the z axis, but only along the x and y axes. In each case, the interface so created was allowed to relax for 2 ns. Properties of interest were then averaged over another run of 5 ns. In order to check the validity of the previous process, the cell was elongated along the z axis (up to 100 Å) while applying the boundary conditions in the three directions and keeping the cell dimensions along the x and y axes constant (24.56 Å). The final results remained unchanged.

3. Results and discussion
As expected, our model predicts a biphasic equilibrium with non-monotonic density profiles at the L/V interface. The longitudinal density profiles are displayed in figure 1a. The simulated interfacial region separating these phases has a non zero thickness and a structure consistent with the large density change across it. The structure is found to be stratified and to depend on the temperature. A strong layering structure is observed at the lowest temperature $T=235 K$, which damps with increasing temperature. At ambient temperature ($T = 325 K$), a structure is still visible. The leading contribution for the damping of the structure, as temperature increases, comes from the capillary waves (CW) broadening of the interface. The theoretical analysis of the CW effects shows that, for any system with infinite transverse size $L_x$, the thermal average of the CW would remove the inhomogeneity of the
density profile $\rho(z)$ that becomes the global average of the density of the system. In other words, as far as the molecular resolution $L_x$ is concerned, the oscillatory density profile would be erased for large molecular resolution whereas, at the sharpest molecular resolution of about $L_x \approx \sigma$, the capillary waves vanish and an "intrinsic" density profile is observed [13]. In our case, the point is the size dependent effect of the CW on the damping of the oscillations for a small transverse size typically used in computer simulations. It is desirable to compare our profiles to available theoretical and experimental results for Hg.

The specific shape of the density profile obtained in this work is qualitatively similar to those calculated from simulations for other potential models [14]. The oscillations penetrate 4 atomic diameters into the bulk liquid. The layering decay length is about 12 Å, independent of the temperature, that is in good agreement with previous observations [15,16]. The first peak is always lower than the second one and a clear asymmetry between maxima and minima with respect to the bulk liquid density is observed. From theoretical or experimental analysis, the main information on the microscopic structure of the interface is given by the ratio $\rho_0/\rho_{\text{bulk}}$, i.e. the two-dimensional density of the first (outermost) layer relative to the bulk density. The values of $\rho_0/\rho_{\text{bulk}}$ obtained from our
simulations are shown in figure 1b as function of the temperature. The results are correlated with the
genral shape of oscillating density profiles in figure 1a, in which the outermost peak is clearly lower
than the inner ones. They are similar to those of Tarazona et al [8], obtained for soft-core potentials,
whose ratio $\rho_0/\rho_{\text{bulk}} < 1$ is decreasing with increasing temperature. It should be stressed that the
opposite behavior might be observed with the "mercury-like" potential [8] that exhibits a rapid
increase of $\rho_0/\rho_{\text{bulk}}$ with temperature.

A second test for our model is the description of the interfacial structure. In figure 2, we display the
transverse pair correlation function (details for practical calculations can be found elsewhere [10])
calculated for the first two outer layers corresponding to the region that encloses the first two density
peaks in the longitudinal density profile. For the layer beneath the outermost one in the L/V interface,
g(r) is almost the same as the pair correlation function in the central region (bulk liquid). In contrast,
g(r) of the outermost layer is different from that of the bulk. Both the reduction of the peak amplitudes
and the increase in peak separation go in the expected direction, in good agreement with previous
theoretical works [10].

Figure 2. Tranverse pair correlation functions at $T = 235$ K for the outermost
layer, second layer and central region.

Contrary to the confrontation between theoretical results, the direct comparison with experiment is
more delicate for several reasons. One of them is the interconnection between the ionic and electronic
densities probed by X-ray reflectivity. Another is the difficulty to estimate the relevant linear
transverse size $L_x$, over which the local density profile is averaged in the measurements, since it
depends on the experimental set up. For Hg, the X-ray reflectivity window has been estimated [17] to
be about 1000 Å ($\approx 300\sigma$). Unfortunately, this transverse size is much larger than the feasible
computer simulations. The results from the fits of X-ray reflectivity experiments [1,2] on Hg and Ga
show quite different results, with values of $\rho_0/\rho_{\text{bulk}}$ always greater than 1. Nevertheless, the inversion
of the X-ray reflectivity data that yields the density on the vapor side is subjected to considerable
experimental uncertainty. As attested in the literature [5,11], even the highest purity liquids may have
enough impurities (e.g. HgO) to give profound effect on the surface properties. Hence, accurate \textit{ab initio}
simulation [4,18] that is a real numerical experiment, can provide valuable information to clarify
this point. In a recent study of Na, the heights of outermost peaks have been found to be comparable
(not higher) to those of the second layer peaks. In addition, previous theoretical predictions [10] for
the liquid metals display a first layer clearly lower than the others, and calculations from density-functional [19] also present the same trend as our density profiles, implying $\rho_0/\rho_{\text{Bulk}} < 1$. Moreover, extrapolation performed up to $L_x \approx 300 \sigma$ shows that the amplitudes should reduce with respect to the "intrinsic" profiles by a factor 4. This assumption has been confirmed in a recent letter [5], since removing the CW effects in the fit of the density profiles does the amplitude of the oscillations much more stronger and disabled from obtaining the best-fit of the reflectivity measurements.

We argue that the discrepancy between the predicted and observed density profiles is due to a combination of the inaccuracy of the experimental results and the limitations of the theoretical model.

4. Conclusions
Simulations calculations have been performed to explore the L/V interface of mercury. The interionic potential used in this work is an improved version of the "mercury-like" potential developed by Tarazona et al. [3,8,19], since layering observation is not preempted by solidification. Our results are in good agreement with previous theoretical analysis. The present work seems to confirm the statements of [5]. As far as a molecular liquid has low melting point and high critical point it must to behave like a liquid metal, except that it does not, of course, present an electron gas. Thus, this system may be described by a broad and shallow potential model similar to the one defined in equation (1). So, our potential model stands at the frontier of metallic and nonmetallic systems, because it has been shown to describe accurately the static Hg properties in the dense metal phase and in the metal-nonmetal transition as well. Further work is needed to study systems other than metals in which the shape of the effective interionic potential may lead to low melting points and to strong liquid surface layering.

Acknowledgments
The authors would like to express their sincere thanks to E. Chacon and P. Tarazona for useful discussions. The CINES (project C20060922810) and the Pôle Messin de Modélisation et Simulation are gratefully acknowledged for providing us with computer time.

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