Exact Solution of the Debye-Hückel Equations for a Polarized Electrode

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A recent solution of the Debye-Hückel equations for a single polarized electrode obtained by Breyer and Gutmann is revised to yield an exact solution of this problem. This solution is compared with an earlier result of H. Müller derived from different initial equations and the solutions are shown to be identical.

The present solution applies only to the diffuse part of the double layer of electrolyte theory and yields the following expression for the mean local potential within the material as a function of the distance x from a polarized anode

$$\psi=(2kT/e)\ln\{\coth[\tfrac{1}{2}(x/L_D+\sinh^{-1}\{\operatorname{csch}(eV_0/2kT)\})]\},$$

where L_D is the Debye length and V_0 the potential applied between electrode and charge-containing material.

A STATIC solution of the Debye-Hückel equations has recently been given by Breyer and Gutmann[1] for a polarized electrode which leads to an expression for charge density that diverges immediately at the electrode. In the present work, we shall show how this nonphysical result may be avoided and shall discuss the derivation of the correct solution of the problem with reference to an earlier correct solution obtained from different initial equations by Müller[2] and summarized by Grahame.[3] This problem is of particular interest because it may be solved exactly in terms of elementary transcendental functions and may be applied quite accurately to other physical situations whose exact solutions are either unobtainable or are considerably more complicated.[4]

Let us consider unit area of a semi-infinite extent of material containing univalent noncombining mobile charge carriers and extending indefinitely in the $+x$ direction from the ideal polarized electrode at $x=0$. In order that the potential and electric field strength within the material be positive quantities decreasing as x increases, we shall choose the polarized electrode to be the anode; the mathematical solution of the space-charge problem is, of course, independent of this choice. If we denote the local concentrations of positive and negative charge carriers by $p(x,t)$ and $n(x,t)$, respectively, the Debye-Hückel equations may be written

$$\frac{\partial n}{\partial t}=\mu_n\frac{\partial}{\partial x}\left[\frac{kT}{e}\frac{\partial n}{\partial x}+n\mathcal{E}\right], \tag{1}$$

$$\frac{\partial p}{\partial t}=\mu_p\frac{\partial}{\partial x}\left[\frac{kT}{e}\frac{\partial p}{\partial x}-p\mathcal{E}\right], \tag{2}$$

where μ_p and μ_n are the carrier mobilities and $\mathcal{E}$ is the local electric field strength within the medium. It is assumed to be composed of a homogeneous Laplacian part E and an inhomogeneous contribution $-d\psi/dx$ arising from possible inhomogeneous charge distribution in the material. Here ψ is the local potential arising from such a distribution, and its level is selected by specifying $\psi=0$ at $x=\infty$. The electric fields satisfy the relations

$$\mathcal{E}=E-d\psi/dx, \tag{3}$$

$$\int_0^\infty \mathcal{E}dx=-V_0, \tag{4}$$

and

$$\frac{d^2\psi}{dx^2}=\frac{4\pi e}{\epsilon}(n-p). \tag{5}$$

Here V_0 is any dc potential applied between the anode at $x=0$ and ground at $x=\infty$. Equation (5) is Poisson's equation; ϵ is the dielectric constant of the material in the absence of free charges.

The following boundary conditions apply to the present problem. Since we shall be concerned with the equilibrium space-charge distribution produced by a dc applied potential, we shall assume that this potential has been applied sufficiently long that equilibrium has been attained. Then, $\partial n/\partial t=\partial p/\partial t=0$. Further, at $x=\infty$ there will be no space-charge and the charge concentrations will have their mutual bulk value c_0. Thus, we also have $\psi=d\psi/dx=d^2\psi/dx^2=0$ at $x=\infty$. At $x=0$, the anode is polarized. Thus, it is blocking for both positive and negative carriers and no mass current can pass from material into electrode or vice versa. For electrolytes, there will be a double layer at this electrode and ions will be prevented from approaching arbitrarily close to the electrode. For the present, we shall neglect this complication but will discuss it later.

It will now be convenient to introduce the following normalized variables: $n^*=n/c_0$; $p^*=p/c_0$; $\psi^*=\psi/(kT/e)$; $V_0^*=V_0/(kT/e)$; $\mathcal{E}^*=\mathcal{E}/(kT/eL_D)$; $E^*=E/(kT/eL_D)$; $z=x/L_D$. In these expressions L_D is the Debye length and is given by

$$L_D=[\epsilon kT/8\pi e^2c_0]^{\frac{1}{2}}. \tag{6}$$

In terms of normalized variables, the equations now

[1] B. Breyer and F. Gutmann, J. Chem. Phys. 21, 1323 (1953).
[2] H. Müller, Cold Spring Harbor Symposia Quant. Biol. 1, 1 (1933).
[3] D. C. Grahame, Chem. Revs. 41, 441 (1947).
[4] See the succeeding paper: J. R. Macdonald, J. Chem. Phys. 22, 000 (1954).

become

$$\frac{d}{dz}\left[\frac{dn^*}{dz}+n^*\mathcal{E}^*\right]=0, \tag{1a}$$

$$\frac{d}{dz}\left[\frac{dp^*}{dz}-p^*\mathcal{E}^*\right]=0, \tag{2a}$$

$$\mathcal{E}^*=E^*-d\psi^*/dz, \tag{3a}$$

$$\int_0^\infty \mathcal{E}^* dz=-V_0^*, \tag{4a}$$

$$\frac{d^2\psi^*}{dz^2}=\tfrac{1}{2}(n^*-p^*). \tag{5a}$$

Equations (1a) and (2a) may be immediately integrated to give

$$\frac{dn^*}{dz}+n^*\mathcal{E}^*=A, \tag{6}$$

$$\frac{dp^*}{dz}-p^*\mathcal{E}^*=B, \tag{7}$$

where A and B are constants. These constants are directly proportional to j_n/μ_n and j_p/μ_p, respectively, where the j's are carrier convection current densities. Since the electrode is blocking for carriers of both charges, the convection currents are individually zero at $z=0$. Since the above integration indicates that the currents are constant, they must also be zero at $z=\infty$, and A and B are identically zero. The value of $\mathcal{E}^*$ at $z=\infty$ is E^* and dn^*/dz and dp^*/dz are zero there. Thus, Eqs. (6) and (7) indicate that E^* is zero at $z=\infty$, and therefore is zero at all points within the medium.

When final equilibrium is established, no current flows and the externally applied potential is balanced by an equal potential produced by the final space-charge distribution within the material. There is then no Laplacian field E^* within the medium. We have discussed the reasons why E^* must be zero in some detail because, by not taking it zero, Breyer and Gutmann[1] were led to the erroneous conclusion that their solution of the space-charge problem was more general than that of Müller[2] and Grahame[3] (who do not introduce E^*), in spite of the fact that their final solution did not involve E^* at all. It might also be pointed out in this connection that taking $|E^*|>0$ requires the application of an infinite potential V_0, as shown by Eq. (4).

With E^*, A, and B all zero, we are now in a position to solve the differential equations and compare the solution of Breyer and Gutmann with the correct solution. From (6) and (7) we obtain

$$\frac{1}{n^*}\frac{dn^*}{dz}=\frac{d}{dz}(\ln n^*)=-\frac{1}{p^*}\frac{dp^*}{dz}=-\frac{d}{dz}(\ln p^*)=\frac{d\psi^*}{dz}. \tag{8}$$

Thus, $\ln(n^*p^*)=$constant. At $z=\infty$, $n^*p^*=1$ so the constant is zero and $n^*p^*=1$ for all z. We also obtain from (8)

$$n^*=e^{\psi^*}, \tag{9}$$

$$p^*=e^{-\psi^*}, \tag{10}$$

with the help of the limiting values $n^*=p^*=1$ at $z=\infty$. Substituting (9) and (10) in (5a), one finds

$$\frac{d^2\psi^*}{dz^2}\equiv\frac{1}{2}\frac{d}{d\psi^*}\left(\frac{d\psi^*}{dz}\right)^2=\sinh\psi^*. \tag{11}$$

This equation may now be solved for ψ^*; this was the course followed by Müller[2] and Grahame.[3] Müller did not start his analysis with the Debye-Hückel equations, however, as in the present work, but instead used only Poisson's equation and Boltzmann distribution functions for n^* and p^*. The justification for the Boltzmann distribution assumption is discussed by both Müller and Grahame. Since Eqs. (9) and (10) are just such distributions for n^* and p^*, we see that the Debye-Hückel equations are consistent with such choice and should lead to the same solution as that obtained by Müller. For ψ^*, Müller obtains as the solution to (11) (written in the present notation and applying to a polarized anode)

$$\psi^*=4\tanh^{-1}[e^{-(z+\alpha)}], \tag{12}$$

where α is an integration constant.

The fundamental equations may also be solved in a different way. If we differentiate (8) with respect to z and substitute the result in (5a), we obtain, after using $n^*p^*=1$,

$$\frac{d^2n^*}{dz^2}=\frac{1}{n^*}\left(\frac{dn^*}{dz}\right)^2+\frac{n^{*2}}{2}-\frac{1}{2}. \tag{13}$$

This equation may be directly integrated[5] to yield

$$\left(\frac{dn^*}{dz}\right)^2=n^{*3}-2n^{*2}+n^*\equiv n^*(n^*-1)^2, \tag{14}$$

where the constant of integration has been evaluated through the use of the boundary conditions at $z=\infty$. Equation (14) may now be integrated by elementary methods and yields

$$n^*=\coth^2[\tfrac{1}{2}(z+\alpha)], \tag{15}$$

where α is again (the same) integration constant. Equation (9) now gives

$$\psi^*=\ln n^*=2\ln\coth[\tfrac{1}{2}(z+\alpha)]. \tag{16}$$

Breyer and Gutmann obtained a differential equation analogous to (14) but one that involved E. After neglecting all terms in E, they solved the equation in terms of an elliptic function which simplified to give the

[5] E. L. Ince, *Ordinary Differential Equations* (Dover Publications, New York, 1944), p. 335.

result (15) but with the omission of α. As we have seen above, the introduction of elliptic functions is an unnecessary complication. The neglect of α has serious consequences, for if α is zero, both n^* and ψ^* approach infinity at $z=0$. We shall show below how α may be evaluated to avoid this catastrophe. Applying the solution (with α omitted) only up to some minimum value of z $(=z_0)$ greater than zero is still incorrect since the potential at z_0 predicted by this solution will depend only on the value of z_0. However, the actual potential at z_0 is related to that applied across the system. Breyer and Gutmann compared their solution for ψ with that of Grahame[3] (with the omission of the integration constant from Grahame's result) and found that series expansions of both results indicated that they were essentially the same for small z. It was not recognized that since the two solutions were derived from the same initial equations (if E is taken zero) the solutions should be identical. In spite of the apparent difference in the forms of the expressions for ψ^* in (12) and (16), it may be shown that the expressions are in fact mathematically identical for a given α.

Now we may evaluate the constant α in terms of the applied potential V_0. Such evaluation was unnecessary for Grahame's purposes and so was not carried out by him. For mathematical convenience we assume that charge carriers (ions, electrons, ion vacancies, etc.) can approach arbitrarily close to the polarized electrode; physically, this condition cannot, of course, be completely realized. If the carriers can reach the $z=0$ point, then the entire potential V_0 between $z=0$ and $z=\infty$ is effective in establishing the space-charge distribution. Then $V_0=\psi(0)-\psi(\infty)=\psi(0)$. We obtain

$$V_0^*=2\ln\coth(\alpha/2). \tag{17}$$

The solution of this equation for α yields

$$\alpha=\sinh^{-1}[\operatorname{csch}(V_0^*/2)]. \tag{18}$$

On substituting this value of α into Eq. (16) for ψ^*, one obtains the complete, exact, mathematical solution of the original equations. The resulting normalized internal field strength, determined from Eqs. (3a), (16), and (18) is then

$$\mathcal{E}^*=2\operatorname{csch}\{z+\operatorname{csch}^{-1}(\sinh\tfrac{1}{2}V_0^*)\}. \tag{19}$$

It will be noted that ψ^* and $\mathcal{E}^*$ are functions of the two variables (x/L_D) and (eV_0/kT). When (V_0/T) is zero, there is no space-charge region. As (V_0/T) increases from zero, a space-charge layer starts to form at and near the polarized electrode. The dependence of the present solution on applied potential and position in the double layer and its application to physical situations will be further discussed in the succeeding paper.[4]