Nonlocal electrostatic approach to the problem of a double layer at a metal-electrolyte interface

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Present theories of the capacity of the metal-electrolyte interface are discussed with particular emphasis on the contribution of the metal. A unified treatment of the interface is presented in which the potential distribution is calculated from nonlocal electrostatics. Two models are treated in detail: In the first model the boundary between the metal and the electrolyte is considered as sharp; it is shown that such a model is difficult to reconcile with the experimental data. The second model allows for the spill-over of the metal electrons into the solvent. Rough estimates show that this type of model is more in line with experimental results.

I. INTRODUCTION

The distribution of the electrostatic potential at the metal electrode-electrolyte interface, usually referred to as the "double-layer problem", has been the subject of electrochemical research, both theoretical and experimental, for several decades. This continued interest in this area is due to the important role which the double layer plays in all processes of adsorption and charge transfer at electrodes, and its resulting influence on such technologically important processes as electrocatalysis and corrosion.

In spite of the intensive research in this area, existing theories of the double layer have taken little notice of recent advances in the related areas of solid-state and surface physics. Thus, it is still customary to consider the metal as a region of constant potential, though it has been known for some time that metals have a finite screening length which is only slightly smaller than the thickness of the Helmholtz layer. Also, the solvent is generally treated as a dielectric with a permittivity varying rapidly over the extension of one or two solvent molecules, a view which is hardly compatible with

contemporary models of dielectrics.

So it seems desirable to introduce modern concepts of the dielectric behavior of metals and polar solvents into double-layer theory. In this paper we shall discuss some of the older theories from this point of view, and propose a new theoretical approach to the problem, which is based on the concepts of nonlocal electrostatics, a convenient tool to describe the structure of the dielectric medium. Thereby we can account for the structure of the solvent and the electrode in our model in a consistent manner.

Since the introduction of nonlocal electrostatics complicates the mathematics of the problem considerably, we shall restrict our present work to the region of small electric fields, where the response of the system is linear, i.e., to potentials near the point of zero charge (PZC), and we shall further assume that there is no specific adsorption at the electrode.

II. THE GOUY-CHAPMAN-STERN THEORY AND SOME EXTENSIONS

The classical theory of Gouy,[1] Chapman,[2] and Stern[3] (GCS) is still the basis of most experimental

and theoretical work on the double layer. In order to set our subsequent calculations into the right perspective, we shall briefly recall the main points of this theory.

In the GCS theory the interfacial region is divided into three parts (see Fig. 1). The metal (region I, $x < 0$) is treated as a perfect conductor, so that the electrostatic potential φ is constant in this region. The adjacent layer of solvent molecules constitutes the Helmhotz layer (region II, $0 < x < L$), which in the absence of specific adsorption is impenetrable to ions and is thus free of charge. The dielectric properties of this region are supposed to differ from those of the bulk electrolyte (region III, $L < x$). In the latter region the potential φ is determined from the Poisson-Boltzmann equation, which predicts a roughly exponential decrease of φ with the Debye length, originally introduced by Gouy as a characteristic parameter.

From the division of the electrolyte into two separate regions it follows immediately that the inverse capacitance $1/C$ of the double layer splits into contributions $1/C_H$ from the Helmholtz layer and $1/C_d$ from the diffuse layer in region III:

$$1/C = 1/C_H + 1/C_d \ . \tag{2.1}$$

Since region II is free of charge, its capacity C_H is independent of the electrolyte concentration, and is given by

$$C_H = \frac{\epsilon_*}{4\pi L} \ , \tag{2.2}$$

where ϵ_* is the "effective dielectric constant" of the Helmholtz layer. The diffuse layer capacity C_d, in contrast, depends strongly on the electrolyte concentration. In the region near the PZC, to which we restrict our consideration, it is:

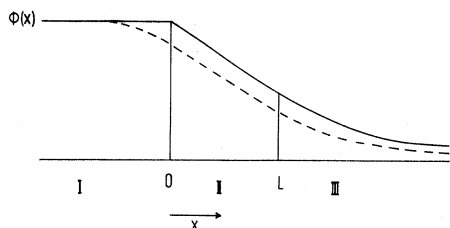$$C_d = \frac{\epsilon_s \kappa}{4\pi} \ . \tag{2.3}$$

FIG. 1. Potential distribution at the interface metal-electrolyte in the GCS theory (solid line) and in a model allowing for field penetration into the metal (broken line). Region I: metal; region II: Helmholtz layer; and region III: bulk electrolyte.

κ is the inverse Debye length of the electrolyte, which varies with the square root of the concentration, and ϵ_s is the bulk dielectric constant of the solvent.

It should be noted that the Poisson-Boltzmann equation, on which the GCS theory is based, holds strictly only at low electrolyte concentrations. More exact statistical-mechanical treatments have been attempted (see, e.g., Ref. 4); in the limit of low electrolyte concentrations they reduce to the GCS theory, so that Eq. (2.3) can be considered as a limiting law.

Equations (2.1)−(2.3) can be tested experimentally[5−7] by studying the capacity as a function of the electrolyte concentration. The best studied system is NaF in aqueous solution in contact with a mercury electrode, which very probably has no specific adsorption. Parsons[8] suggested that a plot of $1/C$ vs $1/C_d$ at various electrolyte concentrations is a good test of the GCS theory. For the above-mentioned system one obtains the predicted linear plot over a broad range of electrolyte concentrations with a concentration-independent part $C_* = 20 \ \mu\text{F}/\text{cm}^2$ at the PZC. If this is identified with the Helmholtz capacity C_H, one obtains $L/\epsilon_* = 0.3$ Å. The thickness L of the Helmholtz layer is usually estimated as $L \cong 4$ Å, which gives for the effective dielectric constant $\epsilon_* \approx 12$, a reasonable value at first glance.

In any case these experiments indicate that there is a concentration-independent contribution $1/C_*$ to the inverse capacity of the double layer. An alternative interpretation of $1/C_*$ was given earlier by Rice.[9] He noted that the electrostatic potential in the metal is not constant, but varies over a distance of the order of the Thomas-Fermi screening length. Consequently, the metal also gives a contribution $1/C_M$ to the inverse interfacial capacity. Using a free-electron model for the metal, Rice obtained

$$\frac{1}{4\pi C_M} = \frac{1}{\kappa_{\text{TF}}^0 \sqrt{\epsilon_b}} \ , \tag{2.4}$$

where κ_{TF}^0 is the inverse Thomas-Fermi screening length of the free-electron gas. ϵ_b is the background dielectric constant of the ion cores; Rice estimated this as $\epsilon_b \approx 8$ from the polarizability of mercury halides. This value is, however, surprisingly high from the viewpoint of the modern theory of solids, according to which ϵ_b is associated with fast interband transitions. For simple metals like mercury we should expect ϵ_b to be of the order of unity. (See *Note added in proof.*) Only for

TABLE I. Experimental values for the inverse capacities $1/4\pi C_*$ and calculated values for the Thomas-Fermi screening lengths of several metal-water interfaces. The data for C_* were taken from Ref. 29, κ_0^{-1} was calculated from Ref. 30.

Metal	Sb	Bi	Hg	Pb	Sn	Cd	In	Ga
$\dfrac{1}{4\pi C_*}$ (Å)	0.37	0.34	0.3	0.27	0.23	0.17	0.11	0.07
κ_0^{-1} (Å)	0.496	0.508	0.488	0.51	0.505	0.546	0.526	0.502

semimetals like bismuth with a small gap, or for certain transition metals with small, closely lying d bands, can ϵ_b reach values of 10 or so. In Table I we give the Thomas-Fermi lengths and the experimental values of $1/4\pi C_*$ for several s-p metals of electrochemical interest. An inspection shows that Rice's formula is at variance with the experimental data: It generally predicts too high values for the inverse capacity; particularly the data for Ga, In, and Cd are much smaller than one would calculate from Eq. (2.4). Also, the experimental data show no obvious correlation between the inverse capacity $1/4\pi C_*$ and ϵ_b. While the liquid metal mercury and the semimetal bismuth have about the same value of $1/4\pi C_*$, we would expect their background dielectric constant ϵ_b to differ considerably, as outlined above.

We are thus faced with a paradox. From a theoretical point of view it would be reasonable to combine the work of Rice with the GCS theory and postulate three contributions, $1/C_M$, $1/C_H$, and $1/C_d$ to the inverse capacity, of which $1/C_M$ and $1/C_H$ are concentration independent. However, such a theory, although physically plausible, contradicts the experimental data,[10] since $1/C_M + 1/C_H$ is considerably greater than the experimental value $1/C_*$.

Most research workers in this area have taken the view that the Helmholtz capacity alone gives C_*. The main argument for this point of view comes from the strong potential dependence of C_* observed experimentally. The metal capacity as given by Eq. (2.4) is practically independent of the electrode potential while the Helmholtz capacity C_H depends on the applied potential through the effective dielectric constant ϵ_*, which depends on the potential through saturation effects.

Still, the situation is far from satisfactory since it is not at all clear why the metal should give no contribution. A tentative explanation for this was offered by Mott and Watts-Tobin,[11] who suggested that the boundary between the metal and the elec-

trolyte is not abrupt, but that there might be some interpenetration between the electrons and the solvent molecules. However, this idea, which would modify the current views of the Helmholtz layer, was not pursued further. Later work in this area has mostly concentrated in constructing more detailed models for the Helmholtz layer (see, e.g., Refs. 12 and 13). While such work has led to a better understanding of the potential dependence of C_*, it has not been able to resolve the paradox discussed above. Instead, this problem has generally been ignored.

III. A NONLOCAL ELECTROSTATIC MODEL WITH A SHARP INTERFACE

A. Basic equations

In the following two sections we shall calculate the interfacial capacity from a nonlocal electrostatic model. We are thus interested in the electrostatic potential as a function of the external charge on the electrode. Now, it is well known in electrochemistry, that due to the presence of solvent dipole layers, the electrostatic potential in the interfacial region is not zero or constant at the potential of zero charge. Physicists generally tend to ignore this fact[9,14] for the reason that it has no effect on the capacity. We shall follow the physicist's practice here; this means explicitly that in the following we denote by $\phi(x)$ the electrostatic potential minus its value at the pzc. The corresponding convention is used for the fields $\vec{E}(x)$ and $\vec{D}(x)$.

In nonlocal electrostatics the dielectric displacement $\vec{D}(x)$ is not simply proportional to the electric field $\vec{E}(x)$ at the same point, but depends also on the electric field in the neighboring region

$$\vec{D}(x) = \int_{-\infty}^{\infty} \epsilon(x,x')\vec{E}(x')dx' , \qquad (3.1)$$

where $\epsilon(x,x')$ is the nonlocal dielectric function of the medium that correlates the displacement and the field at different points in space, and thus re-

flects the structure of the medium. Since, in our case the electric potential varies only in the x direction, we need to consider the one-dimensional case only.

Since the system metal-solvent is not homogeneous, the dielectric function $\epsilon(x,x')$ depends on x and x' separately, while in a homogeneous phase it is only a function of $|x-x'|$. In this section we assume that the metal and the solvent are separated by a sharp interface, so that $\epsilon(x,x')$ correlates only points belonging to the same subsystem. So the dielectric function separates into two parts, ϵ_M for the metal and ϵ_s for the solvent, with the properties

$$\epsilon_M(x,x')\neq 0 \quad \text{only if } x \leq 0 \text{ and } x' \leq 0 ,$$
$$\epsilon_s(x,x')\neq 0 \quad \text{only if } x \geq 0 \text{ and } x' \geq 0 .$$
(3.2)

As in ordinary electrostatics, the potential $\phi(x)$ is obtained by solving the Poisson equation, which now reads

$$\frac{dD}{dx} = -\frac{d}{dx}\int_{-\infty}^{\infty}\epsilon(x,x')\frac{d\phi}{dx'}dx' = 4\pi\rho(x) . \quad (3.3)$$

For a sharp interface this equation splits up into one equation for the solvent and one for the metal. For the solvent we use a modified GCS model. The Poisson equation then takes on the form

$$\frac{d}{dx}\int_0^{\infty}\epsilon_s(x,x')\frac{d\phi}{dx'}dx'$$
$$= \kappa_0^2\phi(x)\Theta(x-L) \quad \text{for } x \geq 0 , \quad (3.4)$$

where κ_0 is the inverse Debye length for an electrolyte with a solvent dielectric constant of unity.

For the metal we incorporate the screening effect of the free electrons into the dielectric function. In this convention the metal is charge free, so that its dielectric displacement D_M is constant:

$$\int_{-\infty}^0 \epsilon_M(x,x')\frac{d\phi}{dx'}dx'$$
$$= -D_M = \text{const} \quad \text{for } x \leq 0 . \quad (3.5)$$

Equations (3.4) and (3.5) must be supplemented by boundary conditions. If U is the total potential drop across the interface, we have

$$\phi(-\infty)=U, \quad \phi(\infty)=0, \quad \phi(x), \ D(x)$$

continuous at $x=0$ as boundary conditions. They determine a unique solution of the integro-differential equations.

We can use the condition of continuity of the dielectric displacement to derive a useful expression for its value D_M in the metal in terms of the potential in the solvent. Combining Eqs. (3.3) and (3.4), and integrating once, gives

$$D_M = \kappa^2\int_L^{\infty}dx\,\phi(x) . \quad (3.6)$$

The inverse capacity $1/C$ of the interface is then determined from

$$1/C = \frac{4\pi U}{D_M} . \quad (3.7a)$$

It splits up into a metal and a solvent contribution:

$$1/C_M = \frac{4\pi[U-\phi(0)]}{D_M}, \quad 1/C_s = \frac{4\pi\phi(0)}{D} . \quad (3.7b)$$

B. The solvent capacity in the limit of small κ_0

Since the Poisson-Boltzmann equation, on which our present treatment is based, applies strictly only to low electrolyte concentrations, we shall restrict ourselves to this case, thereby reducing the complexity of the problem. Specifically, we assume that κ^{-1} is greater than both the thickness L of the Helmholtz layer and the characteristic decay length of the dielectric function $\epsilon(x,x')$, which we denote by l_ϵ. As far as $\epsilon(x,x')$ is concerned, we shall keep our treatment quite general.

Under these conditions, Eq. (3.5) for the potential in the solvent can be solved by means of the singular perturbation technique;[15] that is, we seek a solution of the form

$$\phi(x)=\phi(0)\sum_{n=1}^{\infty}[\kappa^n\varphi_n(x)+\kappa^{n-1}\Psi_{n-1}(\kappa x)] , \quad (3.8)$$

where the functions $\varphi_n(x)$ are exponentially small in the region $x \sim \kappa^{-1}$ and the $\Psi_n(\kappa x)$ are almost constant at $x \simeq l_\epsilon \ll \kappa^{-1}$.

Substituting Eq. (3.8) into (3.5), and equating terms with the same order in κ, we obtain a series of equations for φ_n and Ψ_n. These can be solved by considering separately the regions of small x and large x, and matching the solutions in the intermediate region. This procedure is carried out in Appendix A, where the solution is derived explicitly up to the order of κ^2. The resulting expression for the solvent capacity is:

$$\frac{1}{4\pi C_s} = \frac{1}{\epsilon_s\kappa} + \frac{L+l}{\epsilon_s} - \frac{\Gamma\kappa}{\epsilon_s} + O(\kappa^2) , \quad (3.9)$$

where l is a length characteristic for the range of the spatial dispersion of the dielectric function and Γ is a constant; both l and Γ are defined in Appendix A.

The first term is simply the capacity of the diffuse layer as in the GCS theory. The second term contains both the capacity of the Helmholtz layer and a contribution due to the spatial dispersion of the dielectric function. It is interesting to note that up to this order in κ, the latter term is simply that of a capacitor with a plate separation l. Note also that in contrast to Eq. (2.2) our result contains the bulk dielectric constant ϵ_s in the concentration-independent term. The third term predicts that in the plot of $1/C$ vs $1/C_d$ a deviation from linearity should be observed for large κ, i.e., for large concentrations or small values of $1/C_d$. A deviation of this kind has indeed been observed experimentally in some cases, e.g., by Parsons and Zobel[8] for the interphase between mercury and an aqueous solution of NaH_2PO_4. However, since this deviation occurs at high electrolyte concentrations of the order of 1 M, where our theory may no longer be adequate, it is not certain that this is the effect predicted by our Eq. (3.9). For a given dielectric function of the solvent, the capacity C_s can thus in principle be calculated, the concentration independent term being given by the second term in Eq. (3.9). In Appendix B this is demonstrated for a simple model function, and the order of magnitude of C_s is estimated. These results are further discussed below.

C. The metal capacity in the specular reflection model

We noted above that in the presence of a boundary the dielectric function $\epsilon_M(x,x')$ of the metal differs from the bulk function $\epsilon_M(x-x')$. A useful model, which approximates the former through the latter, is the assumption of specular reflection[16-19]:

$$\epsilon_M(x,x')=\epsilon_M(x-x')-\epsilon_M(x+x') . \qquad (3.10)$$

This is a reasonable model for a medium with a sharp interface. We shall use it to derive a simple expression for the capacity of a metal electrode with an arbitrary bulk dielectric constant. For this purpose it is convenient to extend formally the electrostatic potential $\phi(x)$ in the metal, which is defined on the negative axis $x<0$, to the right by the definition

$$\bar{\phi}(x)=\begin{cases}\phi(x) & \text{for } x<0 \\ \phi(-x) & \text{for } x>0 .\end{cases} \qquad (3.11)$$

Substituting Eqs. (3.10) and (3.11) into our basic equation (3.4) for the metal, we obtain

$$\frac{d}{dx}\int_{-\infty}^{\infty}dx'\epsilon_M(x-x')\frac{d\bar{\phi}(x')}{dx'}=0 . \qquad (3.12)$$

We split $\epsilon(x-x')$ into its local and its nonlocal part

$$\epsilon_M(x-x')=\epsilon_b\delta(x-x')+\tilde{\epsilon}(x-x') \qquad (3.13)$$

and extract the constant part U from the potential

$$\varphi(x)=\bar{\phi}(x)-U . \qquad (3.14)$$

Substituting these definitions into Eq. (3.12) and integrating by parts gives

$$\epsilon_b\varphi''(x)+\int_{-\infty}^{\infty}dx'\epsilon(x-x')\varphi''(x')=2\tilde{\epsilon}(x)\varphi'(-0) . \qquad (3.15)$$

This equation is easily solved by Fourier transformation. Taking account of the discontinuity of $\varphi'(x)$ at $x=0$, we obtain

$$\varphi(x)=-\frac{\epsilon_b\varphi'(-0)}{\pi}\int_{-\infty}^{\infty}e^{ikx}\frac{dk}{k^2\epsilon_M(k)} , \qquad (3.16)$$

where $\epsilon_M(k)$ is the Fourier transform of $\epsilon_M(x-x')$. At the interface we have in particular

$$\varphi(0)=\bar{\phi}(0)-U=-\epsilon_b\varphi'(-0)L_M , \qquad (3.17)$$

where

$$L_M=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dk}{k^2\epsilon_M(k)}=\frac{2}{\pi}\int_0^{\infty}\frac{dk}{k^2\epsilon_M(k)} \qquad (3.18)$$

has the dimensions of a length. In the second step of Eq. (3.18) use has been made of the fact that $\epsilon_M(k)$ is an even function. In our model the dielectric displacement D of the metal is constant. It is conveniently evaluated at the interface $x=0$; here the nonlocal part of $\epsilon(x-x')$ cancels, so that

$$D=\epsilon_b\varphi'(-0) . \qquad (3.19)$$

This gives for the inverse capacity the surprisingly simple result

$$\frac{1}{4\pi C_M}=L_M . \qquad (3.20)$$

This characteristic length L_M has been studied in different physical contexts and has been calculated for various model dielectric functions including those of Lindhard, Hubbard, and Sham (see Ref. 20). A particularly simple expression is obtained in the Thomas-Fermi approximations, which give

$$L_M = \frac{1}{\sqrt{\epsilon_b} \kappa_{TF}^0} , \tag{3.21}$$

where κ_{TF}^0 is the inverse Thomas-Fermi screening length for a free-electron gas in vacuum. Both this and the other models mentioned give similar values for L_M, which for simple metals lie in the region of $0.3-0.8$ Å.

D. Discussion

Combining the results of Secs. III B and III C, the concentration-independent part of the inverse interfacial capacity is

$$\frac{1}{4\pi C_*} = L_M + \frac{L+l}{\epsilon_s} . \tag{3.22}$$

If we compare this result with the experimental value for the mercury-sodium fluoride system at the pzc, we are once again faced with the paradox discussed in Sec. II: The predicted value is too big. For mercury we have $L_M \approx 0.5$ Å, taking $\epsilon_b \approx 1$. The extension of the Helmholtz layer is about $L \approx 4$ Å so that $L/\epsilon_s \approx 0.05$ Å. The contribution l/ϵ_s due to space dispersion is estimated in Appendix B; the smallest reasonable estimate is $l/\epsilon_s \approx 0.2$ Å. This gives a theoretical estimate which is more than twice as large as the experimental value $1/4\pi C_* = 0.3$ Å. Moreover, this discrepancy is not only found with mercury, which according to Bloch and Rice[21] might have anomalous surface properties. In Table I we compare experimental values for the inverse capacity $1/4\pi C_*$ of several electrode systems with the Thomas-Fermi lengths, and in all cases the latter are bigger.

It is difficult to see how the theoretical estimate derived from our model could be made smaller. One escape would be to postulate a larger background dielectric constant ϵ_b for metals, say $\epsilon_b \approx 10$ for Hg, or $\epsilon_b \approx 50$ for Ga. Since such high values are not realistic for bulk metals, they could only be due to a surface effect. This could be envisaged in such a way, that the screening of the electric field is largely effected by the tails of the electronic wave functions spilling over the geometrical surface of the metal. In this region the first layer of solvent molecules would contribute to the background dielectric constant ϵ_b, and could well raise it to the required order of magnitude. Such a picture is, however, not consistent with a sharp interface between the metal and the electrolyte as we have assumed in this section. So our above estimate indicates that a sharp interface model is not applicable to the mercury-water and

to the other metal-water interfaces given in Table I.

For other solvents the situation appears somewhat more favorable. For instance, for a solution of sodium fluoride in acetonitrile in contact with mercury, the experimental value (Ref. 22) is $1/4\pi C_* \approx 0.6$ Å, which could just be reconciled with the above estimate. However, since in these estimates we took the smallest possible values for the contributions to the inverse capacity, some deviation from the sharp interface model is likely also in this case. So it seems necessary to lay the foundations of a model with a diffuse interface, allowing for a spilling over of the metal electrons into the solvent. This will be done in the next section.

IV. THE MODEL WITH A DIFFUSE INTERFACE

During the last decade the structure of the metal-vacuum interface has been investigated intensively from a theoretical point of view. The variation of the electronic density $\rho_e(x)$ near the metal surface was calculated within various approaches. It was shown that outside the positive ionic background $\rho_e(x)$ drops to zero over a distance of several angströms. Both the linear and the nonlinear response of the electronic density to an external electric field were analyzed.[23-26] In particular the influence of the electronic tails on the capacity of the interface was considered; the results varied only little from that for the usual model with a sharp surface. The main effect is that the effective surface is shifted somewhat with respect to the first layer of the ionic cores.

A theoretical description of the metal-polar solvent interface is considerably more difficult. No attempt has yet been made to calculate the electronic density of the metal and its penetration into the solvent. The explicit form of the dielectric function $\epsilon(x,x')$, in the interfacial region, is unknown. Therefore, in this section we shall make a general analysis of the capacity in terms of the general properties of $\epsilon(x,x')$, using concrete model functions only for illustration.

We describe the dielectric properties of the system metal-electrolyte by a single dielectric function $\epsilon(x,x')$. Far from the interface, $\epsilon(x,x')$ reduces to the dielectric function of the solvent and the metal, respectively; and in the interfacial region, it depends strongly on the properties of the boundary. In this general case, our basic relations (3.11) and (3.3) remain valid, while the Poisson-Boltzmann

equations (3.4) and (3.5) are combined into one equation:

$$\frac{\partial}{\partial x} \int_{-\infty}^{\infty} \epsilon(x,x') \frac{\partial \phi}{\partial x'} = \kappa_0^2 \phi(x) \Theta(x-L) . \quad (4.1)$$

Similarly, the inverse dielectric function $\epsilon^{-1}(x,x')$ is now defined through

$$\int_{-\infty}^{\infty} \epsilon(x,x') \epsilon^{-1}(x',x'') dx' = \delta(x-x'') . \quad (4.2)$$

The boundary conditions are the same as before. Equation (4.1) is solved in Appendix C for the case of a large Debye length of the solvent by an iterative method. The resulting capacity is

$$\frac{1}{4\pi C} = \frac{1}{\epsilon \kappa} + \frac{R}{\epsilon} - \frac{\kappa}{\epsilon}(2R_1 + \frac{s}{4}) , \quad (4.3)$$

where the characteristic length R of the system is given by

$$R = \int_{-\infty}^{\infty} dx \left[\left[\int_{-\infty}^{\infty} dx' \epsilon \epsilon^{-1}(x,x') \right] - \Theta(x-L) \right] ,$$

$$(4.4)$$

and R_1 is defined in Appendix C.

For illustration we consider the following simple model, in which

$$\epsilon(x,x') = \epsilon(x)\delta(x-x')$$

$$- \int_{\max(x,x')}^{\infty} \kappa^0 \Theta(L-x'') dx'' , \quad (4.5)$$

where

$$\epsilon(x) = \begin{cases} 1 & \text{for } x < 0 \\ \epsilon_* & \text{for } 0 \le x < L \\ \epsilon_s & \text{for } x \ge L . \end{cases} \quad (4.6)$$

This gives the following expression for the inverse capacity:

$$\frac{1}{4\pi C_*} = \frac{1}{\kappa^0} \frac{1 + \epsilon_*^{-1/2} \tanh \dfrac{\kappa^0 L}{\sqrt{\epsilon_*}}}{1 + \epsilon_*^{1/2} \tanh \dfrac{\kappa^0 L}{\sqrt{\epsilon_*}}} . \quad (4.7)$$

The physical meaning of this model is that the electronic density of the metal extends a distance L into the solvent, which in this region has an effective dielectric constant ϵ_*. This leads to an appreciable reduction of the inverse capacity $1/C_*$ which is illustrated in Fig. 2. Of course, this model is too simple to be a realistic description of the interface, but it shows that the penetration of the metal electrons into the solvent leads to the desired reduction of the constant part of the inverse capacity.

V. CONCLUSIONS

In our work above we have treated the interface metal electrode-liquid electrolyte by the method of nonlocal electrostatics, and obtained expressions for the concentration-independent part of the interfa-
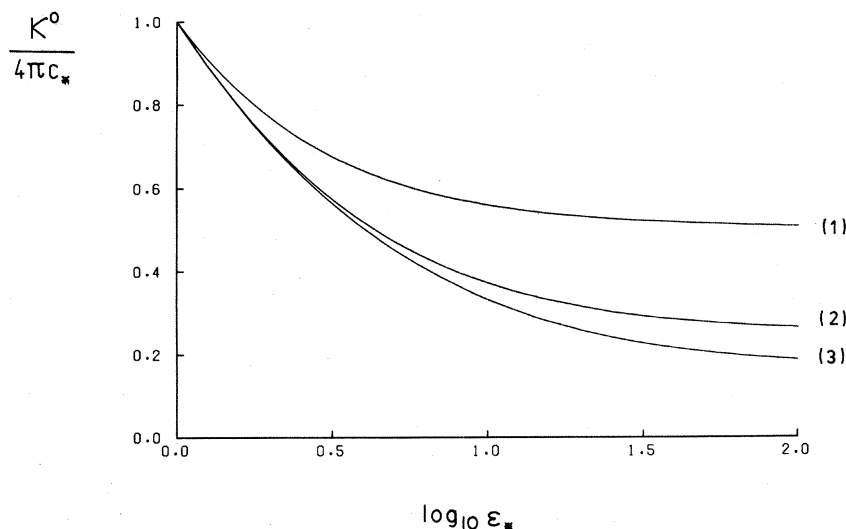

FIG. 2. The normalized inverse capacity $\kappa^0/4\pi C_*$ as a function of the effective dielectric constant ϵ_* according to Eq. (4.7) for three different values of $\kappa^0 L$: (1) $\kappa^0 L = 1$; (2) $\kappa^0 L = 3$; (3) $\kappa^0 L = 5$.

cial capacity. The main advantages of our model over the exisiting theories are:

(1) It represents a unified formalism by which we can treat both the two bulk phases and the interface.

(2) It is a convenient means for taking the structure of the system into account.

(3) It avoids the dubious concept of a dielectric constant varying rapidly over a distance of several angströms.

(4) The corresponding concept has been used successfully in solid-state and surface physics, so that our treatment forms a bridge to these closely related subjects.

A disadvantage of the method is its relative mathematical complexity, which restricted our present work to potentials near the PZC and to the limit of small electrolyte concentrations. The crucial quantity in nonlocal electrostatics is the dielectric function $\epsilon(x,x')$. While for a bulk metal and a bulk solvent reasonable models for this function exist, only little is known about its behavior in the interfacial region. We have therefore attempted to keep our treatment quite general, and used specific model functions for $\epsilon(x,x')$ only to obtain numerical estimates. Ultimately, such an explicit expression for $\epsilon(x,x')$ must come from a microscopic model of the interface.

In the first part of our work we have made the assumption, inherent in practically all theories of the double layer, that the metal and the solvent are separated by a sharp interface. The most important conclusion which we draw from this study is that such a model is incompatible with the experimental data. This result is largely independent of the models which one takes for the subsystems. For all the various approximations to $\epsilon(x,x')$ of the metal which have been used in solid-state physics the contribution of the metal to the inverse capacity is too large. So a realistic model of the interface must allow for a diffuse interface, which lets the metal electrons spill over the geometrical surface and interact with the solvent molecules. In Sec. IV we have presented a general framework which can take such effects into account. Such a model will give interfacial capacities which are more in line with the experimental results for the following reason. When the electronic tails penetrate into the solvent over a distance of $1-3$ Å, then the shielding of the electric field by the electrons occurs in a region where the presence of the solvent molecules provides for a relatively high background dielectric constant. Thus the contribution of the metal electrons to the inverse capacity is considerably reduced and brought closer to the experimental values. While we think that these results are important, a detailed, quantitative theory of the interphase is still lacking. For this it is necessary to go beyond the phenomenological approach, which we have used here, and to construct a quantum-mechanical model of the interphase on the microscopic level. This seems no easy task. While for metals and metal surfaces reasonable quantum-mechanical models exist, the electronic properties of solvents are understood to a far smaller degree. We hope that this work points the way in which future research should be directed.

Note added in proof. ϵ_b of mercury has recently estimated as 2 [see G. W. Ford and W. H. Weber, Surf. Sci. 110, L587 (1981)].

ACKNOWLEDGMENT

APPENDIX A: CALCULATION OF THE POTENTIAL BY SINGULAR PERTURBATION THEORY

Substituting Eq. (3.8) into (3.4) gives

$$\frac{d}{dx} \sum_{n=1}^{\infty} \kappa^n \int_0^{\infty} dx' \epsilon(x,x')[\varphi_n'(x')+\psi_{n-1}'(\kappa x')] = \epsilon\Theta(x-L)\left[\sum_{n=3}^{\infty} \kappa^n \varphi_{n-2}(x) + \sum_{n=2}^{\infty} \kappa^n \psi_{n-2}(\kappa x)\right]. \quad (A1)$$

We shall consider this equation separately in the regions of small and large x.

1. $x < l_\epsilon << \kappa^{-1}$

The main contributions to the integrals come from the region $x' \leq l_\epsilon << \kappa^{-1}$. Therefore, the ψ_n in Eq. (A1) can be expanded into a Taylor series about $\kappa x = 0$. Equation (A1) is then reduced to

$$\sum_{n=1}^{\infty} \kappa^n \frac{d}{dx} \int_0^{\infty} dx' \, \epsilon(x,x') \varphi_n'(x') + \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \frac{\kappa^{n+m}}{m!} \psi_{n-1}^{(m+1)}(0) \frac{d}{dx} \int_0^{\infty} dx' \, x'^m \epsilon(x,x')$$

$$= \epsilon \Theta(x-L) \left[\sum_{n=3}^{\infty} \kappa^n \varphi_{n-2}(x) + \sum_{n=2}^{\infty} \sum_{m=0}^{\infty} \frac{\kappa^{n+m}}{m!} \psi_{n-2}^{(m)}(0) x^m \right] . \quad \text{(A2)}$$

This can be split into a series of equations by equating terms with the same power in κ. We write down the first two equations explicitly:

$$\frac{d}{dx} \int_0^{\infty} dy \, \epsilon(x,y) \varphi_1'(y) + \psi_0'(0) \frac{d}{dx} \int_0^{\infty} dy \, \epsilon(x,y) = 0 , \quad \text{(A3)}$$

$$\frac{d}{dx} \int_0^{\infty} dy \epsilon(x,y) \varphi_2'(y) + \psi_1'(0) \frac{d}{dx} \int_0^{\infty} dy \epsilon(x,y) + \psi_0''(0) \int_0^{\infty} dy \epsilon(x,y) y = \epsilon \Theta(x-L) \psi_0(0) . \quad \text{(A4)}$$

2. $x \sim \kappa^{-1}$

In this region the φ_n functions are small and can be neglected. The main contribution to the integral comes from the region close to x, where $|x-y| \leq l_\epsilon$. Therefore, the ψ_n can be expanded about the point κx. Also, we note, that for $x,y \gg l_\epsilon$ we have $\epsilon_s(x,y) = \epsilon_s(x-y)$, since the effect of the boundary is no longer felt. From this it follows that the moments

$$\int_0^{\infty} dy \epsilon_s(x-y)(x-y)^m \approx \int_{-\infty}^{\infty} dy \epsilon_s(y) y^m \equiv M^{(m)} , \quad \text{(A5)}$$

are constants. In particular, $M^{(0)} = \epsilon_s$, and all odd moments vanish, since $\epsilon(x)$ is an even function. Taking these considerations into account, we obtain for the potential:

$$\sum_{n=1}^{\infty} \sum_{k=0}^{\infty} \kappa^{n+2k+1} \frac{M^{(2k)}}{(2k)!} \psi_{n-1}^{(2k+2)}(\kappa x)$$

$$= \epsilon \sum_{n=2}^{\infty} \kappa^n \psi_{n-2}(\kappa x) . \quad \text{(A6)}$$

The first three equations in powers of κ are

$$\psi_0''(\kappa x) = \psi_0(\kappa x) , \quad \text{(A7)}$$

$$\psi_1''(\kappa x) = \psi_1(\kappa x) , \quad \text{(A8)}$$

$$\psi_2''(\kappa x) = \psi_2(\kappa x) - \frac{M^{(2)}}{2\epsilon} \psi_0^{(IV)}(\kappa x) . \quad \text{(A9)}$$

Their solutions are

$$\psi_0(y) = \psi_0(0) e^{-y} , \quad \text{(A10)}$$

$$\psi_1(y) = \psi_1(0) e^{-y} , \quad \text{(A11)}$$

$$\psi_2(y) = \left[\psi_2(0) + \psi_0(0) \frac{M^{(2)}}{4\epsilon} y \right] e^{-y} . \quad \text{(A12)}$$

From (A10)−(A12) it follows that

$$\psi_0'(0) = -\psi_0'(0) = -\psi_0(0), \quad \psi_1'(0) = -\psi_1(0) . \quad \text{(A13)}$$

Let us return to Eqs. (A3) and (A4). Integrating once and using (A13), we obtain

$$\int_0^{\infty} dy \, \epsilon(x,y) \varphi_1'(y) = \psi_0(0) \int_0^{\infty} dy \, \epsilon(x,y) + C_0 , \quad \text{(A14)}$$

$$\int_0^{\infty} dy \, \epsilon(x,y) \varphi_2'(y) = \psi_1(0) \int_0^{\infty} dy \, \epsilon(x,y)$$

$$- \psi_0(0) \int_0^{\infty} dy \epsilon(x,y) y$$

$$+ \epsilon \Theta(x-L)(x-L) \psi_0(0) + C_1 . \quad \text{(A15)}$$

The constants C_0 and C_1 can be found from the values of the integrals at infinity. We have

$$\lim_{x \to \infty} \int_0^{\infty} dy \, \epsilon(x,y) \varphi_1'(y) = 0 ,$$

$$\lim_{x \to \infty} \int_0^{\infty} dy \, \epsilon(x,y) dy = x\epsilon , \quad \text{(A16)}$$

so that

$$C_0 = -\epsilon \psi_0(0), \quad C_1 = -\epsilon \psi_1(0) + \epsilon L \psi_0(0) . \quad \text{(A17)}$$

We now apply the inverse dielectric function $\epsilon_s^{-1}(x,x')$ defined by the relation:

$$\int_0^{\infty} dx \, \epsilon_s^{-1}(x'',x) \epsilon_s(x,x') = \delta(x'-x''), \quad x',x'' > 0 . \quad \text{(A18)}$$

Then,

$$\varphi_1'(x) = -\psi_0(0) \int_0^{\infty} dy \, [\epsilon_s^{-1}(x,y)\epsilon - \delta(x-y)] , \quad \text{(A19)}$$

$$\varphi_2'(x) = -\psi_1(0) \int_0^\infty dy \, [\epsilon_2^{-1}(x,y)\epsilon - \delta(x-y)] + \psi_0(0) \int_0^\infty dy \{ \epsilon_s^{-1}(x,y)\epsilon[L\Theta(L-y)+y\Theta(y-L)] - y\delta(x-y) \} \, .$$

(A20)

At this point it is convenient to introduce the following notations:

$$l(x) = \int_x^\infty dx'' \int_0^\infty dx' [\epsilon_s^{-1}(x'',x')\epsilon_s - \delta(x''-x')] \, ,$$

(A21)

$$l = l(0) \, ,$$

(A22)

$$S(x) = \int_x^\infty dx'' \int_0^\infty dx' \{ \epsilon_s^{-1}(x'',x')\epsilon_s[x'\Theta(x'-L)+L\Theta(L-x'')] - x'\delta(x'-x'') \} \, ,$$

(A23)

$$S = S(0) \, ,$$

(A24)

$$s = \frac{1}{\epsilon_s} \int_{-\infty}^\infty dy \, y^2 \epsilon_s(y = x - x') = -\frac{1}{\epsilon_s} \frac{d^2 \epsilon_s(k)}{dk^2} \bigg|_{k=0} \, ,$$

(A25)

$$t = \int_L^\infty l(x) dx \, .$$

(A26)

With the aid of these definitions the terms for the potential can be written in a concise form. Integrating Eqs. (A19) and (A20) over x gives

$$\varphi_1(x) = \psi_0(0)l(x) \, ,$$

(A27)

$$\varphi_2(x) = \psi_1(0)l(x) - \psi_0(0)S(x) \, .$$

(A28)

The equations (A10)−(A12), (A27), and (A28), together with Eq. (3.8), determine the distribution of the electrostatic potential $\phi(x)$, which is expressed through the dielectric function $\epsilon(x,x')$ and the still undetermined constants $\psi_n(0)$. The latter can be determined by considering Eq. (3.8) at the point $x=0$, which gives

$$\psi_0(0) = 1 \, ,$$

(A29a)

$$\psi_1(0) = -\varphi_1(0) = -l \, ,$$

(A29b)

$$\psi_2(0) = -\varphi_2(0) = l^2 + S \, .$$

(A29c)

Inserting these terms into Eq. (3.8), we obtain for the potential up to second order:

$$\phi(x) = \phi(0) \left[\kappa l(x) - \kappa^2[ll(x)+S(x)] + e^{-\kappa x} \left(1 - \kappa l + \kappa^2 l^2 + \kappa^2 - \kappa^3 \frac{s}{4} x \right) \right] \, .$$

(A30)

In order to calculate the corresponding capacity we next require the dielectric displacement D_M in the metal, which according to Eq. (3.6) is obtained from the potential by integrating over x:

$$D_M = \epsilon \kappa \phi(0) \left[1 - \kappa(l+L) + \kappa^2 \left(l^2 + S + lL + \frac{L^2}{2} + t + \frac{s}{4} \right) \right] + O(\kappa^4) \, .$$

(A31)

Making use of Eq. (3.7b), we obtain finally for the capacity of the solvent:

$$\frac{1}{4\pi C_s} = \frac{1}{\epsilon_s \kappa} + \frac{l+L}{\epsilon_s} - \frac{\Gamma}{\epsilon_s} \kappa + O(\kappa^2) \, ,$$

(A32)

where

$$\Gamma = \gamma + s/4 = S + t - \tfrac{1}{2}L^2 - Ll + s/4 \, ,$$

(A33a)

$$\gamma = S + t - \tfrac{1}{2}L^2 - Ll = \left[\int_0^\infty dx \int_L^\infty dx' + \int_L^\infty dx' \int_0^\infty dx \right](x'-L)[\epsilon_s \epsilon_s^{-1}(x,x') - \delta(x-x') \, .$$

(A33b)

APPENDIX B: THE SOLVENT CAPACITY C_s IN THE SHARP INTERPHASE MODEL, CALCULATED FOR A MODEL DIELECTRIC FUNCTION

As an illustration of our general equations (3.17) for the solvent capacity we consider a model, in which the dielectric function $\epsilon(x,y)$ is expressed through the corresponding function $\epsilon(x-y)$ for the bulk solvent in the form

$$\epsilon(x,y)=\epsilon(x-y)-\rho\epsilon(x+y) ,$$

$$x,y>0, \quad 0\leq\rho\leq1 . \tag{B1}$$

This is somewhat more general than the specular reflection model used in Sec. III C, which corresponds to $\rho=1$. For the physical meaning of this approximation, and particularly of the reflection coefficient ρ, we refer to Ref. 27.

A simple but useful model function for the dielectric function $\epsilon(x-y)$ of the bulk solvent is the Inkson model.[28] In the one-dimensional case this reduces to

$$\epsilon(x-y)=\delta(x-y)+\frac{\epsilon-1}{2\Lambda\sqrt{\epsilon}}\exp\left[-\frac{|x-y|}{\Lambda\sqrt{\epsilon}}\right] ,$$

$$\tag{B2}$$

where Λ is the characteristic correlation length of the spatial dispersion. The inverse dielectric function for (B1) and (B2) is[26]

$$\epsilon^{-1}(x,y)=\delta(x-y)-\left[1-\frac{1}{\epsilon}\right]\frac{1}{2\Lambda}(e^{-|x-y|/\Lambda}$$

$$+\Theta e^{-x+y/\Lambda}) ,$$

$$\tag{B3}$$

where

$$\Theta=\frac{\sqrt{\epsilon}-1-\rho(\sqrt{\epsilon}+1)}{\sqrt{\epsilon}+1-\rho(\sqrt{\epsilon}-1)} . \tag{B4}$$

This gives for the characteristic parameters l, γ, and s

$$l=(\epsilon_s-1)\frac{1-\Theta}{2}\Lambda , \tag{B5a}$$

$$s=2(\epsilon_s-1)\Lambda^2 , \tag{B5b}$$

$$\gamma=-(\epsilon-1)\Lambda^2[1-(1-\Theta)e^{-L/\Lambda}] . \tag{B5c}$$

The corresponding expression for the capacity is

$$\frac{1}{4\pi C_s}=\frac{1}{\epsilon_s\kappa}+\frac{L}{\epsilon_s}+\left[1-\frac{1}{\epsilon_s}\right]\frac{1-\Theta}{2}\Lambda$$

$$+\kappa\Lambda^2\left[1-\frac{1}{\epsilon_s}\right][\tfrac{1}{2}-(1-\Theta)e^{-L/\Lambda}] .$$

$$\tag{B6}$$

We are particularly interested in the contribution C_*^{dis} of the space dispersion to the concentration-independent part C_* of the capacity. Making use of the fact, that generally $\epsilon_s\gg1$, and $0\leq\rho\leq1$, we obtain the relation

$$\frac{\Lambda}{\sqrt{\epsilon}}\leq\frac{1}{4\pi C_*^{\text{dis}}}=\left[1-\frac{1}{\epsilon_s}\right]\frac{1-\Theta}{2}\Lambda\leq\Lambda . \tag{B7}$$

The correlation lengths of solvents generally lie in the region of $2-10$ Å, the minimum value being determined by a molecular diameter. Thus the smallest reasonable estimate for the contribution of the space dispersion is

$$\frac{1}{4\pi C_*^{\text{dis}}}\geq0.2 \text{ Å} . \tag{B8}$$

APPENDIX C: ITERATIVE SOLUTION FOR THE POTENTIAL IN A SYSTEM WITH A DIFFUSE INTERFACE

We shall now derive an expression for the capacity in the model with a diffuse interface restricting our treatment again to the case of large κ^{-1}. For this purpose it is convenient to rewrite our basic equations in the following form:

$$D(x)=D-\epsilon\kappa^2\int_L^x dx'\,\phi(x'), \quad x>L \tag{C1}$$

where

$$D=\lim_{x\to-\infty}D(x) ,$$

$$\frac{d\phi}{dx}=-\int_{-\infty}^{\infty}dx'\,\epsilon^{-1}(x,x')D(x') , \tag{C2}$$

$$\phi(x)=U+\int_{-\infty}^{x}dx'\,\phi'(x') . \tag{C3}$$

We shall again consider the regions of large and small x separately.

1. The region of large x

At $x\sim\kappa^{-1}$ we may expand $\phi'(x')$ about x:

$$\phi'(x')=\phi'(x)+(x-x')\phi''(x)$$

$$+\tfrac{1}{2}(x-x')^2\phi'''(x) \cdots , \tag{C4}$$

and $\epsilon(x,x')$ may be replaced by the bulk solvent dielectric function $\epsilon_s(x-x')$. Equation (4.1) can then be written in the form

$$\phi''(x)+\frac{s}{2}\phi^{\mathrm{IV}}(x)=\kappa^2\phi(x) , \qquad \text{(C5)}$$

where s has already been defined in Eq. (3.13). For $s\kappa^2 \ll 1$ the solution of this equation is

$$\phi(x)=\psi\exp[-\kappa(x-L)(1-\kappa^2 s/2)^{1/2}]$$

$$\approx\psi\left[1-(x-L)\kappa\left[1-\frac{\kappa^2}{4}s\right]+\frac{\kappa^2(x-L)^2}{2}+\cdots\right] .$$

$$\text{(C6)}$$

ψ is an undetermined constant, which will be obtained by matching this solution with the one for short distances.

2. The region of small x

For $x \ll \kappa^{-1}$ we solve the system of equations (C1)–(C3) by iteration. The zero-order solution is

obtained by neglecting the integral in (C1) and setting $D_0(x)=D=$ const. Substituting this value into Eq. (C2) gives

$$\phi_0'(x)=-D\int_{-\infty}^{\infty}dx'\,\epsilon^{-1}(x,x') . \qquad \text{(C7)}$$

It is convenient to introduce the function

$$\xi(x)=\int_{-\infty}^{\infty}\epsilon\epsilon^{-1}(x,x')dx'-\Theta(x-L) . \qquad \text{(C8)}$$

This is now substituted into Eq. (C7). After integration we obtain for the zero-order approximation

$$\phi_0(x)=U-\frac{D}{\epsilon}(x-L)+\frac{D}{\epsilon}[R(x)-R] , \qquad \text{(C9)}$$

where

$$R(x)=\int_x^{\infty}dx'\,\xi(x'), \quad R=R(-\infty) . \qquad \text{(C10)}$$

The next-order approximation is obtained by substituting (C9) into (C1), and subsequently into (C21) and (C3). After some straightforward but tedious calculations we obtain the following asymptotic expansion for $\phi_1(x)$ in the region $L \ll x \ll \kappa^{-1}$:

$$\phi_1(x)=U(1+\kappa^2 R_1)-\frac{D}{\epsilon}\left[R-\kappa^2 R_0\int_L^{\infty}dx\,R(x)+\frac{\kappa^2}{2}R_2+\kappa^2 RR_1\right.$$

$$\left.+\kappa^2\int_{-\infty}^{\infty}dx''\int_L^{\infty}dx'\,\epsilon\epsilon^{-1}(x'',x')\int_{x'}^{\infty}du\,R(u)\right]$$

$$-(x-L)\frac{D}{\epsilon}\left[1-\kappa^2\int_L^{\infty}dx'\,R(x')-\frac{\kappa^2}{2}s\right]+O(x-L)^2 , \qquad \text{(C11)}$$

where

$$R_n=\int_{-\infty}^{\infty}dx\,\xi n(x)$$

and

$$\xi_n(x)=\int_L^{\infty}dx'\epsilon\epsilon^{-1}(x,x')(x'-L)^n-\Theta(x-L)\times\begin{cases}1 & \text{for } n=0 \\ x-L & \text{for } n=1 \\ (x-L)^2-s & \text{for } n=2\end{cases} . \qquad \text{(C12)}$$

3. Matching the solutions

The solutions (C6) and (C12) are now matched by equating the coefficients with the same power in $(x-L)$. Considering the zero and first order terms we obtain:

$$\psi=U(1+\kappa^2 R_1)-\frac{D}{\epsilon}\left[R-\kappa^2 D_0\int_L^{\infty}dx\,R(x)+\kappa^2 RR_1+\frac{\kappa^2}{2}R_2+\kappa^2\int_{-\infty}^{\infty}dx''\int_L^{\infty}dx'\,\epsilon\epsilon^{-1}(x'',x')\int_{x'}^{\infty}dx\,R(x)\right] ,$$

$$\text{(C13)}$$

$$\frac{D}{\epsilon}\left[1-\kappa^2\int_L^\infty dx\, R(x)-(\kappa^2/2)s\right]=\psi\kappa[1-(\kappa^2/4)s]\,. \tag{C14}$$

These two equations determine the unknown constants ψ and D. The resulting expression for the inverse capacity is

$$\frac{1}{4\pi C}=\frac{U}{D}=\frac{1}{\epsilon\kappa}+\frac{R}{\epsilon}-\frac{\kappa}{\epsilon}\left[s/4+R_1+\int_L^\infty R(x)dx\right]+O(\kappa^2)\,. \tag{C15}$$

For the special case of sharp interface this result reduces to that derived in Appendix A.

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