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Quantum theory of the double layer: Model including solvent structure

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We describe a microscopic theory of the electrons at the surface of an electrode-electrolyte interface in which no specific adsorption of ions takes place at the electrode surface. Unlike some earlier models, our calculations allow for the possibility that the distance from the metal to the solvent molecules can change when the potential on the electrode is changed. In the work described here, we report calculations on a model which improves on our previous work by including more detail concerning the electronic and molecular structure of the solvent. By including these features, we remove some arbitrary features of our previous model and improve the agreement between experiment and our calculations for the differential capacitance of the interface between an *sp* metal and a dilute electrolyte.

I. INTRODUCTION

The differential capacitance of the double layer at a metal-electrolyte surface has been studied experimentally and theoretically for more than a century. Until recently, one could summarize theoretical thinking concerning this quantity in terms of the Stern-Gouy-Chapman model[1] which described the interface (when there is no specific ion adsorption at the surface) as consisting of a region of electrolyte described by the Gouy-Chapman theory and a compact layer inside the second Helmholtz plane which arose from a monolayer of tightly bound solvent molecules and which behaved as a second capacitor of capacitance per unit area C_c in series with the Gouy-Chapman capacitance. The metal was modeled as a classical conductor. In this model the differential capacitance could then be written as

$$1/C_d = 1/C_c + 1/C_{\mathrm{GC}} \tag{1}$$

in which the compact and Gouy-Chapman layers, respectively, contribute differential capacitances C_c and C_{GC}. C_c was assumed to be independent of the ionic concentration of the electrolyte. The form of Eq. (1) has been substantiated in many experiments. The charge dependence of the compact capacity has however, been difficult to model theoretically. Until recently, most theories of the compact layer treated the metal as a classical conductor and attributed this potential dependence of C_c entirely to nonlinear polarization of the solvent layer near the interface. These theories had some success in reproducing the experimental capacitance but a recent review by Guidelli[2] makes it clear that there is a serious discrepancy between essentially all forms of these theories and experiment on the anodic side of the point of zero charge. While we agree that the polarization state of the first layer of solvent plays an important role in determining the differential capacitance, we[3] and others[4,5] have recently noted that a complete picture of the capacitance of the electrode-electrolyte interface must include the properties of the electrons of the metal electrode and the nature of their interaction with the solvent.

Prior to the work reported here, we have published two papers in which the effects of these electrons on the differential capacitance were estimated using models of increasing sophistication.[3,6] In each of these papers, the key feature, not present in most other work on this problem, is that our calculations allow the positions of the solvent molecules to relax relative to the metal surface as the charge on the electrode changes. This feature turns out to be essential to our explanation of the main qualitative features of the observed differential capacitance. It is also this feature which differentiates this problem from that of a metal-oxide junction. In the latter, solid-solid problem, the relaxation of the position of the oxide relative to the metal as the charge on the interface changes is not a key feature in accounting for the electrostatic properties of the interface, as we believe it is in the metal electrolyte interface. In our first paper,[3] we assumed, following work of Theophilos and Modinos[7] on the vacuum-metal interface, that the electron density distribution responded to a change of charge on the electrode by translating in or out of the metal without changing shape. This simple assumption permitted a correct prediction of the sign and order of magnitude of the change of the differential capacitance with charge.

In our second paper on this subject,[6] we made a more complete model based on the same physical ideas as described in more detail below and at the beginning of the next section. That theory incorporated the effects of applied voltages upon the metal's electrons and the solvent equilibrium position and accounted qualitatively and semiquantitatively for the differential capacitance in the experimentally accessible range of surface charge. In Ref. 6, we presented quantitative, self-consistent calculations of the electronic structure. The model for the metal was the jellium plus pseudopotential model previously used by Lang and Kohn[8] while the solvent was supposed to affect the electrons of the metal through a pseudopotential, taken to be a "step potential" whose position was determined by minimization of the surface energy.

Though the calculations based on the model of Ref. 6 gave results which were in encouragingly good qualitative and sometimes semiquantitative agreement with experiments, they contained some deficiencies: The assumption of a "step potential" barrier was arbitrary, and did not take account of the nonuniformity of the solvent density near the surface. The height of the barrier was a parameter, not predicted by the model. Furthermore, there was no clear connection between the position of the square barrier and the number density and the polarization density associated with the solvent. In the present paper we present calculations which remedy these deficiencies and improve the agreement with experiment on *sp* metals.

In Sec. II we review the model of Ref. 6. In Sec. III we indicate how we have modified it to include more detailed information on solvent molecular structure. In Sec. IV we describe how we have obtained a pseudopotential to describe the electronic structure of the solvent. In Sec. V we give results and compare them with experiment. Section VI contains conclusions and discussion.

II. DESCRIPTION OF THE EARLIER MODEL

In our earlier model[6] the energy $E(\sigma,x_2)$ per unit area of the interface was calculated from the expression

$$E(\sigma,x_2) = E_s(\sigma,x_2) + E_{\mathrm{att}}(\sigma,x_2) - \phi(\sigma,x_2+d)\sigma/2 + E_{\mathrm{ps}} + E_{\mathrm{core-sol}} . \quad (2)$$

We used Eq. (2) to calculate the position x_2 of the square barrier as a function of σ, the charge per unit area on the metal side of the interface. [In the new model, described in Secs. III–V below, a position x_w will play the role of x_2 in Eq. (2) and a position x_2, defined in Sec. V and related to x_w, will be used to calculate the compact part of the differential capacitance.] In Eq. (2), $E_s(\sigma,x_2)$ is the surface energy of the jellium-step potential system with charge σ per unit area induced on the surface. In Ref. 6, $E_s(\sigma,x_2)$ was calculated self-consistently using the local density approximation. The energy E_{att} describes the long range mutual attraction of the solvent and the metal which is clearly left out of the step potential form for the pseudopotential. In Ref. 6 and in the present work we use the dipole-image interaction for E_{att}. In the model of this paper, however, we will not adjust the magnitude of the solvent dipole in E_{att} as we did in Ref. 6 in order to obtain a reasonable binding energy and equilibrium position of the solvent. In this paper we will use the experimentally known value of the dipole moment of water in E_{att}. $\phi(\sigma,x_2+d)$ in Eq. (2) is the electrostatic potential at the point x_2+d. x_2+d is a point beyond which the electron density is essentially zero. The term $-\phi(\sigma,x_2+d)\sigma/2$ describes the electrostatic interaction of the ions of the electrolyte with the metal and is derived in Appendix B of Ref. 6. E_{ps} is an energy due to a pseudopotential correction to the jellium approximation arising from ion cores of the metal crystal face and $E_{\mathrm{core-sol}}$ describes the solvent-metal ion-core interaction. These last two terms, E_{ps} and $E_{\mathrm{core-sol}}$ will not be used in the present model. Since only the derivative of the total energy with respect to x_2 was of interest, terms independent of x_2 have been left out of Eq. (2) as discussed in Ref 6.

The self-consistent calculation which was done in order to determine the functions $E_s(\sigma,x_2)$, $\phi(\sigma,x_2)$, and the first moment $\bar{x}(\sigma,x_2)$ of the charge induced on the metal is described in Ref 6. We used the Kohn-Sham[9] version of the variational principle originally formulated by Hohenberg and Kohn[10] in which the variational function $n_m(x)$ (the electron density) is described in terms of "orbitals" $\phi_\lambda(x)$ which obey the Hartree-like equation (atomic units)

$$[-\tfrac{1}{2}\nabla^2 + v(n_m)]\phi_\lambda = \epsilon_\lambda\phi_\lambda . \quad (3)$$

n_m is the density of electrons. Here $v(n_m)$ includes a Hartree term, an exchange and correlation term, v_{xc}, a term due to the positive jellium background, v_{bkg}, and a term v_{sol} due to the interaction between the electrons arising from the metal and the solvent molecules:

$$v(n_m) = \int d\mathbf{r}' n_m(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + v_{\mathrm{xc}} + v_{\mathrm{bkg}} + v_{\mathrm{sol}} . \quad (4)$$

The key difference between the present model and that described in Ref. 6 is the form used for v_{sol}. In Ref. 6 we chose the form

$$v_{\mathrm{sol}} = V_0\Theta(x-x_2) , \quad (5)$$

in which Θ is the Heaviside function. This term was supposed to arise from the interaction of the electrons arising from the metal with the molecules of the solvent. As mentioned above, it has two defects: the quantity V_0 is not determined from first principles but is a parameter and the "step" form of Eq. (5) does not take full account of solvent structure near the electrode. Here we will remedy these defects by averaging a pseudopotential describing the interaction of a solvent molecule with the electrons arising from the metal over a solvent molecule distribution containing an approximate account of the inhomogeneities near the surface. In the following two sections we will describe first how this averaging is performed in order to obtain v_{sol} and second how the pseudopotential is obtained.

III. MODEL INCLUDING SHORT-RANGE SOLVENT STRUCTURE

To produce a model in which the short-range structure of the solvent and its interaction with the metal are treated in a more microscopic and detailed manner, we have developed a pseudopotential $V_{\mathrm{ps}}(\mathbf{r}-\mathbf{R}_i,\mathbf{\Omega}_i)$ which describes the interaction of the electrons of the metal with a molecule of the solvent. In $V_{\mathrm{ps}}(\mathbf{r}-\mathbf{R}_i,\mathbf{\Omega}_i)$, $\mathbf{r}$ is the electron position, $\mathbf{R}_i$ is the position of the center of mass of a solvent molecule, and $\mathbf{\Omega}_i$ is the orientation of the dipole moment of the solvent molecule. The derivation of this pseudopotential and the form we are currently using for it are described in the next section. In deriving V_{ps} we have replaced the water molecules of the solvent by spherically symmetric neon atoms (with the same number of electrons as H_2O) plus a long range dipole potential. In addition to the linearly additive part $V_{\mathrm{ps}}(\mathbf{r}-\mathbf{R},\mathbf{\Omega})$, the net pseudopotential developed here also has a nonlinear, exchange and correlation part V_{xc}. In this section we describe how V_{ps} and V_{xc} are used to construct v_{sol}. To obtain the contribution of $V_{\mathrm{ps}}(\mathbf{r}-\mathbf{R}_i,\mathbf{\Omega}_i)$ to v_{sol}, we average the pseudopotential over the positions $\mathbf{R}_i$ of the solvent molecules weighted to take account of solvent inhomogeneity and also over the position coordinates z,y which are transverse to the interface. Denoting the resulting average by $(\dots)_{\text{av}}$ we have a contribution to v_{sol} of

$$\begin{aligned}\left[\sum_i V_{\text{ps}}(\mathbf{r}-\mathbf{R}_i,\mathbf{\Omega}_i)\right]_{\text{av}} &= \frac{1}{A}\int d\mathbf{R}\,d\mathbf{\Omega}\,P(\mathbf{R},\mathbf{\Omega})\int dz\int dy V_{\text{ps}}(\mathbf{r}-\mathbf{R},\mathbf{\Omega})\\ &=\rho_s\int dX\,d\mathbf{\Omega}\,g(X,\mathbf{\Omega})\bar{V}_{\text{ps}}(x-X,\mathbf{\Omega}). \end{aligned}\qquad (6)$$

Here A is the surface area;

$$P(\mathbf{R},\mathbf{\Omega}) = \sum_i \delta(\mathbf{R}-\mathbf{R}_i)\delta(\mathbf{\Omega}-\mathbf{\Omega}_i),$$

$$g(X,\mathbf{\Omega}) = \frac{1}{\rho_s}\int dZ\,dY\,P(\mathbf{R},\mathbf{\Omega}), \qquad (7)$$

and

$$\bar{V}_{\text{ps}}(x-X,\mathbf{\Omega}) = (1/A)\int dz\,dy\;V_{\text{ps}}(\mathbf{r}-\mathbf{R},\mathbf{\Omega}), \qquad (8)$$

where ρ_s is the (three-dimensional) bulk solvent density. For the correlation function $g(X,\mathbf{\Omega})$ we are using the mean spherical approximation[11] for a liquid of hard sphere atoms with point dipoles against a hard wall at position x_w. The resultant total energy is minimized with respect to x_w. This can be regarded as a first iteration in an iterative calculation in which the electron density would be used to modify the form of $g(x)$ in later stages. In the mean spherical approximation, $g(X,\mathbf{\Omega})$ can be written

$$g(X-x_w,\mathbf{\Omega}) = g_0(X-x_w) + g_D(X-x_w)\cos\theta, \qquad (9)$$

where θ is the angle between the normal to the surface and the direction of $\mathbf{\Omega}$. In Figs. 1 and 2 we show $g_0(x)$ and $g_D(x)$ as given by the calculations of Ref. 11.

The form chosen for $V_{\text{ps}}(\mathbf{r}-\mathbf{R}_i)$ as described in Sec. IV below takes the form

$$\bar{V}_{\text{ps}}(x,\mathbf{\Omega}) = \bar{V}_{\text{ps},1}(x) + \bar{V}_{\text{xc}}(x) + \bar{V}_D(x)\cos\theta, \qquad (10)$$

where the bar above $\bar{V}$ means a transverse average and the subscript 1 on $\bar{V}_{\text{ps},1}$ means the part of the pseudopotential which is linear in the metal electron density n_m (see below) and $\bar{V}_{\text{xc}}$ is the exchange and correlation part of the pseudopotential. In Eq. (10), $\bar{V}_D(x)$ is the transverse average of the dipolar field due to the point dipole on the solvent molecules. We write this as

$$\bar{V}_D = \frac{p}{A}\int dz\int dy\;V_D(|\mathbf{r}-\mathbf{R}|),$$

where

$$V_D(r) = (1-e^{-(r/r_0)^5})\left[\frac{1}{r^3}\right].$$

The cutoff function $e^{-(r/r_0)^5}$ removes the unphysical divergence in V_D as $r\rightarrow 0$ and p is the magnitude of the dipole moment taken here to be that of water. Combining Eqs. (6), (9), and (10) gives the pseudopotential as

$$\begin{aligned} v_{\text{sol}}(x-x_w) &= \left[\sum_i V_{\text{ps}}(\mathbf{r}-\mathbf{R}_i,\mathbf{\Omega}_i)\right]_{\text{av}}\\ &=\rho_s\left[\int dX\,g_0(X-x_w)\bar{V}_{\text{ps}}(x-X)+\tfrac{1}{3}\int dX\,g_D(X-x_w)\bar{V}_D(x-X)\right]. \end{aligned}\qquad (11)$$

[Here and elsewhere, potentials denoted with an unbarred, capital letter V refer to functions of the radial coordinate referred to a solvent molecule center, potentials denoted with a barred $\bar{V}$ refer to a potential which has been transversely averaged as in Eq. (8), and potentials denoted with a small v have been averaged over solvent molecule positions using the correlation functions as in Eq. (11).] The first of the two terms in the potential in Eq. (11) is shown in Fig. 3 using the forms given in the next section and the results in Fig. 1.

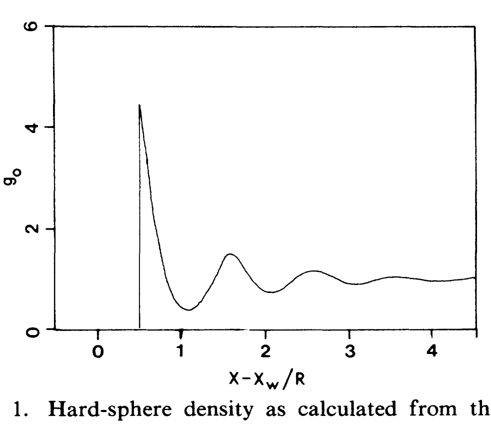

FIG. 1. Hard-sphere density as calculated from the mean spherical approximation as in Ref. 11. Here $x-x_w$ is the distance of the center of a sphere from the hard wall at x_w and R is the diameter of the spheres.

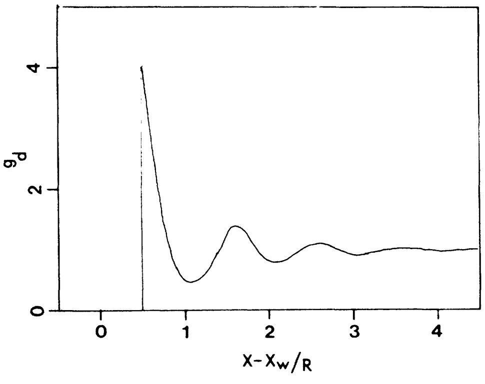

FIG. 2. Dipole correlation function $g_d(x-x_w)$ as calculated in Ref. 11.

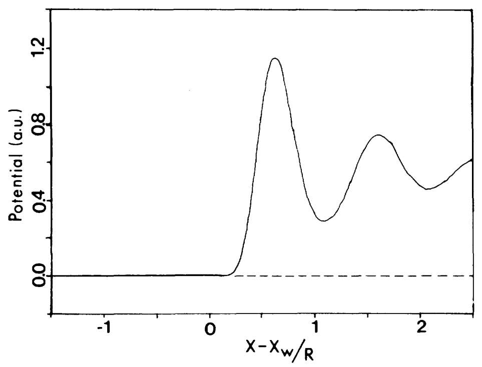

FIG. 3. Averaged linear part of the pseudopotential $v_{\text{sol}}(x)$ as given by Eq. (11).

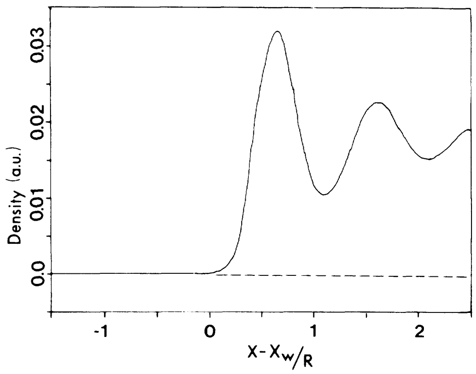

FIG. 4. Transversely averaged electron density associated with solvent molecules as given by Eq. (14).

As explained in Sec. IV below, in addition to the first two terms in Eq. (11), the short-range electron-solvent interaction must include the exchange and correlation potential v_{xc} which is not linearly additive in the sense that

$$V_{\text{xc}}(n_m+n_s)\neq V_{\text{xc}}(n_m)+V_{\text{xc}}(n_s).$$

This exchange and correlation potential takes the form

$$\bar{V}_{\text{xc}}(x) = \frac{1}{A}\int dz\,dy V_{\text{xc}}[n_s(\mathbf{x})+n_m(x)], \qquad (12)$$

where

$$n_s(\mathbf{r}) = \sum_i n_0(\mathbf{r}-\mathbf{R}_i)$$

is the electron density associated with the solvent molecules and $n_m(x)$ is the density of electrons associated with the metal. We have shown that, for the problem of interest, the solvent averaged form of Eq. (12) can be adequately approximated by

$$\begin{aligned} v_{\text{xc}}(x) &= V_{\text{xc}}\left[\frac{1}{A}\int dz\,dy\, n_s(\mathbf{r})+n_m(x)\right] \\ &= V_{\text{xc}}[\bar{n}_s(x-x_w)+n_m(x)], \qquad (13) \end{aligned}$$

where

$$\bar{n}_s(x-x_w) = \rho_s\int dX\, g_0(X-x_w)\int dz\,dy\sum_i n_0(\mathbf{r}-\mathbf{R}_i). \qquad (14)$$

$\bar{n}_s(x)$ is shown in Fig. 4.

IV. MODEL SOLVENT PSEUDOPOTENTIAL

To complete the description of the model discussed in the preceding section we explain here how the interaction of metal electrons with solvent molecules is described by a pseudopotential. The method is similar to one described by Hamann, Schluter, and Chiang[12] but we have adapted it to the problem at hand. As mentioned above we will describe the method here for a neon atom, adding a dipole potential to the neon pseudopotential in order to obtain our model solvent "molecule." To use a pseudopotential to replace the entire solvent molecule we require that the wave functions describing the electrons associated with the solvent molecules remain fixed in the configuration they have in some reference state. Though this "frozen core" approximation is not very accurate for hydrogen bonding molecules such as H_2O, it is essential for a one dimensional calculation of the sort we are doing here. The reference state chosen for construction of the pseudopotential is that of a neon atom far enough from a metal surface so that the potential in the region near the neon atom due to the metal is approximately zero. The solution to the all electron problem for the reference state then reduces to first solving the all electron, local density equations for an isolated neon atom, obtaining both the neon atom electron density, $n_0(r)$, and effective potential $V[n_0(r)]$. The electronic density associated with electrons from the metal can then be described by local density approximation "wave functions" ϕ_E^0 which can be expanded in the region surrounding the neon atom as

$$\phi_E^0 = \sum_{l,m} A^{lm}R_l^0(r)Y_{lm}(\theta,\phi).$$

Here $R_l^0(r) = u_l^0/r$ is given by the solution to the radial Schrödinger equation (atomic units):

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+2V[n_0(r)-E]\right]u_l^0(r) = 0. \qquad (15)$$

Following a procedure like that in Ref. 12, we find a nodeless "pseudo-wave-function" u_l^{ps} which is required to have the properties that (1) u_l^{ps} becomes the same as u_l^0 for large enough r, (2) the net charge associated with the pseudo-wave-function and u_l^0 are the same, and (3) u_l^{ps} goes to zero as r^{l+1} at r:

$$u_l^{\text{ps}}(r) = u_l^0(r) \quad \text{for all } r \gg r_c, \qquad (16)$$

$$\int_0^R [u_l^{\text{ps}}(r)]^2 dr = \int_0^R [u_l^0(r)]^2 dr \quad \text{for } R>>r_c, \qquad (17)$$

$$u_l^{\text{ps}}(r) \propto r^{l+1} \quad \text{as } r\to 0. \qquad (18)$$

Here, r_c is a "core" radius which is a parameter of the pseudopotential, and R is any finite radius large enough so that the two wave functions are equal for all larger values of r. The method is only fully consistent if the results are not strongly dependent on r_c. In this work, we have created such a pseudo-wave-function by requiring that $u_l^{\text{ps}}(r)$ minimize the functional $G[u_l(r)]$ given by

$$G[u_l(r)] = \int \left[-u_l \frac{d^2u_l}{dr^2} + \frac{l(l+1)}{2r^2} u_l^2 - Eu_l^2 + V[n_0(r)][1-f(r)]u_l^2 \right] dr$$

$$+ \beta \int (u_l - u_l^0)^2 [1-f(r)] dr + \lambda \int u^2 f(r) dr,$$

where $f(r)$ satisfies

$$f(r) \rightarrow \begin{cases} 0 & r >> r_c \\ 1 & r < r_c . \end{cases}$$

[In our calculations we choose $f(r) = e^{-(r/r_c)^4}$.] Here λ is a Lagrange multiplier determined by requiring that u_l satisfies condition (17) above and the term containing β forces u_l to go to u_l^0 for $r \gg r_c$. We took $\beta = |E|$. The equation satisfied by $u_l(r)$ under these conditions is

$$\frac{d^2u_l}{dr^2} - \frac{l(l+1)}{r^2} u_l + 2(E-\beta)u_l - 2\{V[n_0(r)][1-f(r)] + (\lambda+\beta)f(r)\}u_l(r) = -2\beta u_l^0 [1-f(r)].$$

The procedure is now to solve this equation for $u_l(r)$ and then invert the equation

$$\left[\frac{d^2u_l}{dr^2} - \frac{l(l+1)}{r^2} \right] u_l + 2[E - V_l(r)]u_l = 0$$

in order to obtain the partial wave pseudopotential $V_l(r)$. The corresponding potential

$$V'_{\text{ps}}(\mathbf{r},\mathbf{r}') = \sum_{l=0}^{\infty} V_l(r) \sum_{m=-l}^{l} Y_{ml}(\hat{\mathbf{r}}) Y_{ml}^{*}(\hat{\mathbf{r}}')$$

is the correct pseudopotential in the "reference state" when the molecule is far from the metal. For the present case we have shown that it is sufficiently accurate to take $V'_{\text{ps}}(\mathbf{r},\mathbf{r}') = V'_0(r)\delta(\mathbf{r}-\mathbf{r}')$. In Fig. 5 we show the pseudo and true wave functions for $E = -0.15$ a.u. and $r_c = 1.3$ a.u. In Fig. 6 we show $V_0(r)$ for various values of the parameter r_c in the function f.

The resulting pseudopotential V_0 only takes account of that part of the exchange and correlation potential which arises from that part of the electron density which is given by the core density $n_0(r)$. To take account of the full exchange and correlation energy in a way which takes full account of the nonlinearity of the exchange and correlation energy as a function of electron density, we follow Ref. 13: We subtract the exchange and correlation potential due to $n_0(r)$ alone from V_0 and then add the full exchange and correlation potential arising from the full electron density $n_0(\mathbf{r})+n_m(\mathbf{r})$ back in to give the full exchange and correlation potential used in the solution of the Kohn-Sham equations. Here $n_m(\mathbf{r})$ is the density of valence or "metal" electrons. The resulting pseudopoten-

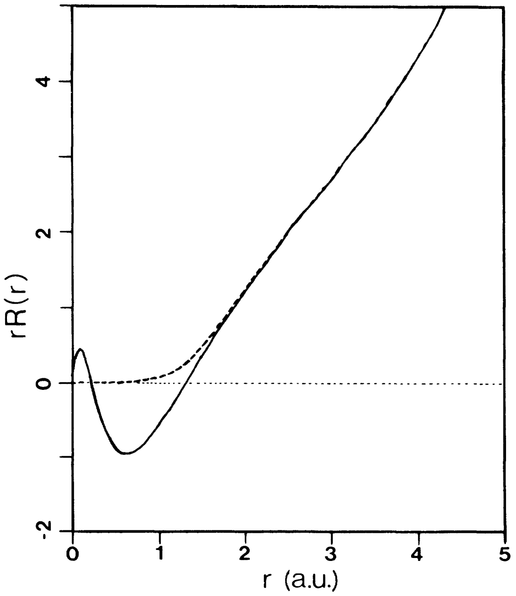

FIG. 5. Real and pseudowave functions for $E = -0.15$ a.u. and $r_c = 1.3$ a.u.

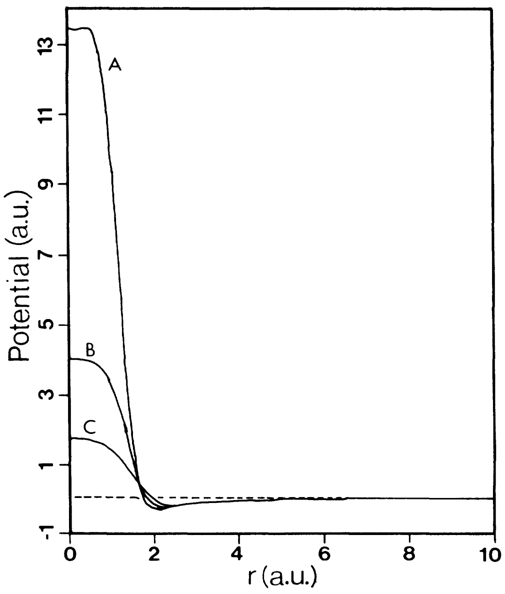

FIG. 6. The pseudopotential $V'_0(r)$ for $E = -0.15$ a.u. and (a) $r_c = 1.2938$ a.u., (b) $r_c = 1.5$ a.u., and (c) $r_c = 1.7$ a.u.

tial is a sum of a "linear" (or charge independent) part $\bar{V}_{\mathrm{ps},1}(x)$ given by

$$\bar{V}_{\mathrm{ps},1}(x) = (1/A)\int \{V_0'(r) - V_{\mathrm{xc}}[n_0(r)]\}\,dy\,dz \qquad (19)$$

and an exchange and correlation part $\bar{V}_{\mathrm{xc}}(x)$ given by

$$\bar{V}_{\mathrm{xc}}(x) = (1/A)\int dy \int dz\, V_{\mathrm{xc}}\left[n_m(x) + \sum_i n_0(\mathbf{r}-\mathbf{R}_i)\right],$$

where the sum is over solvent positions. The integrand of the right-hand side of Eq. (19) is shown for $E=-0.15$, $r_c=1.3$ a.u. in Fig. 7. In practice, n_m is essentially zero very near the nucleus of each solvent molecule, so that we can truncate $n_0(\mathbf{r}-\mathbf{R}_i)$ in that region, since the potential will not be used there. We take the form $n_0(r)=A\sin(Br)/r$ near the core and match it smoothly to the exact n_0 at a radius r_0 which is near r_c.

As mentioned in the preceding section, $V_{\mathrm{xc}}[n_m(x)+n_s(\mathbf{r})]$ is not a linear function of its argument so that averaging it over the transverse position coordinates of the solvent molecules is not straightforward. We have shown numerically by evaluating the average for an ordered array of molecules that the approximation [see Eqs. (4), (13), and (14)]

$$\begin{aligned} v_{\mathrm{xc}} &= (1/A)\int dz\,dy\, V_{\mathrm{xc}}[n_s(\mathbf{r}) + n_m(x)] \\ &= V_{\mathrm{xc}}\left[(1/A)\int dz\,dy\, n_s(\mathbf{r}) + n_m(x)\right] \end{aligned}$$

is accurate to within about 10%. Here $n_s(\mathbf{r}) = \sum_i n_0(\mathbf{r}-\mathbf{R}_i)$ where the molecules are at positions $\mathbf{R}_i$. Unfortunately, if we use the pseudopotential defined by this procedure to calculate the binding energy of a neon atom to a metal surface, then we find that the result depends on the parameter r_c as it should not in pseudopotential theory. We have chosen to deal with this difficulty by choosing a value of r_c for use in the calculations described in the next section in such a way that the binding energy of neon atoms alone (with no dipole term added to the pseudopotential) to the metal surface is consistent with all electron calculations[14] of rare-gas atoms on jellium surfaces.

V. CALCULATION OF $x_w(\sigma)$ AND THE CAPACITANCE

The calculation of $x_w(\sigma)$ and the electronic contribution to the compact layer capacitance now proceed in essentially the same way as in Ref. 6: For a given σ and a series of values of x_w, all the terms in Eq. (2) are computed [except that in the present model we leave out contributions from E_{ps} and $E_{\mathrm{core-sol}}$ and in Eq. (2) x_2 is replaced everywhere by x_w]. The resultant energy as a function of x_w for fixed σ is then fitted to a polynomial in x_w from which the minimum $x_w(\sigma)$ is extracted for that σ. In this way we obtain the function $x_w(\sigma)$ and so obtain the equilibrium position of the solvent distribution. We have chosen in the present work to focus attention on *sp* metals for which the jellium model is most reliable. The pseudopotential corrections for the metal ion cores are not expected to be very large for the systems with which we compare (at least away from the strongly anodic region) and for this reason we do not include the terms E_{ps} and $E_{\mathrm{core-sol}}(\sigma,x_2)$ in this total energy calculation. As in Ref. 6, we include the dipole-image interaction as a correction. Here however, we do not adjust the value of the dipole moment and we integrate the dipole-image interaction over the solvent distribution as given by the MSA hard-sphere results. In Fig. 8 we show the values of $x_w(\sigma)$ cal-

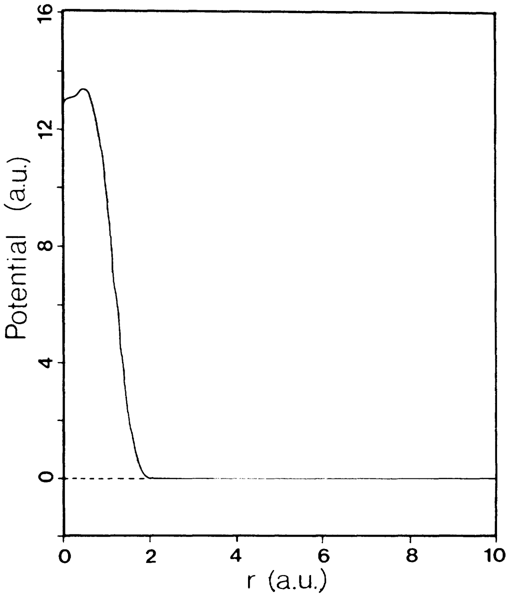

FIG. 7. The "linear part" of the pseudopotential with $E=-0.15$ a.u. and $r_c=1.3$ a.u. See Eq. (19) and the accompanying text.

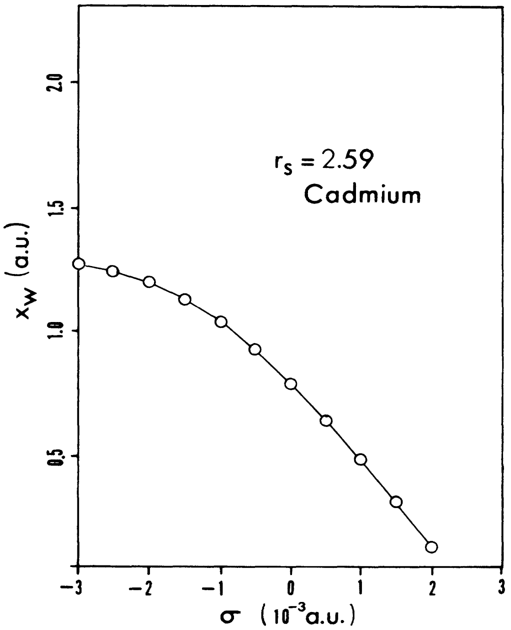

FIG. 8. Values of the distance x_w as a function of the charge per unit area on the metal for Cd, calculated using the model described in the text.

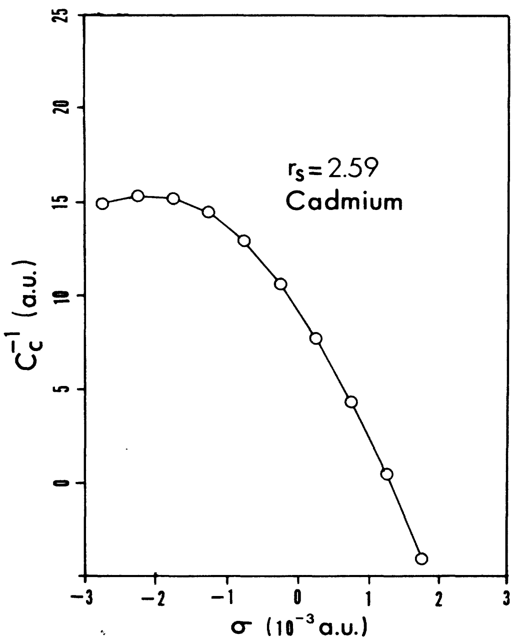

FIG. 9. The inverse compact capacitance as a function of the charge per unit area on the metal for Cd, calculated using the model described in the text.

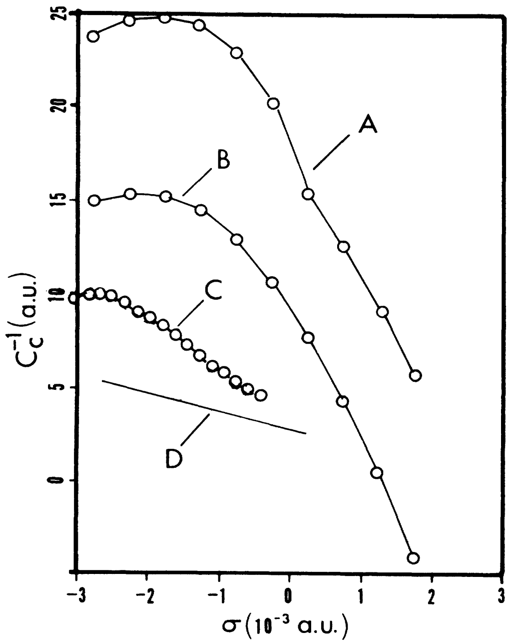

FIG. 10. Comparison of C_c^{-1} for the three models studied to date and the experimental results for Cd: (a) the prediction of Ref.6, where the solvent pseudopotential was modeled by a step function; (b) the prediction of the present model, described in the text; (c) experimental results; (d) the slope predicted by the simple "slide" model also described in Ref. 6.

culated in this manner for Cd.

In order to calculate the compact differential capacitance, one needs to know[15] $\bar{x}(\sigma)$, the first moment of the charge induced upon the metal, and $x_2(\sigma)$, the starting point of an equivalent Gouy-Chapman electrolyte. The point $\bar{x}(\sigma)$ is obtained from the self-consistent charge densities as described in Ref. 6. The point $x_2(\sigma)$ is the position at which to place the edge of an ideal Gouy-Chapman electrolyte in place of the true electrolyte charge distributions in order to obtain the same total potential drop.[15] The MSA hard-sphere-plus-dipole distribution functions allow calculation of $x_2(\sigma)$ relative to the hard wall position in the limit as $\sigma \rightarrow 0$. Here we assume that this position for x_2 remains fixed with respect to the solvent distribution over the range of induced charge considered and so differs from x_w by a known constant. This is analogous to the assumption in Ref. 6 that $x_2(\sigma)$ was fixed to the edge of the square barrier, and relies largely on the assumption that the polarization density is linear in σ. Thus the present model offers the added advantage that the position of x_2 relative to the pseudopotential is calculated from the model rather than being guessed at. The inverse compact differential capacitance is then given by[15]

$$C_c^{-1}(\sigma) = \frac{d}{d\sigma}\{\sigma[x_2(\sigma) - \bar{x}(\sigma)]\} .$$

The results for the inverse compact differential capacitance, expressed as a graph of $1/C_c$ as a function of charge σ are shown in Fig. 9, and they are compared with experiments[16] on Cd electrodes and with the results of the model of Ref. 6 in Fig. 10.

VI. DISCUSSION AND CONCLUSIONS

Inspection of Fig. 10 indicates that the inclusion of solvent structure and more detailed information about the solvent-electron interaction has resulted in quite significant improvement in the power of the model to predict the right values for the observed differential capacitance of the Cd-electrolyte interface. This improvement, which is also obtained for other *sp* metals, is particularly encouraging in view of the fact that the new model for the solvent is somewhat less arbitrary than the preceding one as well as being more detailed. It should, however, be pointed out that at least one free parameter remains because we are forced to adjust r_c in the pseudopotential in order to give the right binding energy for neon to a metal surface.

In future work on this model it will be necessary to include saturation effects in the dipolar response of the solvent in this model and to improve the model employed to calculate $E_{\text{long-range}}$. We have discussed both these points before.[6] The former effect can be expected to account for the observed temperature dependence of the differential capacitance and the latter will remove the arbitrary character of the assumptions employed in that term. Finally, it will be useful to explore the consequences of the transverse averaging employed in this paper by developing a fully three-dimensional model. This is of particular importance in view of the fact that most experimental electrochemical interfaces are far from being perfect single crystal faces while the solvent is undoubtedly highly disordered. Despite these caveats, we do not anticipate that the basic physics of the model will require major revision as a consequence of such considerations.

ACKNOWLEDGMENT

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