Density Profiles at a Water/Liquid Mercury Interface

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A molecular dynamics simulation of the water/liquid mercury interface has been performed. The potentials describing the water-metal interactions are derived from *ab initio* calculations of a water molecule on a mercury cluster. The mercury-mercury potential is based on pseudopotential theory. As a first result the density profiles of the mercury, oxygen, and hydrogen atoms are presented.

In this note, first results of a molecular dynamics simulation of the interface between water and liquid mercury are reported. The water-water interactions are described by the BJH water model [1]. The potential energy between two mercury atoms is taken from a simulation of pure liquid mercury based on pseudopotential theory [2]. The interaction between the mercury atoms and water are derived from *ab initio* calculations of the adsorption energy of a water molecule on a mercury cluster [3]. The parameterized potential for Hg–O and Hg–H have been employed in the simulation of water near a solid mercury surface [4].

The basic box with sidelengths of $L_x = 24.00$ Å, $L_y = 25.98$ Å, and $L_z = 69.80$ Å contained 750 water molecules and 880 mercury atoms with periodic boundary conditions in all three directions. The interface simulation was started from a configuration where the basic periodic boxes from a pure mercury and a pure water simulation were combined at a distance of 3 Å, which is approximately the position of the potential minimum for the water-mercury interaction. During the equilibration period the dimensions of the combined box were changed until the average density at the center of the water as well as of the mercury phase showed the density of the pure substances. The NVE ensemble simulation was integrated in time steps of 0.1 fs and extended over 40 ps at a temperature of 299 K.

The density profiles for mercury, oxygen, and hydrogen, averaged over both interfaces, are depicted in Figure 1. The xy plane at $z = 0$ Å is defined as the

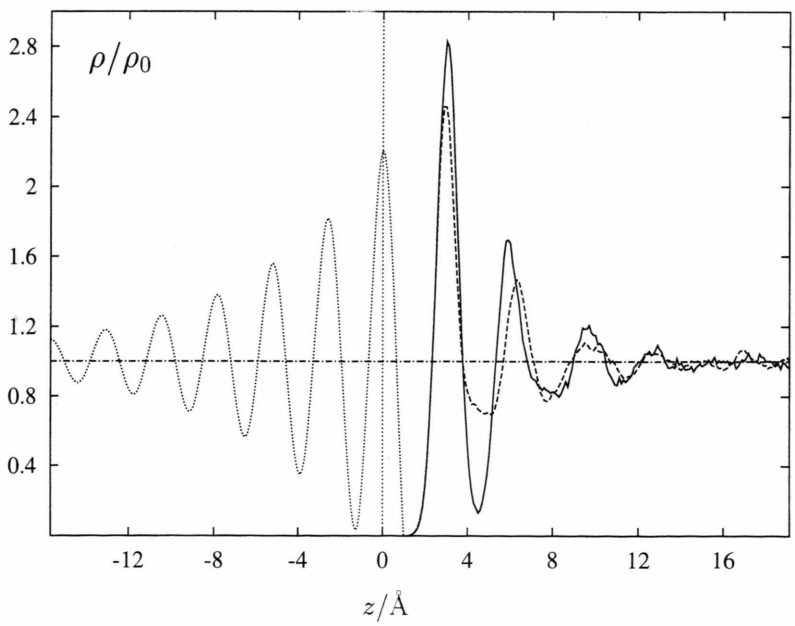

Fig. 1. Relative densities of mercury (dotted lined), oxygen (solid line), and hydrogen atoms (dashed line) as a function of the distance from the mercury surface. The surface at $z = 0$ Å is defined as the average value of the first layer of mercury atoms.

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average position of the first layer of mercury atoms. The mercury density profile can be presented by the analytical form

$$\varrho/\varrho_0 = 1.0 + 1.2\exp(0.15\,z)\cos(2.4\,z). \qquad (1)$$

Both, the oxygen and hydrogen density profiles show two pronounced maxima and a small, third maximum. The height of the first two maxima is significantly reduced compared to the surface of solid mercury [4] or to the surface of platinum (100) [5]. As the oxygen and hydrogen density profiles do not coincide, it follows that the potential drop at the interface is significantly different from zero.

The number of mercury atoms at the interface was 72 while that of water molecules was 73. This implies that each mercury atom has adsorbed one water molecule.

The mercury density profile can be compared with a theoretical study of a mercury/vapor interface [6] and an experimental investigation of a mercury/water interface [7]. In these studies an oscillatory density profile with an oscillation length similar to our result but with a smaller decay length was found.

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