Interfacial Solutions of the Poisson-Boltzmann Equation

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The linearized Poisson-Boltzmann equation is considered for boundary conditions corresponding to a fixed point-charge ion near the planar boundary between an electrolytic solution and a dielectric substrate. Use of the Fourier expansion for this fixed charge density allows the mean potential to be synthesized in the form of a simple quadrature. Subsequently, it is possible to compute the reversible work necessary to displace the ion atmosphere surrounding this charge into one hemisphere as the charge is brought up to the interface from the interior of the electrolyte phase. Implications for ionic adsorption processes are discussed. The result of a similar analysis for the mean potential surrounding a point dipole oriented normally to the boundary is also presented.

I

The molecular structure at the interface between an electrolytic solution and an immersed solid body (often an electrode for an electrochemical process) is regarded, under general circumstances, as strongly controlled by several simultaneously operative factors. Electrostatic charge on the solid and the consequent large interfacial electric fields can markedly orient polar solvent molecules, and thus produce local dielectric saturation. Specific chemical bonding forces give rise to a strongly bound monolayer (the inner or Helmholtz region of the electrical double layer) whose composition depends critically on the chemical differences between various ions and substrate materials. Additionally, it may be shown that the finite size of ions in the electrolyte plays an important role in establishing even the qualitative character of the charge distribution in the diffuse (or Gouy) charge layer of the interfacial region.

The point of view in the present article will be to investigate a model illustrating only a single aspect of the interfacial structure problem. Specifically, we choose to analyze the form and nature of the non-spherical average potential and charge surrounding a point ion near the solution-substrate interface. In the special case that this ion resides at the boundary between the two phases, the resulting distribution of charge and the potential refer to that portion of the Gouy layer induced by a single ion adsorbed at the surface. By working entirely within the regime of the linear Poisson-Boltzmann equation, the diffuse charge distribution set up by an assembly of adsorbed ions is a linear combination of the single-ion distributions. In this manner, it is possible to avoid the commonly made assumption that the Gouy portion of the double layer is produced by a uniformly distributed surface charge.

It is hoped, in later use of more realistic models of interfacial structure, in which neither the linear Poisson-Boltzmann equation is regarded as valid, nor in which solvent and substrate molecular nature are neglected, that the straightforward answers obtained here may shed some light on the qualitative nature of actual ion distributions.

The relevant solutions to the linear Poisson-Boltzmann equation are obtained as simple quadratures which, though not standard integral forms, are nevertheless amenable to ready numerical analysis in specific cases of interest. Schmutzer has obtained an alternative quadrature solution to the same potential problem considered here, in terms of modified Hankel functions. There does not appear to be any simple transformation of our representation into his, but rather the two expressions are apparently independent integral representations of solution to the same boundary value problem. The last section of this paper indicates by illustration, however, that the present approach does exhibit ease of generalization to other related boundary value problems with the linear Poisson-Boltzmann equation; there, the potential and charge surrounding a normally oriented dipole in the interfacial region are likewise cast in simple quadrature form.

In addition, the present analysis leads to a computation of the reversible work necessary to force the ion atmosphere (spherically symmetric in the bulk electrolyte) of an ion to be adsorbed at the substrate-electrolyte interface, into one hemisphere. It is pointed out how this reversible work, as well as the shielded Coulomb interaction between pairs of adsorbed ions at the interface (which follows immediately from our general solutions), affect isotherms at this surface.

II

Figure 1 indicates schematically the interfacial region with which we shall be concerned. The y-z plane of a rectangular Cartesian coordinate system is the boundary between semi-infinite dielectric substrate and...
electrolyte phases. The positive \( x \) axis, normal to this plane, is oriented into the electrolyte. \( D_s \) and \( D_r \) will denote respectively the dielectric constants of substrate \( (x<0) \) and electrolyte \( (x>0) \). A point ion with electrostatic charge \( Ze \) (\( Z \) is an integer, and \( e \) is the protonic charge) is located at \( x_c \) on the \( x \) axis in the electrolyte region. Our initial task is to compute the average charge density \( \rho(r) \) and potential \( \psi(r) \) at any position \( r \) in the vicinity of this fixed ion.

As shown in Fig. 1, it is convenient to divide space into three distinct regions: I, II, and III. The first represents the entire dielectric substrate, and since it is assumed that no electrolyte can penetrate this region, \( \rho(r) \) must identically vanish there. Accordingly, the potential in I, which will henceforth be denoted for clarity by \( \psi(I)(r) \), satisfies Laplace’s equation

\[
\nabla \psi(I)(r) = 0 \quad (\text{region I}) .
\]

For regions II and III separated by the plane \( x=x_c \), and which are characterized by potentials \( \psi(II)(r) \) and \( \psi(III)(r) \), respectively, we adopt the approach of the well-known dilute electrolyte theory of Debye and Hückel,\(^4\) wherein these functions are supposed to satisfy the linearized Poisson-Boltzmann equation

\[
\nabla \psi(II)(r) = e^2 \psi(II)(r) \quad (0 \leq x \leq x_c),
\]

\[
\nabla \psi(III)(r) = e^2 \psi(III)(r) \quad (x_c < x),
\]

\[\kappa = \text{the usual Debye parameter},\]

\[
e^2 = \frac{4\pi}{D_s k_B T} \sum_{i=1}^{n} c_i (Z_i e)^2,
\]

for an n-species electrolyte whose ions of charge \( Z_i e \) have number density \( c_i \); \( k_B \) is Boltzmann’s constant, and \( T \) the absolute temperature. Consistent with, and implicit in derivation of the linear Poisson-Boltzmann equation is the simple proportionality between mean potential and charge density. Thus, for both regions II and III occupied by dilute electrolyte,

\[\rho(r) = - (e^2 D_s / 4\pi) \psi(II,III)(r) \quad (x \geq 0), \quad (4)\]

For each position vector \( r \) measured from the origin of the Cartesian coordinate system,

\[r = x u_x + y u_y + z u_z,\]

\((u_x, u_y, \text{and } u_z \text{ are the unit vectors along the three axes}), \text{ we may define an associated two-dimensional vector } \mathbf{s} \text{ as the projection of } \mathbf{r} \text{ into the } y-z \text{ plane,}\]

\[s = y u_y + z u_z.\]

The fixed point charge \( Ze \) in the plane \( x = x_c \) is therefore equivalent to a charge density \( \sigma(\mathbf{s}) \) in this latter plane, which is

\[a(s) = Ze \delta(\mathbf{s}),\]

\(\delta(\mathbf{s})\) is the two-dimensional Dirac delta function.

\[\]

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\(^4\) P. Debye and E. Hückel, Physik. Z. 24, 185, 305 (1923).

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For the purposes of later mathematical convenience, the delta function appearing in Eq. (6) is decomposed into its Fourier components. For this reason, it is desirable to introduce a large rectangular periodicity area \( A \) onto the interfacial surface which, by translation in the \( y \) and \( z \) directions, generates an infinite array of “unit cells.” At distance \( x_c \) above the center of each of these cells will appear either the original point charge \( Ze \), or one of its periodicity images. In view of the two-dimensional periodicity thus imposed on our problem, the Fourier decomposition of \( \sigma(\mathbf{s}) \) involves summation over a discrete set of two-dimensional vectors \( k \) which form the reciprocal lattice\(^5\) to the initial unit cell subdivision of the interface

\[
\sigma(\mathbf{s}) = \sum_k \sigma_k \exp(i k \cdot \mathbf{s}),
\]

\[\sigma_k = Ze / A,\]

On this account, \( \sigma(\mathbf{s}) \) as written here is automatically periodic with the unit cell period. Eventually, of course! we shall take the limit of infinitely large \( A \), so as truly to isolate the original charge.

We now proceed to exploit the linearity of differential Eqs. (1) and (2). The mean potential in the interfacial region induced by a sum of several charge distributions, predicted on the basis of (1) and (2) with appropriate boundary conditions, is precisely equal to the sum of separately induced mean potentials for each charge distribution taken individually. Equation (7) has exactly this form; it analyzes a point charge \( Ze \) into a sequence of running waves with amplitudes \( \sigma_k \). Our task therefore will be

\[\]

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\(^5\) L. Brillouin, Wave Propagation in Periodic Structures (Dover Publications, New York. 1953), Chap. VI.
Table I. Values of the integral $I(\alpha)$, Eq. (22), obtained by numerical integration, and the corresponding reduced atmosphere displacement work, $aI(\alpha) + \frac{1}{2}$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$-I(\alpha)$</th>
<th>$aI(\alpha) + \frac{1}{2}$</th>
</tr>
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<tr>
<td>0.0</td>
<td>0.0000</td>
<td>0.5000</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.9414</td>
<td>-0.3473</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0000</td>
<td>-0.5000</td>
</tr>
</tbody>
</table>

to solve Eqs. (1) and (2) for a single unit amplitude running wave charge distribution, $\exp(ik\cdot s)$, and subsequently to build up the solution of interest (that is, for the point charge) by summing over all wave vectors $k$.

When the plane $x=x_0$ bears only charge density $\exp(ik\cdot s)$, the potentials in regions I, II, and III will be denoted by $\psi(I)$, $\psi(II)$, and $\psi(III)$. In directions parallel to the interface, each of these three functions must exhibit the same periodicity as the inducing charge itself. Using the fact that the potential must vanish at $x=\pm \infty$, it is easy to see that the general solutions to Eqs. (1) and (2) must have the forms

$$\psi(I)(r) = \psi(I) \exp[ik\cdot s + \frac{1}{2} k^2 x],$$

$$\psi(II)(r) = B_k(II) \exp[ik\cdot s + (k^2 + \kappa^2)\frac{1}{2} x],$$

$$\psi(III)(r) = B_k(III) \exp[ik\cdot s - (k^2 + \kappa^2)\frac{1}{2} x].$$

That these are the proper functional forms may readily be verified by insertion in the relevant differential equation.

The four multiplicative constants $B_k(I)$, $B_k(II, \mp)$, $B_k(II, \pm)$, and $B_k(III)$, must be chosen so that the functions (8) satisfy the usual electrostatic boundary conditions across the two surfaces $x=0$ and $x=x_0$. Specifically, one must demand continuity of potential at both of these planes; furthermore, the normal component of dielectric displacement must be continuous across $x=0$, but must suffer a discontinuity of $4\pi \exp(ik\cdot s)$ in passing $x=x_0$ in the direction of the positive $x$ axis. Application of these conditions to Eqs. (8) leads to a set of four simultaneous linear equations in the $B_k$'s

$$B_k(I) = B_k(II, \pm) + B_k(II, \mp),$$

$$B_k(III) = B_k(II, \pm) \exp[2(k^2 + \kappa^2)\frac{1}{2} x] + B_k(II, \mp),$$

$$B_k(II, \pm) = \frac{4\pi}{D_k(k^2 + \kappa^2)\frac{1}{2}} \exp\left[-(k^2 + \kappa^2)\frac{1}{2} x\right] + B_k(II, \mp),$$

$$B_k(II, \mp) = \frac{4\pi}{D_k(k^2 + \kappa^2)\frac{1}{2}} \exp\left[-(k^2 + \kappa^2)\frac{1}{2} x\right],$$

The four Eqs. (9) may be solved to yield:

$$B_k(II, \pm) = \frac{2\pi}{D_k(k^2 + \kappa^2)\frac{1}{2}} \exp\left[-(k^2 + \kappa^2)\frac{1}{2} x\right],$$

$$B_k(II, \mp) = \frac{2\pi}{D_k(k^2 + \kappa^2)\frac{1}{2}} \left[ D_k(k^2 + \kappa^2)\frac{1}{2} + D_k\frac{1}{k} \right] \cdot \exp\left[-(k^2 + \kappa^2)\frac{1}{2} x\right].$$

With these multiplicative constants now completely determined, one may proceed to synthesize the desired potential for the point charge. As already indicated, one needs only to form the linear combination

$$\psi(\cdot)(r) = \sum_k \sigma_k \psi_k(\cdot)(r); \quad \psi = I, \ II, \ III.$$

In doing so, we may simultaneously pass to the infinite limit, so that the $k$-sum in (11) may be replaced as usual by an integral over a continuous two-dimensional variable $k$.

$$\sum_k \to \frac{A}{(2\pi)^{\frac{1}{2}}} \int d^2 k.$$

If results (10) and (8) are substituted into (11), in the integral limit (12), the potential in region I is found by straightforward manipulation to be

$$\psi(I)(r) = 2Ze_k \alpha \frac{J_0(\kappa x) \cdot L}{\int D_k(1+F^2)\frac{1}{2} + D_k} \cdot \exp\left[-(\kappa x) \cdot (1+F^2)\frac{1}{2} + (\kappa x) \cdot l\right] dl, s = l, \quad k = |k|,$$

where $J_0$ is the zeroth order Bessel function. In obtaining expression (13), polar coordinates in $k$-space have been introduced, and the angular variable has been
eliminated by means of the identity

$$2\pi J_0(\lambda) = \int_0^{2\pi} d\theta \exp(i\lambda \cos \theta).$$  \hspace{1cm} (14)

In an entirely similar manner, the potential in regions II and III may be obtained. For both these regions occupied by electrolyte, one finds the single expression

$$\psi_{\text{II,III}}(r) = \frac{Z_0}{D_e} \int_0^{\infty} J_0[\kappa (s)/l] \frac{D_e(1+s^2) - D_s}{D_s(1+s^2) + D_s} dl \cdot \exp[-\kappa (x-x_e)(1+s^2)].$$  \hspace{1cm} (15)

The quadratures (13) and (1.5) together therefore constitute the solution to the problem under consideration. Unfortunately, these integrals are not elementary standard forms, so they cannot be explicitly integrated. It is of some interest, however, to note that Eq. (1.5) leads to an interesting Bessel function identity in the limit \(x, s\) very large. For in this case the point charge has essentially been removed into the bulk of the electrolyte phase, and its mean potential is well known to be just the shielded Coulomb potential.4 In this limit, therefore, we find from Eq. (15)

$$\frac{Ze}{D_s} \exp(-\kappa l) = \frac{Z_0}{D_e} \int_0^{\infty} J_0[\kappa (s)/l] \frac{D_e(1+s^2) - D_s}{D_s(1+s^2) + D_s} dl \cdot \exp[-\kappa (x-x_e)(1+s^2)].$$  \hspace{1cm} (16)

We now turn attention to the specific case \(x_e=0\), corresponding to adsorption of the point ion at the solution-substrate interface. In this event, the “ion atmosphere” of the adsorbed charge is entirely confined to one hemisphere, and its charge density [through (4)] is determined by the form of \(\psi_{\text{III}}(r)\) with \(x_e\) set equal to zero (we shall now suppress the Roman superscript)

$$\psi(r) = 2Ze \int_0^{\infty} \frac{J_0[\kappa (s)/l]}{D_e(1+s^2) + D_s} dl \cdot \exp[-\kappa (x-x_e)(1+s^2)].$$  \hspace{1cm} (17)

If the electrolyte were infinitely dilute \((\kappa \to \infty)\), the electrostatic potential would satisfy Laplace’s equation in both phases. In that case, the potential in the electrolyte region would be expressible as a sum of two Coulomb potentials, one for the actual charge \(Ze\) (at \(x_e\)), and another for the apparent “image” charge \([\frac{(D_e-D_s)}{(D_e+D_s)}]Ze\) across the interface (at \(x_e\)).5

When the point charge is adsorbed on the substrate surface, it coalesces with its image to produce an effective charge

$$2D_eZe/(D_e+D_s).$$

As a consequence, the zero concentration limit of Eq. (17) is just

$$\psi(r, \kappa=0) = 2Ze/(D_e+D_s) r.$$  \hspace{1cm} (18)

At finite electrolyte concentration, the diffuse atmosphere of charge which forms around the adsorbed ion will tend to shield the “bare” Coulomb interaction (18). In the arbitrary concentration result (17), we may separate the contribution to \(\psi(r)\) attributable to the adsorbed point charge alone, and the diffuse charge atmosphere. On the right side of Eq. (17), we add and subtract the two members of the identity3

$$\kappa \int_0^\infty J_0[\kappa (s)/l] \exp[-(\kappa x)l] dl = 1/l,$$  \hspace{1cm} (19)

to obtain

$$\psi(r) = \frac{2Ze}{(D_e+D_s)} r + 2Ze \int_0^\infty J_0[\kappa (s)/l] \frac{\exp[-(\kappa x)l]}{D_e(1+s^2) + D_s}$$

$$\cdot \left[ \exp[-(\kappa x)(1+s^2)] - \exp[-(\kappa x)/l] \right] dl.$$  \hspace{1cm} (20)

The diffuse atmosphere contribution to \(g(r)\) the integral term in Eq. (20), is in an especially suitable form for numerical analysis in specific cases of interest, on account of the rapid convergence of the integrand to zero, as \(l\) increases.

The shielding produces a finite shift in \(\psi(r)\) at the origin (the position of the adsorbed ion). Specifically,

$$\eta = \lim_{r \to 0} \left[ \psi(r) - \frac{2Ze}{(D_e+D_s) r} \right] = 2Ze I(\alpha)/(D_e+D_s), \quad \alpha = D_e/(D_e+D_s);$$  \hspace{1cm} (21)

where the integral \(I\) is defined

$$I(\alpha) = -\int_0^\infty \frac{\exp[(1+s^2)-l]}{\alpha^2(l+1-s^2)^2} dl.$$  \hspace{1cm} (22)

The corresponding potential shift, \(\eta_0\), if our point ion were located in the bulk of the electrolyte, so that it would be surrounded by a spherically symmetric atmosphere of charge, follows from the Debye-Hückel shielded potential (16)

$$\eta_0 = \lim_{r \to 0} \left[ \frac{(Ze/D_e) \exp(-\kappa l) - (Ze/D_s)}{l} \right] = -Ze/e.$$  \hspace{1cm} (23)

One may regard the adsorption process for a point ion on the substrate surface as occurring by reversible


electrostatic discharge of the ion in the bulk electrolyte, followed by relocation of the discharged ion at the adsorption site, and finally reversible recharging of the ion to its original electrostatic charge. The excess work of adsorption \( W \), resulting from the change in nature of the ion atmosphere shielding from bulk to interface, is just

\[
W = \frac{1}{2}Ze(\eta - \eta_0) - \left( \frac{Ze}{\kappa} \right)^2 \alpha I(\alpha) \quad (24)
\]

Equivalently, this work may be interpreted as work of displacement of the originally spherically symmetric ion atmosphere into one hemisphere. Although our expression (24) for this “atmosphere displacement work” is strictly valid only in the asymptotic limit of infinitely dilute electrolytes (on account of use of the linear Poisson-Boltzmann equation), we speculate that a qualitatively similar result will be of importance in predicting the character of ionic adsorption from the qualitative effect of the displacement work.

The purpose of this last section is to indicate briefly the procedure analogous to that of Sec. II, in the

\[
\int_0^\infty \frac{I_0(ks)kI}{D_x(1+k^2)+D_x} dl.
\]

The properties of the adsorbed nonideal two-dimensional gas may in principle now be computed by constructing a canonical partition function using a total interaction potential which is a sum, over all pairs adsorbed on the surface, of functions \( \varphi \). Finally, we re-emphasize that the average potential in the electrolyte when many point ions have been adsorbed at the surface, is just a linear superposition of shielded potentials of form (17), centered at each of these ions. Once again, this is a consequence of the assumed linearity of the functional equations for \( \varphi \). The resulting picture of the diffuse portion of the electrical double layer near a discrete set of adsorbed ions, will be that of a rather lumpy charge distribution. The “lumpiness” is determined primarily by the value of the dimensionless ratio of the Debye length to the distance between adsorbed ion nearest neighbors. Only for large values of this ratio is it proper to treat the adsorbed charge as uniformly spread over the interface in computing the Gouy layer diffuse charge distribution.

IV

The purpose of this last section is to indicate briefly the procedure analogous to that of Sec. II, in the

case that a point dipole (rather than a point charge) resides at distance $x_c$ from the interface, with its axis normal to this interface. If the magnitude of the dipole moment (pointing toward the interior of the electrolyte) is $\mu$, then the dipole density $\mu(s)$ on the plane $x = x_c$ may be Fourier analyzed into running wave contributions

$$\mu(s) = \mu \delta(s) = \sum_k \mu_k \exp(ik \cdot s), \quad (26)$$

$$\mu_k = \mu / A.$$ 

The mean potential induced by this point dipole once again may be regarded as composed of contributions due to each of the running waves, $\exp(ik \cdot s)$. Consequently, the potentials $\Psi^{(I)}$, $\Psi^{(II)}$, and $\Psi^{(III)}$ associated with each wave vector $k$ still have forms (8) in the three regions I, II, and III. However, the multiplicative constants are different, and instead of the $B'$s, might be denoted by $C^{(I)}_k$, $C^{(II,+)}_k$, $C^{(II,-)}_k$, $C^{(III)}_k$.

The boundary conditions for determination of the $C$'s now specify that the normal component of the dielectric displacement be continuous across both surfaces $x = 0$ and $x = x_c$; also, the mean electrostatic potential, for dipole density $\exp(ik \cdot s)$, must be continuous across $x = 0$, but must experience a discontinuity of $(4\pi / D_e) \exp(ik \cdot s)$ in crossing $x = x_c$ in the positive $x$ direction.

When the four simultaneous linear equations corresponding to these boundary conditions are solved, it is possible as before to synthesize the actual mean potential corresponding to the point dipole. If this is done, and if the periodicity area $A$ is once again allowed to become infinite to replace $k$ summations by integrals, the expressions for the mean potential in the three regions is found to be:

$$\Psi^{(I)}(r) = -\frac{2\mu k^2}{D_e} \int_0^\infty l J_0[(\kappa s)l] \left\{ \exp[\kappa(x-x_c)(1+l^2)\frac{1}{2}] \right\} dl;$$

$$\Psi^{(II)}(r) = -\frac{\mu k^2}{D_e} \int_0^\infty l J_0[(\kappa s)l] \left\{ \exp[-\kappa(x-x_c)(1+l^2)\frac{1}{2}] \right\} dl;$$

$$\Psi^{(III)}(r) = -\frac{\mu k^2}{D_e} \int_0^\infty l J_0[(\kappa s)l] \left\{ \exp[-\kappa(x-x_c)(1+l^2)\frac{1}{2}] \right\} dl. \quad (27)$$

Taking $x_c$ very large amounts to locating the point dipole in the interior of the electrolyte phase. The shielded dipolar potential field in this case is known to be

$$(\mu / D_e) [\kappa + (1/l)] \exp(-\kappa t) \cos \theta,$$

where $\theta$ is the angle to the dipolar axis, and where $t$ has been defined in Eq. (16). Comparing this with results (27) for $\Psi^{(II)}$ and $\Psi^{(III)}$ in the large $x_c$ limit leads to the dipolar analog of integral identity (16)

$$(\mu / D_e) (\kappa + t^{-1}) \exp(-\kappa t) \cos \theta = \mu k^2 / D_e$$

$$\int_0^\infty l J_0[(\kappa s)l] \left\{ \exp[-\kappa x \cdot x \cdot |(1+l^2)\frac{1}{2}] \right\} dl;$$

$$\cos \theta = \frac{(x-x_c)}{t}. \quad (28)$$

**ACKNOWLEDGMENT**

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