Effect of Solvent on Properties of the Liquid Metal Surface

J. P. Badiali
University Pierre et Marie Curie

M. I. Rosinberg
University Pierre et Marie Curie

Jerry Goodisman
Syracuse University

Effect of Solvent on Properties of the Liquid Metal Surface

J.P. Badiali, University Pierre et Marie Curie
M.L. Rosinberg, University Pierre et Marie Curie
J. Goodisman, Syracuse University

Abstract

We calculate the difference in the surface potentials between the free surface of a liquid metal and the same metal in an ideally polarizable interface at the point of zero charge. This difference, $^\delta X_m$, is due to the deformation of the electronic cloud of the metal by the solvent molecules. The simple model used for the free (metal-metal vapor) surface yields qualitatively correct work functions for a number of metals (Hg, Cd, In, Zn, Pb, Ga, A1). Two simple ways to model the metal-solvent interaction are proposed and calculations of $^\delta X_m$ made for each. One, the dielectric film model, considers only an electrostatic interaction between metal electrons and solvent, while the other, the repulsive core model, considers only the exchange repulsion between metal electrons and the cores of solvent molecules. For Zn, Cd and Hg the dielectric film model, with parameters chosen according to conventional electrochemical wisdom, gives values for $^\delta X_m$ which are close to those estimated in the literature. For Ga and A1, the effect of the solvent is much greater because of the larger electron density and smaller ion size. The repulsive core model can give similar results, but there is an arbitrariness in the choice of the barrier strength parameter. Again, Ga is more sensitive to the presence of solvent. The effect of changing certain parameters in both models, and of combining the two, is considered.

(I) Introduction

It is generally accepted that the nature of the metal is important in determining the point of zero charge (pzc) of an ideally polarizable electrode (IPE). The correlation between the pzc and the work function of a metal has been discussed in a number of review articles (for example, refs. 1-3). On the other hand the importance of understanding how the solvent or solution phase of the IPE modifies the surface properties of the metal has long been recognized [4].

At the interface between a metal and its vapor, the concentration profiles of the **[End of page 31]** ions and the electrons are different. This produces a charge separation and a dipolar surface charge distribution which is the origin of the surface potential of the metal, X_m From experimental and theoretical data, Trasatti [5] has estimated that the change in X_m resulting from the modification of the dipolar distribution of Hg by water is a decrease of about 0.33 V. For Cd and Zn, Bockris and Habib [6] estimated the corresponding changes to be $^\delta X_m = --0.45$ and -0.37 V respectively.

To our knowledge, there has been no theoretical calculation of $^\delta X_m$ based on contemporary models of metal structure. In the present paper we calculate this quantity for a number of metals, to verify whether such calculations lead to values of the same order of magnitude as those derived by Bockris and co-workers, and to investigate how $^\delta X_m$ depends on the nature of the metal. Subsequent work will investigate the effect on X_m of charging the electrode. By using the same model for all the metals, we hope to make the comparisons useful. We emphasize at the outset that no parameters are introduced which are specific to the effect under study; values used for all parameters in the model are those given by other workers in the theory of metals.

The model used to describe the metal-vapor interface is presented in Section (II). The calculations in this section yield values for X_m and for the work functions which are compared to those in the literature. The metal-solvent interaction is modeled in two ways in Sections (III) and (IV). In each .case, $^\delta X_m$ is calculated. Further

discussion is given in Section (V). We note that in discussions of the electrochemical interface, the metal has been generallly represented as a charged wall and more or less sophisticated models developed for the electrolyte. Here, we do the reverse and introduce oversimplified models for the electrolyte which forms the metal's environment, treating the metal in some detail.

(II) The Metal-Vapor Interface

Using the density-functional formalism (see below), Lang and Kohn [7] have developed a model which allows the calculation of the electron density profile at a metal surface. From this density profile and that of the ions, one can obtain the work function [8] and, given a model for the interionic interactions, the surface energy. The Lang-Kohn (LK) model first uses a reference system in which the ions are replaced by a continuous positively charged background (jellium). The ionelectron interaction for solid metals is supposed to involve a core pseudopotential repulsion as well as a Coulombic attraction. The difference between the actual interactions between electrons and discrete ions, and interactions between electrons and the jellium, is treated as a perturbation in LK theory. The effect of this perturbation is of great importance for the surface energy of high-density metals, but relatively unimportant for the calculation of the work function.

Smith [9] suggested that, instead of solving a pseudo-Schrodinger equation for the electronic wave functions on jellium, as proposed by LK, one should determine the electron density profile variationally, using the density functional theory. This is done by calculating the surface energy using a function of given form for the **[End of page 32]** electron density profile, and minimizing the surface energy with respect to parameters in the function, which leads to algebraic equations to determine the parameters. Later workers [10-12] have included the pseudopotential part of the ion-electron interaction in such calculations. The electron density profile then varies from metal to metal not only because of differing electron densities but also through the properties of the metal ions (parameters in the pseudopotential).

In the present work, we assume that the ion density profile is sufficiently steep, relative to that of the electrons, to be approximated by a step function (since we are dealing with a liquid, the ions are distributed according to a continous density profile rather than occupying discrete lattice positions, as would be the case for a solid metal):

$$n_+(z) = \bar{n}_+ \theta(-z) \tag{1}$$

Here, if $\bar{n}_+$ is the ion density in bulk metal, for $z < O$, and the Heaviside or step function $\Theta(z)$ is 0 for $z < 0$ and 1 for $z > O$. The electron density profile is taken to be of exponential form:

$$n_-(z) = \bar{n}_-(1 - A\, e^{\alpha z}), \quad z < z_0 \tag{2}$$
$$n_-(z) = \bar{n}_- B\, e^{-\beta z}, \quad z > z_0$$

with

$$\bar{n}_- = Z\bar{n}_+ \tag{3}$$

The charge or valence of an ion is Z, and atomic units are used: $e = m = h = 1$. The unit of length is 5.292 X 10^{-11} m, and of energy 4.359×10^{-18} J. The vapor density is assumed negligible here. The form of eqn. (2) allows the electronic distribution to be non-symmetric relative to $z = 0$. Of the five parameters only two are independent, say α and ß. The others are related to α and ß by the constraints that $n_-(z)$ be continuous and with continuous derivative, and that the metal be electrically neutral:

$$\int [Zn_+(z) - n_-(z)]\, dz = 0 \tag{4}$$

Using these conditions, we have:

$$n_-(z) = \bar{n}_- \left(1 - \frac{e^{\alpha z - 1 + \alpha/\beta}}{1 + \alpha/\beta}\right), \quad z \leq \alpha^{-1} - \beta^{-1} \tag{5}$$
$$n_-(z) = \bar{n}_- \frac{e^{-\beta z - 1 + \beta/\alpha}}{1 + \beta/\alpha}, \quad z > \alpha^{-1} - \beta^{-1}$$

The Friedel-type oscillations [7] which must exist at the the surface are not included in the profile of eqn. (5). However, for the metals of relatively large electron density which interest us, Lang and Kohn have shown that these oscillations are of very small amplitude.

The electron density profile can, in principle, be obtained from the solution to a many-electron Schrodinger equation. The potential energy operator would include **[End of page 33]** the interelectronic repulsion plus a term representing the interaction between electrons and ions, obtained by averaging the single ion-electron potential over the distribution of ions (eqn. 1 in the present case). The great difficulties inherent in such a scheme can be avoided by use of the density-functional formalism, which is based on the theorem that the lowest energy of a many-electron system can be represented by a functional of the electron density. This means that there exists an expression F, involving the electron density and perhaps its derivatives, such that the electron density which minimizes F is the true electron density and the corresponding value of F the energy (apart from the kinetic energy of the heavy particles). Parameters in an electron density function n_- such as eqn. (5) are determined by evaluating F for n_- and minimizing with respect to variation of parameters (α and β in the present case). For an infinite metal the energy is of course infinite, and one has to subtract an infinite homogeneous part which of course does not depend on the parameters of the surface. The quantity to be minimized is thus proportional to the surface energy.

The exact form of F is not known and various approximations to it have been used, such as representation of part of the electronic kinetic energy as the integral over space of $\kappa_k n_-^{5/3}$, which is correct for a homogeneous gas of electrons. Terms representing the electronic exchange and correlation energies are derived similarly, and a kinetic energy contribution proportional to the integral $(\nabla n_-)^2/n_-$ takes the inhomogeneity into account. We use this form of F (see eqns 6-12), which is readily evaluated for the profile eqn. (5).

Invoking the density-functional formalism, we determine the parameters α and β by minimizing the surface energy of the metal, U_s:

$$\left(\frac{\partial U_s(\alpha,\beta)}{\partial \alpha}\right)_\beta = 0; \qquad \left(\frac{\partial U_s(\alpha,\beta)}{\partial \beta}\right)_\alpha = 0 \tag{6}$$

The surface energy is written [12]:

$$U_s = U_{kin} + U_{exc} + U_{inh} + U_{es} + U_{ps} + U_{ion} \tag{7}$$

The electronic kinetic energy contribution is

$$U_{kin} = \kappa_k \int_{-\infty}^{\infty} \left[n_-(z)^{5/3} - \bar{n}_-^{5/3}\theta(-z) \right] dz \tag{8}$$

With $\kappa_k = 3(3\pi^2)^{2/3}/10$. The electronic exchange energy is

$$U_{exc} = -\kappa_a \int_{-\infty}^{\infty} \left[n_-(z)^{4/3} - \bar{n}_-^{4/3}\theta(-z) \right] dz \tag{9}$$

where $\kappa_a = (3/4)(3/\pi)^{1/3}$, and the electronic correlation energy is

$$U_{cor} = -\frac{1}{2}\int_{-\infty}^{\infty}\left[0.115 n_-(z) - 0.0311 n_-(z) \ln_r\left(\frac{3n_-(z)}{4\pi}\right)^{1/3} - 0.115\,\bar{n}_-\theta(z) + \right.$$
$$\left. + 0.0311\bar{n}_-\ln\left(\frac{3\bar{n}_-}{4\pi}\right)^{1/3}\theta(-z) \right] dz$$

[End of page 34] Inhomogeneities in the electron density contribute

$$U_{inh} = (72)^{-1}\int_{-\infty}^{\infty} \left[n_-(z) \right]^{-1}\left[\nabla n_-(z) \right]^2 dz \tag{10}$$

and the electrostatic contribution to the surface energy is

$$U_{es} = \frac{1}{2}\int \frac{\left[Zn_+(z) - n_-(z) \right]\left[Zn_+(z') - n_-(z') \right]}{|\vec{r}-\vec{r}'|} \, dz\, d\vec{r}' \tag{11}$$

because the electrostatic energy of the bulk system vanishes. For the contribution of the pseudopotential, we have:

$$U_{ps} = \int \left[W(|\vec{r}-\vec{r}'|) + |\vec{r}-\vec{r}'|^{-1} \right]\left[Zn_+(z)n_-(z') - Zn_+(z)\bar{n}_-\theta(-z) \right] d\vec{r}'\, dz \tag{12}$$

and we use a pseudopotential of the form given by Heine and Animalu [13]:

$$W(r) = A_0/Z, \quad r < R_m; \qquad W(r) = -r^{-1}, \quad r \geqslant R_m \tag{13}$$

The last term in eqn. (7) involves correlations between ions as well as the short-range (non-electrostatic) ion-ion interaction, owing to" the repulsion between the closed inner shells. It is not needed for the calculation of α and ß, since it is independent of the electronic distribution.

Furthermore, the electrostatic potential in the interface involves only the one particle densities for atoms and ions, not their correlations, so that specification of U_{ion} is not necessary at all in the present work. It could be calculated for a solid metal (of known structure), but presents difficulties for a liquid, since it requires knowledge of the pair distribution functions in the interface.

All the remaining terms in U_s are calculable. Grouping together the terms involving electrons alone, we have:

$$U_{kin} + U_{exc} + U_{inh} = \kappa_k \bar{n}_-^{5/3} \left[\sum_{j=1}^{\infty} \binom{5/3}{j} \frac{(-1)^j}{j\alpha(1+\alpha/\beta)^j} + \frac{1}{\alpha} - \frac{1}{\beta} + \frac{1}{\left(\frac{\beta}{\alpha}+1\right)^{5/3}} \frac{3}{5\beta} \right] -$$

$$- \kappa_a \bar{n}_-^{4/3} \left[\sum_{j=1}^{\infty} \binom{4/3}{j} \frac{(-1)^j}{j\alpha(1+\alpha/\beta)^j} + \frac{1}{\alpha} - \frac{1}{\beta} + \frac{1}{\left(\frac{\beta}{\alpha}+1\right)^{4/3}} \frac{3}{4\beta} \right] + \bar{n}_- \alpha \ln\left(1+\frac{\beta}{\alpha}\right)\frac{1}{72}$$

$$+ \frac{0.0311\bar{n}_-}{6\alpha}\left[\frac{\alpha}{\beta}\ln\left(1+\frac{\beta}{\alpha}\right) + \frac{\alpha}{\beta} - 1 + \sum_{j=1}^{\infty} \frac{(1+\alpha/\beta)^{-j}}{j^2} \right]$$

where

$$\binom{m}{j} = \frac{m(m-1)\dots(m-j+1)}{j!} \tag{14}$$

[End of page 35] The electrostatic interactions between ions and electrons give:

$$U_{es} = -2\pi\bar{n}_-^2 \left[\frac{1}{3\alpha^3} - \frac{5}{6\beta^3} - \frac{1}{2\alpha^2\beta} - \frac{\beta}{2\alpha^3(\alpha+\beta)} + \frac{2\alpha}{\beta^3}\frac{e^{\beta/\alpha-1}}{\alpha+\beta} \right] \quad \text{if } \alpha^{-1} \leqslant \beta^{-1}$$

$$U_{es} = -2\pi\bar{n}_-^2 \left[-\frac{1}{3\alpha^3} - \frac{1}{6\beta^3} - \frac{1}{2\alpha^2\beta} - \frac{\beta}{2\alpha^3(\alpha+\beta)} + \frac{2\beta}{\alpha^3}\frac{e^{\alpha/\beta-1}}{\alpha+\beta} \right] \quad \text{if } \alpha^{-1} \geqslant \beta^{-1} \tag{15}$$

Finally, the pseudopotential contribution is, for $\alpha^{-1} < \text{ß}^{-1}$,

$$U_{ps} = -2\pi\bar{n}_- \left[\left(\frac{A_0 R_m^2}{2} + R_m \right)\left(\frac{1}{2\alpha^2} + \frac{1}{2\beta^2} \right) + \frac{1}{3\beta^3} - \frac{1}{3\alpha^3} + \frac{A_0 R_m^4}{8} + \frac{R_m^3}{6} \right.$$

$$- \frac{A_0}{8}\left(\frac{3}{\alpha^4} + \frac{2}{\alpha^2\beta^2} + \frac{3}{\beta^4} \right) + \frac{e^{\alpha/\beta-1-\alpha R_m}}{\alpha^3(1+\alpha/\beta)}\left(1 + A_0 R_m + \frac{A_0}{\alpha} \right)$$

$$\left. + \frac{e^{\beta/\alpha-1-\beta R_m}}{\beta^3(1+\beta/\alpha)}\left(1 + A_0 R_m + \frac{A_0}{\beta} \right) - 2\frac{e^{\beta/\alpha-1}}{\beta^3(1+\beta/\alpha)} \right] \tag{16}$$

If $\alpha^{-1} > \text{ß}^{-1}$, α and ß are interchanged in the last term.

In Table 1, we have listed the metals studied in the present work, together with the values of the parameters characterizing them: $\bar{n}_-$, A_0, R_{m^*}, and the crystallographic ion radius R_c. Using these values and eqns. (14-16), we have minimized the surface energy to find the parameters of the electron density profile, first assuming $\alpha = \text{ß}$ (giving α_0) and then allowing α and ß to vary separately. The results are shown in Table 1.

Given these values, we can calculate the work function for each metal, which

TABLE 1

Parameters for the metals studied and calculated parameters for electron density profile. Atomic units are used; $\bar{n}_-$, R_c, A_0 and R_m are from ref. 13

	Electron density $\bar{n}_-$	Pseudopotential parameters			Density profile parameters (bare s.)		
		R_c	$-A_0$	R_m	α_0	α	β
Hg	0.01267	2.12	0.97	2.6	0.901	0.846	0.961
Cd	0.01381	1.95	0.88	2.6	0.815	0.764	0.874
In	0.01711	1.74	1.32	2.4	0.800	0.760	0.836
Zn	0.01961	1.57	0.99	2.2	0.861	0.826	0.880
Pb	0.01966	1.59	1.92	2.1	0.834	0.806	0.861
Ga	0.02283	1.17	1.47	2.4	0.862	0.845	0.880
Al	0.02695	1.03	1.38	2.0	0.814	0.803	0.825

[End of page 36] involves two parts: the chemical potential for the electron in a metal, given [12] by

$$\mu_e = 4.7854\bar{n}_-^{2/3} - 0.9847\bar{n}_-^{1/3} - 0.07007 - 0.005167 \ln \bar{n}_-$$

$$+ 2\pi\bar{n}_- R_m^2 \left(1 - \frac{2}{3}\frac{|A_0|}{Z} R_m\right) \tag{17}$$

and the surface potential, calculated from eqns. (1) and (5) to be

$$\chi_m = 2\pi\bar{n}_- \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2}\right) \tag{18}$$

The work function Φ is given by [8]

$$\Phi = -\mu_e + \chi_m \tag{19}$$

Calculated values for μ_e, χ_m and Φ are given in Table 2 (χ^0_m and ϕ^0 are calculated with $\alpha = \beta = \alpha_0$). In the last column, for comparison, are given values for recommended by Trasatti [3].

The values we calculate for Φ are quite close to those obtained by Smith [9] and by Lang and Kohn [8]. In general, there is agreement with Trasatti's [3] values; the case of mercury is exceptional, and will be considered further below. (The present model, of course, is incapable of calculating differences in χ_m and Φ associated with differences in crystallographic orientation; extension of the ideas of the model to do this are possible.) We take the results of Table 2 to indicate that our model is capable of yielding reasonable values for surface properties and is hence useful for discussing changes in these properties due to the environment, e.g. the solvent in the electrochemical interface. We now will see that the model is easily extended to take such interactions into account.

(III) The Dielectric Film Model for the Metal-Solvent Interaction

Two types of models have been used in the literature to study the interaction between a metal and an absorbate. In one type, the interaction between the metal

TABLE 2

Bulk chemical potentials for the electron, calculated surface potentials χ and work functions Φ, in eV. The values χ^0_m and Φ^0 are calculated with $\alpha = \beta$. Recommended experimental values Φ^* taken from Table III of ref. 3

	μ_e	χ^0_m	Φ_0	χ_m	Φ	Φ^*
Hg	1.86	5.34	3.48	5.37	3.51	4.50
Cd	3.55	7.11	3.56	7.13	3.58	4.12
In	5.40	9.15	3.75	9.25	3.65	4.16
Zn	4.67	9.03	4.35	9.25	4.58	4.30
Pb	5.21	9.66	4.45	9.71	4.50	4.24
Ga	6.36	10.50	4.14	10.51	4.15	4.25
Al	9.40	13.91	4.52	13.92	4.51	4.20

[End of page 37] and a single molecule is studied in detail. This is appropriate for low surface coverage. On the other hand, if the surface coverage is high, one can consider the layer of adsorbed molecules as a continuous film

covering the surface. For example the modification of the work function of a metal due to a layer of adsorbed alkali atoms was studied from this viewpoint by Lang [14]

In applying models of this type to the electrochemical interface, it seems reasonable to consider that, in the absence of specific adsorption, the coverage by the solvent is high. This suggests a model of the second type, the solvent in contact with the metal being represented by a film. Its response to charge is characterized by a dielectric constant, whose value must be significantly higher than unity (vacuum value) but less than the bulk value because of orienting effect of local fields. Solvent outside the film is characterized by the still higher bulk value of the dielectric constant. For a highly concentrated solution, this model is shown in Fig. la. It requires values for the two dielectric constants e_1 and e_2 and the two geometric parameters d_1 and d_2. The bulk value of 78 will be used for e_2, in conformity with what is generally accepted in electrochemistry for the dielectric constant of water. The value of e_1 is considerable smaller because of the orienting effect of fields at the
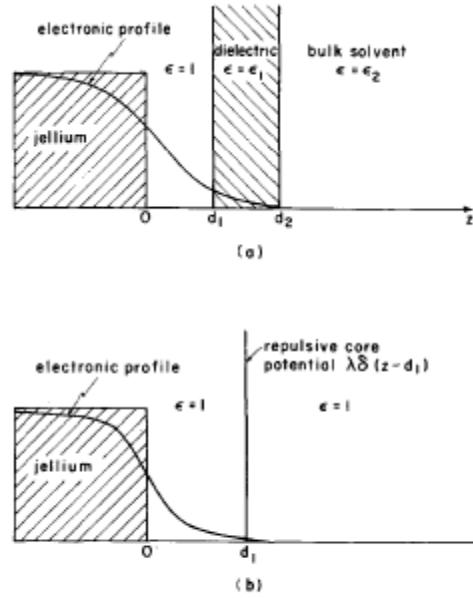

Fig. 1. Models for solvent–metal interactions. (a) Dielectric film model: $d_2 - d_1$ was taken as 0.3 nm, diameter of a water monolayer, and d_1 as the ionic radius for the metal (b) Repulsive core model: d_1 was taken as the midpoint of the water layer of the dielectric film model.

[End of page 38] surface; we take $\varepsilon_1 = 6$, which is often used in the electrochemical literature to characterize the response of the adsorbed layer to electric fields. The thickness of the film, $d_2 - d_1$, should correspond to a monolayer of water. This would make $d_2 - d_1 = 0.3$ nm or 5.67 a.u. For d_1 we use R_c, the crystallographic ion radius for each metal; R_c plus 0.15 nm is then the distance of closeset approach of the center of a water molecule to the surface formed by the metal ions.

The electrons of the metal penetrate into the dielectric film, modifying the electrostatic energy as well as their contribution to the surface potential. By solving Poisson's equation, we obtain the electrostatic energy:

$$U_{es} = -2\pi\bar{n}_-^2 \left[\frac{1}{3\alpha^3} - \frac{5}{6\beta^3} - \frac{1}{2\alpha^2\beta} - \frac{\beta}{2\alpha^3(\alpha+\beta)} + \frac{2\alpha}{\beta^3}\frac{e^{\beta/\alpha-1}}{(\alpha+\beta)} \right.$$
$$\left. + \frac{\alpha^2}{2\beta^3}\left(\frac{e^{\beta/\alpha-1}}{\alpha+\beta}\right)^2 \left(e^{-2\beta d_1}\left(1-\varepsilon_1^{-1}\right)+e^{-2\beta d_2}\left(\varepsilon_1^{-1}-\varepsilon_2^{-1}\right)\right) \right] \quad \text{if } \frac{1}{\alpha}-\frac{1}{\beta}\leqslant 0$$

$$U_{es} = -2\pi\bar{n}_-^2 \left[\frac{-1}{3\alpha^3} - \frac{1}{6\beta^3} - \frac{1}{2\alpha^2\beta} - \frac{\beta}{2\alpha^3(\alpha+\beta)} + \frac{2\beta}{\alpha^3}\frac{e^{\alpha/\beta-1}}{(\beta+\alpha)} \right.$$
$$\left. + \frac{\alpha^2}{2\beta^3}\left(\frac{e^{\beta/\alpha-1}}{\alpha+\beta}\right)^2 \left(e^{-2\beta d_1}\left(1-\varepsilon_1^{-1}\right)+e^{-2\beta d_2}\left(\varepsilon_1^{-1}-\varepsilon_2^{-1}\right)\right) \right] \quad \text{if } \frac{1}{\alpha}-\frac{1}{\beta}\geqslant 0 \quad (20)$$

The surface potential is now

$$\chi_m = 4\pi\bar{n}_- \left[\frac{1}{2}\left(\frac{1}{\alpha^2}+\frac{1}{\beta^2}\right) + \frac{e^{\beta/\alpha-1-\beta d_1}}{\beta^2(1+\beta/\alpha)}\left(\frac{1}{\epsilon_1}-1\right) + \frac{e^{\beta/\alpha-1-\beta d_2}}{\beta^2(1+\beta/\alpha)}\left(\frac{1}{\epsilon_2}-\frac{1}{\epsilon_1}\right)\right]$$

(21)

Using eqn. (20), minimization of the surface energy of the metal in the presence of the dielectric filml was carried out and led to the new values for α and β given in Table 3. Also given are the new surface potentials and the changes:

$$\delta\chi_m = (\chi_m)_{film} - (\chi_m)_{bare}$$

(22)

TABLE 3

Surface parameters α and β and surface potentials χ in the presence of dielectric film, and changes in surface potential. Potentials in eV; other parameters in atomic units. χ_m^0 and $\delta\chi_m^0$ are calculated with $\alpha=\beta=\alpha_0$.

	α_0	χ_m^0	α	β	χ_m	$-\delta\chi_m^0$	$-\delta\chi_m$
Hg	0.892	5.10	0.861	0.926	5.14	0.24	0.24
Cd	0.800	6.75	0.809	0.796	6.68	0.37	0.45
In	0.774	8.70	0.810	0.739	8.62	0.45	0.63
Zn	0.828	8.67	0.883	0.776	8.57	0.35	0.67
Pb	0.807	9.12	0.865	0.754	9.00	0.54	0.71
Ga	0.818	9.79	0.962	0.707	9.50	0.71	1.01
Al	0.761	13.00	0.978	0.613	12.45	0.91	1.47

[End of page 39] The results $X^0{}_m$ and δX^0 are calculated holding $\alpha = \beta = \alpha_0$.

Our calculated values for $\delta X^0{}_m$ and δX_m are quite close to those suggested by Trasatti and Bockris for Hg and Cd [5,6]. However, there are significant changes when β is allowed to be different from α. The metals Ga and Al have the smallest crystallographic ion radii and largest bulk electron densities, so that the effect of the dielectric film on the electron density profile can be expected to be largest for them. It should also be noted that X_m and $\delta X^0{}_m$ are close to each other for the bare surfaces, so that the introduction of the second parameter β (β independent of α) does not change things much, but there is an appreciable difference between δX_m and $\delta X^0{}_m$ for a number of the cases in Table 3.

In Fig. 2, the density profiles for the bare surface and for the surface in the presence of the film are shown for Ga. In the case of Hg, the change is smaller and the optimum profile corresponds to $\alpha \sim \beta$. In the case of Ga, α and β are different and there is clearly an increase of electronic charge in the region of the film.

The model described in this section deals only with electrostatic effects. It does not take into account the exchange repulsion between the electrons of the metal and closed electron shells of the molecules. The model presented in Section (IV) considers such repulsions.
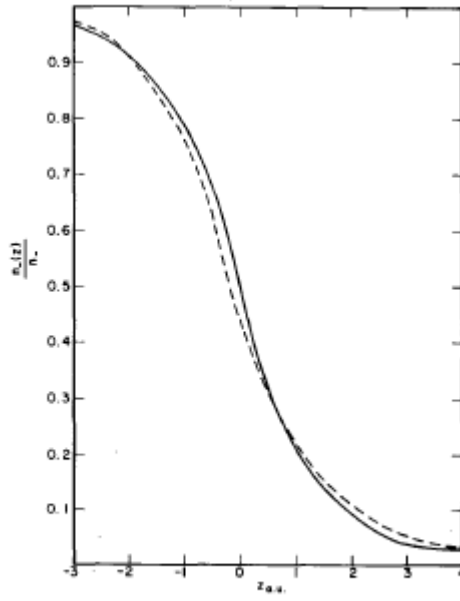
Fig. 2. Electron density profiles for Ga in the absence and in the presence of the dielectric film. (solid and broken curves respectively).

[End of page 40]

(IV) Repulsive Core Model

In studying field emission, Duke and Alferieff [15] suggested that the effect of the repulsion between the electrons and the cores of adsorbed molecules could be considered in terms of Harrison's pseudopotential [16]. In this model, the layer of adsorbed molecules at a distance d_1 from the metal surface interacts with the electrons with a potential $\lambda\delta(z - d_1)$, where δ is the Dirac delta function as shown in Fig. lb. It is not difficult to use this approach to calculate $^\delta X_m$.

The surface energy is simply increased by a term:

$$U_B = \lambda n_-(d_1) = \lambda \frac{\alpha}{\beta} \frac{e^{\beta/\alpha-1}}{1+\alpha/\beta} e^{-\beta d_1} \bar{n}_- \tag{23}$$

All other terms in the energy, including the electrostatic contribution, are unchanged from their values for the bare surface. The expression for X_m is also unchanged from eqn. (18), but the inclusion of the term (23) in the energy expression to be minimized leads to changed values of α and β and hence a changed profile and a different surface potential. We have allowed α and β to vary separately as well as minimizing U_s with a held equal to β. For each metal, we have considered values of λ from 0.15 to 1.917 a.u., the last corresponding to $m\lambda^2/2h^2 = 50$ eV. In each case we have taken d~ as the sum of the crystallographic ion radius and the radius of a water molecule, 0.15 nm.

By comparing the results of Tables4 and 5 with X_m from Table2, one sees the values of $^\delta X_m$ change approximately linearly with λ, with a fall-off from linearity when $m\lambda^2/2h^2$ exceeds 7 eV ($\lambda \sim 0.5$) which is comparable to the Fermi energy for the metals considered here (7-12 eV). As expected, the barrier repels the electrons toward the interior of the metal. In Table4, we have given results for $\lambda = 0.3$; the values of α and β are obviously respectively smaller and greater than those for the bare metal surfaces. For this value of λ ($m\lambda^2/2h^2 = 1.22$ eV) the values of $^\delta X_m$ are similar to that obtained from the dielectric model. Again, Ga and A1 are the metals for which the effect is greatest.

	$\alpha = \beta = \alpha_0$	χ_m^0	$-\delta\chi_m^0$	α	β	χ_m	$-\delta\chi_m$
Hg	0.938	4.92	0.42	0.795	1.118	5.16	0.21
Cd	0.853	6.49	0.63	0.708	1.049	6.60	0.53
In	0.831	8.46	0.68	0.700	1.011	8.57	0.68
Zn	0.889	8.48	0.59	0.764	1.045	8.57	0.68
Pv	0.868	8.91	0.75	0.744	1.026	9.00	0.71
Ga	0.903	9.57	0.95	0.772	1.078	9.68	0.83
Al	0.852	12.73	1.18	0.732	1.023	13.00	0.92

[End of page 41]

	$\lambda = 0.15$			$\lambda = 0.6$		
	α	β	χ_m/V	α	β	χ_m/V
Hg	0.816	1.045	5.24	0.771	1.233	5.07
Cd	0.732	0.953	6.75	0.680	1.205	6.47
In	0.727	0.913	8.78	0.669	1.186	8.37
Zn	0.792	0.954	8.78	0.729	1.210	8.34
Pb	0.772	0.935	9.23	0.710	1.195	8.77
Ga	0.805	0.967	9.96	0.732	1.289	9.41
Al	0.765	0.914	13.39	0.689	1.262	12.60

(V) Discussion

The model, as applied to the bare metal (metal-vapor) interface, gives generally reasonable values for the work function (Table 2). However, the value of Φ in the case of mercury is about 30% lower than that suggested by Trasatti [3]. The difference may be due to an insufficiency in the model or simply to the parameters used in the pseudopotential. As we have noted, the interionic structure is never explicitly introduced, nor are modifications of the work function due to the crystallographic orientation considered. For solids, the replacement of the jellium by an ionic lattice, to take these into account, improves the agreement with experiment [8,11]. For liquids, the surface is characterized by the density profiles of ions and electrons. The former is unknown and we have used a step function for it, which may explain some of the discrepancies with the experimental results.

Furthermore, we have used a pseudopotential of Heine-Animalu form. The values of the parameters to be used for Hg are uncertain. In Table 6 the modifications of Φ, when the well depth A_0 and the radius R_m are changed, are shown. The corresponding changes in $^\delta X_m$, using the dielectric film with $\alpha \neq \beta$, are also given. It appears that $^\delta X_m$ cannot be changed radically by varying these parameters over a reasonable range, although some increase in the magnitude of Φ is possible. Mercury having the smallest electron density of the metals considered, the neglect of Friedel oscillations in using eqn. (5) may be most serious and make for the large error in Φ and other properties.

The interaction between metal electrons and the solvent can be expected to involve both an electrostatic part and a repulsion due to the closed-shell cores. The models presented consider one or the other of these: The electrostatic effect is present in the dielectric film model and the repulsion in the delta-function model. Both models lead to a lowering of the work function of about 0.5 eV, which is the estimated order of magnitude [5,6]. However, the changes in the density profiles are quite different. Clearly, a more complete model should take both effects into account. **[End of page 42]**

TABLE 6

Influence of pseudopotential parameters of mercury on work function Φ and δX_m[a]: A_0 and R_m are pseudopotential parameters; $\Delta\mu_e$ is the change in bulk chemical potential, relative to first line, due to changes in pseudopotential parameters

R_m	$-A_0$	Without film					With film		
		α	β	$\Delta\mu_e$	Φ	X_m	α	β	X_m
2.6	0.97	0.846	0.961		3.48	5.37	0.861	0.926	5.14
2.6	0.95	0.826	0.943	0.25	3.47	5.61	0.841	0.905	5.37
2.6	1.00	0.880	0.988	−0.38	3.50	5.01	0.893	0.959	4.80
2.5	0.97	0.828	0.943	0.26	3.44	5.59	0.843	0.906	5.34
2.7	0.97	0.871	0.982	−0.33	3.54	5.10	0.884	0.950	4.89
3.0	0.97	0.992	1.067	− 1.75	3.96	4.10	1.002	1.047	3.95

[a] Chemical and electrical potentials are in volts; other quantities in atomic units.

We have carried out such calculations for mercury and for aluminium. For the former metal, the barrier with $\lambda = 0.3$, superimposed on the dielectric film, makes $X_m = 5.00$ V, but the profile is close to that for the barrier alone: the best α and β values are 0.800 and 1.098. The change δX_m of -0.37 is somewhat less than the sum of the δX_m values for film and barrier separately (-0.20 and -0.21): indeed, there is some cancellation. For aluminium with $\lambda = 0.15$, 0.3 and 0.6, X_m is changed by -1.87, -2.17 and -2.30V respectively, relative to the bare metal. Again, the effects of the barrier and the film are not additive, with the presence of the film diminishing the effect of the barrier, since δX_m with a film and no barrier is - 1.37 V. We note again that we have no means of deciding what value to use for λ.

In neither model is there a separation in space between the metal and the solution, as is sometimes supposed to exist for the ideally polarizable electrode. However, spatial overlap is compatible with the behavior of IPE [17]. In any case, the concentration of metal electrons is quite low in the first layer of water molecules: for mercury, this concentration is of the order of $3 \times 10^{-4} n\_$ at d_2. As a result, our calculations are not sensitive to the values of ε_2.

As we have mentioned, δX_m is most important for the metals of largest electron density and smallest ionic radius, such as A1 and Ga. To investigate which factor is most significant, we have performed a series of dielectric film calculations for Ga, varying the distance d_1 between jellium and die/ectric from the crystallographic ionic radius of 1.17 a.u. to 2.5 a.u. We always take d_2 as $d_1 +0.3$ nm. For $d_1 = 1.17$, 1.5, 2.0 and 2.5 a.u. the values of δX_m are -- 1.01, --0.81, --0.57 and -0.39 V, so that, to reduce δX_m to a value near that found for Hg by changing dl, the distance of the adsorbed water layer would have to be more than doubled. One could, of course, question the use of $\varepsilon_1 = 6$, which we have used independently of d_1.

The value of e~ reflects the effect of the intense local electric field which leads to dielectric saturation, and $\varepsilon_1 = 6$ is commonly used in calculating the influence of a charge on the metal on the compact inner layer. In the present case, the field in the **[End of page 43]** film is equal to

$$E_t = \frac{4\pi\bar{n}\_ -e^{-\beta z+(\beta/\alpha)-1}}{\beta\varepsilon(1+\beta/\alpha)}$$

For Ga and Hg the fields in the center of the film are equivalent, respectively, to charges of 2.42 and 0.35 /μC cm^{-2}. For such charges, the value $\varepsilon_1 = 6$ seems reasonable, but, because the field for Ga is so much larger, one might consider using a lower value for ε_1. Reducing ε_1 to 2 lowers δX_m to --0.51 V. Our conclusion is still that the change δX_m is significantly larger in size than for Hg. Because of the small size of the ion Ga^{3+} compared to the ion Hg^{2+}, it appears that the effect of the solvent on the charges of the metal is much larger for gallium than for mercury. (In treating the effect of the metal on the solvent, one can, of course, use models [18,19] which dispense with the notion of dielectric constant entirely.)

Possible improvements in the model could involve use of an ionic profile differing from a step, or introduction of an interionic structure characteristic of a liquid metal. In the case of the dielectric film, ε could be made to vary continuously [20,21] according to the local electric field. It has been shown that the variation of the polarization in the interface can have important consequences for the derivation of the Lippmann equation [20].

Models which introduce a continuous variation of e have been proposed by Vorotyntsev and Kornyshev.[21]. We expect, however, to use the present models to discuss the response of the metal to charging of the interface.

Acknowledgement

References

1 R.M. Reeves in J.O'M. Bockris and B.E. Conway (Eds.), Modern Aspects of Electrochemistry, Vol. 9, Butterworths, London, 1974, p. 239.

2 A.N. Frumkin, B. Damaskin, N. Grigoryev and I. Bagotskaya, Electrochim. Acta, 19 (1974) 69, 75.

3 S. Trasatti, in P. Delahay (Ed.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 10, Wiley-Interscience, New York, 1977, p. 213.

4 R. Parsons in J.O'M. Bockris and B.E. Conway (Eds.), Modern Aspects of Electrochemistry, Vol. I, Butterworths, London, 1954, p. 103.

5 S. Trasatti, J. Electroanal. Chem., 33 (1971) 351.

6 J.O'M. Bockris and M.A. Habib, J. Electroanal. Chem., 68 (1976) 367.

7 N.D. Lang and W. Kohn, Phys. Rev, B1 (1970) 4555.

8 N.D. Lang and W. Kohn, Phys. Rev, B3 (1971) 1215.

9 J.R. Smith, Phys. Rev,, 183 (1969) 522.

10 G. Paasch, H. Eschrig and W. John, Phys. Stat. Sol, B51 (1972) 283.

11 R. Monnier and J.P. Perdrew, Phys. Rev., B17 (1978) 2595.

12 J.P. Badiali, A. Lepape and J. Goodisman, Phys. Chem. Liq. 10 (1981) 243.

13 W. Heine and A.O.E. Animalu, Phil. Mag., 12 (1965) 1249.

14 N.D. Lang, Phys. Rev., B4 (1971) 4234.

15 C.B. Duke and M.E. Alferieff, J. Chem. Phys., 16 (1967) 923