Electrostatic Boundary Conditions
At The Surfaces of Debye-Hückel Solutions

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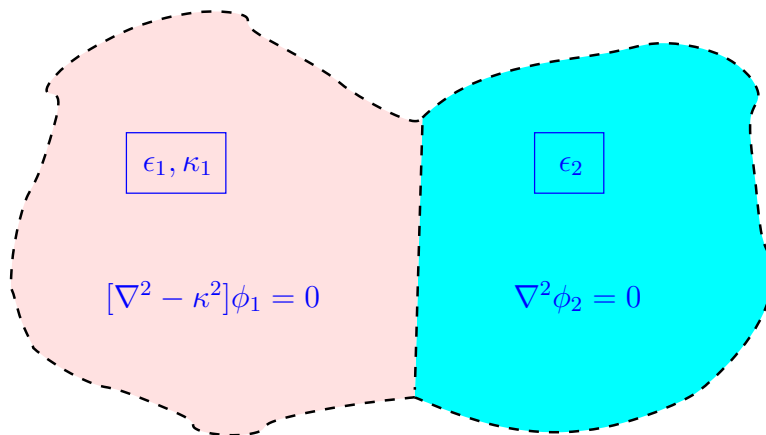
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Contents

Figure 1: Interface between an electrolytic solution and a simple dielectric medium.

1 Overview

What boundary conditions apply at the surface of a Debye-Hückel solution?

We consider the situation depicted in Figure 1. A region filled with electrolytic solution of dielectric constant ϵ_1 and inverse Debye length $\kappa_1 \equiv \kappa$ borders a region of dielectric constant ϵ_2 (and no electrolyte, i.e. $\kappa_2 = 0$.). In the Debye-Hückel approximation, the electrostatic potential in the solution satisfies the Helmholtz equation:

$$\nabla^2 \phi_1 - \kappa^2 \phi_1 = 0, \tag{1}$$

while in the simple dielectric medium we have the Laplace equation:

$$\nabla^2 \phi_2 = 0. \tag{2}$$

The continuity of ϕ at the interface gives us one boundary condition:

$$\phi_1 = \phi_2 \qquad \text{(on the boundary)}.$$

But what boundary conditions hold for the *derivatives* of ϕ, i.e. on the normal electric fields E_{1n} and E_{2n}?

The general answer in the literature seems to be simply to take

$$\epsilon_1 E_{1n} = \epsilon_2 E_{2n} \tag{3}$$

i.e. the same boundary condition that would hold if the solution were a simple dielectric with no electrolyte. At first glance it seems odd that the boundary condition could be completely independent of the presence of screening charges in the solution. In this memo we'll consider some sample problems and try to figure out what's going on. In particular,

- In Section 2, we revisit Maxwell's equations to remind ourselves what *fundamental* boundary conditions are *always* satisfied by the electric fields at *any* interface. We then consider the interface between two simple dielectric media to see how equation (3) arises in that *particular* situation, and note that (3) fails to hold if there is any additional bound surface charge at the interface.

- In Section 3, we consider problems involving interfaces between electrolytic and non-electrolytic (simple dielectric) media. Using only the fundamental Maxwell equations and some statistical reasoning we investigate the density of bound ionic charges at these interfaces and critique the use of the approximate boundary condition (3).

- In Section 4 we consider the electrostatics of some simple problems involving charged sheets in dielectric solutions. We find that an electrolytic solution *perfectly screens* the field of a charge sheet at distances comparable to the Debye length. (Note: This stuff turned out not to be particularly relevant to the rest of the memo, but we figured we'd keep it in just for fun.)

2 Back To Basics: What Maxwell's Equations Tell Us

2.1 The Fundamental Truth Is $E_1 - E_2 = \sigma/\epsilon_0$

First let's go all the way back to the drawing board and recall what Maxwell's equations tell us must *always* be true about electric fields at interfaces. As shown in Figure 2, we consider a two-dimensional interface separating two regions. The region below the boundary contains some charge density $\rho(\mathbf{x})$, while there is no charge above the boundary. The boundary itself contains a bound surface charge σ. We draw the standard cylindrical Gaussian surface straddling the boundary and apply Gauss' law:

$$\oint \mathbf{E} \cdot d\mathbf{A} = \frac{Q}{\epsilon_0} \tag{4}$$

where the surface integral is over the surface of the pillbox and Q is the total charge contained inside it. If the pillbox is short and narrow compared to the length scales of the problem geometry, the electric field normal to the *side* walls will have no variation over the surface of the pillbox and will thus contribute nothing to the LHS of (4), while the electric fields normal to the *end* walls are constant over those walls and may be pulled out of the integral, yielding

$$\oint \mathbf{E} \cdot d\mathbf{A} = \left[E_{2n}\left(\frac{L}{2}\right) - E_{1n}\left(-\frac{L}{2}\right) \right] \cdot A$$
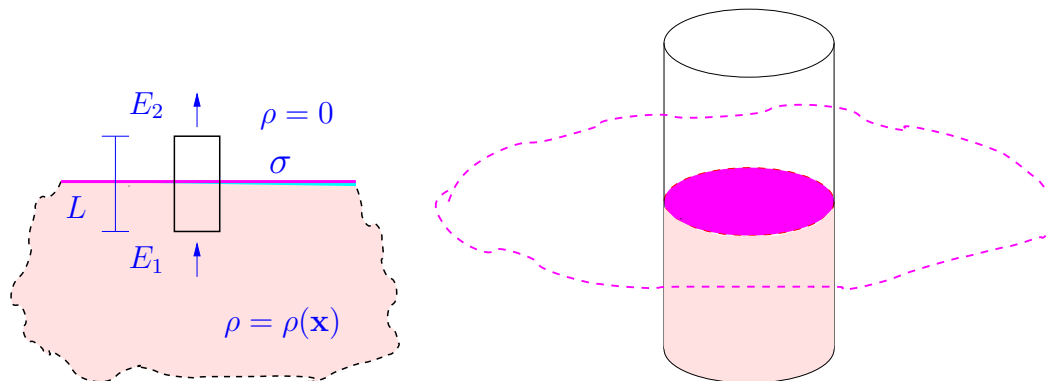
Figure 2: Gaussian pillbox straddling the boundary between two regions. There are two contributions to the total charge inside the pillbox: the bound surface charge σ on the interface, and the volume charge density ρ contained in the lower portion of the pillbox.

where A is the area of the endcap of the cylindrical pillbox, E_{in} is the component of the field in region i normal to the endcap of the pillbox, and the argument of E_{in} refers to the distance from the interface at which the field is to be evaluated.

Meanwhile, the RHS of (4) will contain two terms: a contribution from the bound surface charge on the interface, and a contribution from the volume charge density ρ contained in the lower part of the pillbox:

$$\frac{Q}{\epsilon_0} = A \cdot \frac{\sigma}{\epsilon_0} + \frac{A}{\epsilon_0} \cdot \int_{-L/2}^{0} \rho(z)dz$$

where we have ignored the variation of ρ over the transverse dimension of the pillbox, and taken z as the variable running along its length.

Assembling the two parts of equation (4), we obtain

$$E_{2n}\left(\frac{L}{2}\right) - E_{1n}\left(-\frac{L}{2}\right) = \frac{\sigma}{\epsilon_0} + \frac{1}{\epsilon_0} \int_{-L/2}^{0} \rho(z)dz$$

The important observation here is that the first term on the RHS is *independent* of L, while the second term *vanishes* as $L \to 0$, as long as the charge distribution ρ is nonsingular. By reducing the length of the pillbox we can reduce its content of volume charge ρ as much as we like, but the surface charge σ will always be there. In the limit $L \to 0$ we obtain simply

$$E_{2n}(0^+) - E_{1n}(0^-) = \frac{\sigma}{\epsilon_0}, \tag{5}$$

independent of the properties of the two regions and of any charges that may exist therein.

There is a simpler way to understand equation (5). Let E_{Sn} be the normal component of the electric field arising from the surface charge on the interface, while E_{0n} is the normal component of the electric field arising from all *other* charges in the universe. Then clearly E_{0n} points in the *same* direction on both sides of the interface, while E_{Sn} points in *different* directions. We have

$$E_{1n} = E_{0n} - E_{Sn}, \qquad E_{2n} = E_{0n} + E_{Sn} \tag{6}$$

so

$$E_{2n} - E_{1n} = 2E_{Sn}.$$

But E_{Sn} is just $\sigma/2\epsilon_0$, the field of a charged sheet. This leads us right back to (5), again without reference to any properties of the respective media.

So (5) is the fundamental mathematical statement dictated by Gauss' law, the one condition that must hold in all situations. Let's now see what form it takes in various special cases.

2.2 For Simple Dielectric Media We Find $\epsilon_1 E_1 = \epsilon_2 E_2$

First let's consider the interface between two simple (non-electrolytic) dielectric media, as in Figure (1) with $\kappa = 0$. What does (5) tell us in this case?

To begin we recall that a dielectric is *defined* as a medium that, in the presence of an electric field $\mathbf{E}$, exhibits a dipole moment per unit volume equal to

$$\mathbf{P} = (\epsilon_r - 1)\epsilon_0 \mathbf{E},$$

which means that when the outward normal electric field at a surface of the medium is E_n, that surface develops a surface charge equal to [1]

$$\sigma = (\epsilon_r - 1)\epsilon_0 E_n. \tag{7}$$

Note that E_n here is the field arising from all external charges *and from the surface charge (7) to which it gives rise*, so equation (7) is not an immediate recipe for determining σ, but rather a statement that must be satisfied self-consistently.

To do so, let the fields E_{1n} and E_{2n} be directed as in Figure 1, and decompose these fields as in (6). The net surface charge that develops at the interface contains contributions of the type (7) from both sides of the boundary:

$$\sigma = +(\epsilon_1 - 1)\epsilon_0 E_{1n} - (\epsilon_2 - 1)\epsilon_0 E_{2n} \tag{8}$$

$$= (\epsilon_1 - 1)\epsilon_0 \left(E_{0n} - \frac{\sigma}{2\epsilon_0} \right) - (\epsilon_2 - 1)\epsilon_0 \left(E_{0n} + \frac{\sigma}{2\epsilon_0} \right). \tag{9}$$

---

[1]Note that if the electric field at the surface points away from the bulk of the medium, the surface charge that appears is *positive*. We can understand this mnemonically by picturing the bound positive charges in the material being pushed by the electric field as far as they will go, i.e. to the surface, where they stop.

Solving for σ, we obtain

$$\sigma = 2\epsilon_0 \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) E_{0n}$$

and inserting into (6) we find

$$
\begin{aligned}
E_{1n} &= \left[1 - \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right] E_{0n} \\
&= \left[\frac{2\epsilon_2}{\epsilon_1 + \epsilon_2} \right] E_{0n}
\end{aligned}
\tag{10}
$$

and

$$
\begin{aligned}
E_{2n} &= \left[1 + \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right] E_{0n} \\
&= \left[\frac{2\epsilon_1}{\epsilon_1 + \epsilon_2} \right] E_{0n}.
\end{aligned}
\tag{11}
$$

Using (10) and (11) we can now eliminate the partial field E_{0n} to obtain a relation between the *total* fields on either side of the interface:

$$\epsilon_1 E_{1n} = \epsilon_2 E_{2n}. \tag{12}$$

We note that there is nothing *fundamental* about this relation, and that its content is simply that of (5) together with the specific prescription (7) for dielectric media.

2.3 If There Is Additional Surface Charge then $\epsilon_1 E_1 \neq \epsilon_2 E_2$!

What happens if, in addition to the polarization surface charge appearing at the interface between dielectric media, there is an additional *fixed* surface charge σ' there? For example, suppose we spray a fixed surface charge density onto a two-dimensional sheet of Saran wrap and insert it at the interface between the two media. Does (12) still hold?

With all definitions as in the previous section, we note that equation (9) for the total surface charge at the interface should now be modified to read

$$
\begin{aligned}
\sigma &= (\epsilon_1 - 1)\epsilon_0 E_{1n} - (\epsilon_1 - 1)\epsilon_0 E_{2n} + \sigma' \\
&= (\epsilon_1 - 1)\epsilon_0 \left(E_{0n} - \frac{\sigma}{2\epsilon_0} \right) - (\epsilon_2 - 1)\epsilon_0 \left(E_{0n} + \frac{\sigma}{2\epsilon_0} \right) + \sigma'.
\end{aligned}
$$

Solving as before, we find that the total surface charge on the interface is

$$\sigma = 2\epsilon_0 \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) E_{0n} + \left(\frac{2}{\epsilon_1 + \epsilon_2} \right) \sigma',$$

the fields are

$$E_{1n} = \left(\frac{2\epsilon_2}{\epsilon_1 + \epsilon_2}\right) E_{0n} - \left(\frac{1}{\epsilon_1 + \epsilon_2}\right) \frac{\sigma'}{\epsilon_0}$$

$$E_{2n} = \left(\frac{2\epsilon_1}{\epsilon_1 + \epsilon_2}\right) E_{0n} + \left(\frac{1}{\epsilon_1 + \epsilon_2}\right) \frac{\sigma'}{\epsilon_0},$$

and the boundary condition (12) is generalized to read

$$\epsilon_2 E_{2n} - \epsilon_1 E_{1n} = \frac{\sigma'}{\epsilon_0}. \tag{13}$$

We note that this has all been a longwinded justification of the simpler way of thinking about dielectric problems, in which the procedure is simply to (1) ignore all bound polarization charges and solve for the fictitious field (the **D** field) that would exist if only the "free" charges in the problem were retained; and then (2) obtain the **E** field, which includes the effects of the bound polarization charges, simply by multiplying **D** by the reduction factor $1/\epsilon$, where ϵ may be different in different regions.

3 Problems Involving Solution-Dielectric Interfaces

In the previous section we recalled the fundamental boundary condition (5) prescribed by Maxwell's laws, and noted the particular form (12) it takes at the interface between simple dielectrics. What is corresponding form taken by (5) at the interface between a Debye-Hückel solution and a simple dielectric?

3.1 Point Charge In Spherical Cavity In Solution

As a first example, we consider the situation depicted in Figure 3. A spherical dielectric, with relative dielectric constant ϵ_c, radius R, and a point charge Q at its center, is placed inside a Debye-Hückel solution with inverse Debye length κ and dielectric constant ϵ_s. For the moment we take $\epsilon_s = \epsilon_c = 1$. What are the electric fields in the cavity and in the solution? We will address this problem using both electrostatic and statistical mechanical reasoning.

Electrostatics The potential inside the cavity is that of the point charge plus terms accounting for the contributions of all charges on the boundary of and outside the cavity:

$$\phi(r) = \frac{Q}{4\pi\epsilon_0 r} + A + Br, \qquad r < R \tag{14}$$

where $A + Br$ is the general spherically symmetric solution of the Laplace equation.
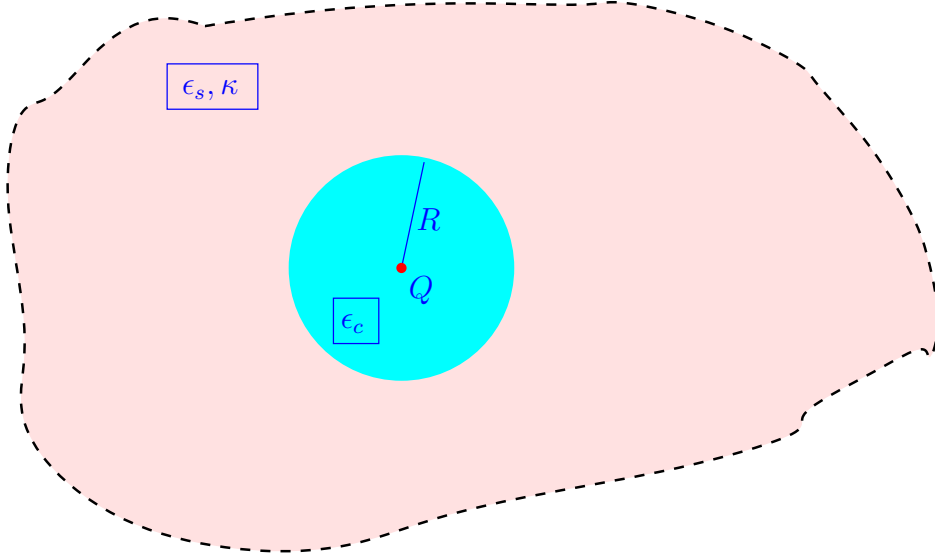
Figure 3: Point charge inside spherical dielectric cavity in Debye-Hückel solution.

Outside the cavity the potential is given by the spherically symmetric solution of the Helmholtz equation:

$$\phi(\mathbf{r}) = C\frac{e^{-\kappa r}}{r}, \qquad r > R. \tag{15}$$

We now determine the constants A, B, and C in (14) and (15). We begin by noting immediately that $B = 0$. Indeed, in view of the spherical symmetry of the problem, we may think of the charges on the boundary and outside the sphere as being organized into concentric spherical shells of charge density $\sigma(r)$, with $\sigma(r)$ falling off with r but constant over any one of the shells. But the potential of a uniform sphere of surface charge is *constant* on the interior of the sphere. Indeed, a shell of radius a with surface charge σ gives rise to a potential

$$\phi(r) = \frac{\sigma}{4\pi\epsilon_0} \int \frac{a^2 \sin\theta d\theta d\phi}{\sqrt{a^2 + r^2 - 2ra\cos\theta}} = \begin{cases} \dfrac{a\sigma}{\epsilon_0}, & r < a \\[2ex] \dfrac{a\sigma}{\epsilon_0}\left(\dfrac{a}{r}\right), & r > a. \end{cases} \tag{16}$$

Hence $B = 0$ in (14), while A is just the sum of the potentials $a\sigma(a)/\epsilon_0$ of all the concentric spherical shells of charge in the solvent. To evaluate this, we think of the charges external to the cavity as consisting of a surface charge σ_R on the surface of the cavity plus a volume charge $\rho(r)$ in the bulk of the solution. The

latter is given simply by

$$\rho(r) = -\epsilon_0 \nabla^2 \phi$$
$$= -\epsilon_0 \kappa^2 C \frac{e^{-\kappa r}}{r}.$$

from (15). We think of ρ as being comprised of a series of concentric spherical shells of thickness dr and surface charge density

$$\sigma(r) = \rho(r)dr = -\epsilon_0 \kappa^2 C \frac{e^{-\kappa r}}{r} dr.$$

Then A in (14) is

$$A = \frac{R\sigma_R}{\epsilon_0} + \int_R^\infty \frac{r\rho(r)dr}{\epsilon_0}$$
$$= \frac{R\sigma_R}{\epsilon_0} - \kappa^2 C \int_R^\infty e^{-\kappa r} dr$$
$$= \frac{R\sigma_R}{\epsilon_0} - \kappa C e^{-\kappa R}.$$

This gives us one relation between the constants A, C, and σ_R. A second relation is obtained from the continuity of ϕ at the interface:

$$\frac{Q}{4\pi\epsilon_0 R} + A = C \frac{e^{-\kappa R}}{R}.$$

Combining both relations yields

$$C = \left(\frac{1}{4\pi\epsilon_0}\right) \left(\frac{e^{\kappa R}}{1 + \kappa R}\right) \left(Q + 4\pi R^2 \sigma_R\right). \tag{17}$$

which we note is in fact the same relation we obtain from applying (5) to the fields (14) and (15). If we relax the assumption that $\epsilon_s = \epsilon_c = 1$ then (17) is modified to read

$$C = \left(\frac{\epsilon_c}{\epsilon_s}\right) \left(\frac{1}{4\pi\epsilon_0}\right) \left(\frac{e^{\kappa R}}{1 + \kappa R}\right) \left(Q + 4\pi R^2 \sigma_R\right). \tag{18}$$

Equation (18) is one equation relating the two unknowns C and σ_R. If σ_R were zero (or small compared to $Q/4\pi R^2$) we would be done. The general practice in the literature seems to be to *assume* this to be true, in which case (12) is the appropriate boundary condition at the interface. However, there would seem to be no *a priori* justification for the assumption, and indeed intuitively we would expect it to fail – we would expect ions from the solution, attracted to the charge Q, to swim in to the cavity surface and adhere there, forming a layer of bound surface charge. If such a layer exists, i.e. if σ_R is nonzero in (18), then we need a second relation between C and σ_R. To find one we turn to statistical mechanics.

Statistical Mechanics   To find the charge density on the cavity surface we think of the ions in the solution as forming ideal noninteracting Boltzmann gases, one for each type of ion. One phase of this gas is adsorbed on the 2D surface of the cavity, while the remainder exists in the 3D bulk of the solution. The two phases are in thermal, mechanical, and chemical equilibrium in the presence of the electrostatic field (15), and we seek to determine the density of ions adsorbed on the surface as a function of the density of ions in the bulk.

   We work in the canonical ensemble, and initially consider only one species of ion. If there are a total of N of these ions in the system, of which N_S are adsorbed on the surface, then the partition functions of the surface and bulk phases are

$$Z_S = \frac{1}{N_S!} \left(Z_{1S} \right)^{N_S}$$

$$Z_B = \frac{1}{(N - N_S)!} \left(Z_{1B} \right)^{(N - N_S)}$$

and the free energies are

$$F_S = -kTN_S \ln Z_{1S} + kTN_S \log N_S - kTN_S$$
$$F_B = -kTN_B \ln Z_{1B} + kT(N - N_S) \log(N - N_s) - kT(N - N_S).$$

The condition for phase equilibrium is

$$\frac{\partial}{\partial N_S}(F_S + F_B) = 0 \qquad \Longrightarrow \qquad \frac{N_S}{N - N_S} \approx \frac{N_S}{N} = \frac{Z_{1S}}{Z_{1B}}. \qquad (19)$$

Here Z_{1S} and Z_{1B} are the partition functions for a single ion in the surface phase and in the bulk phase, which, for an ion of mass m and charge q, are given by

$$Z_{1S} = \int \frac{d^2 r d^2 p}{(2\pi\hbar)^2} e^{-\beta \left(\frac{p^2}{2m} + q\phi(R) \right)}$$

$$= \frac{A}{\lambda^2} e^{-\beta q\phi(R)}$$

$$Z_{1B} = \int \frac{d^3 r d^3 p}{(2\pi\hbar)^3} e^{-\beta \left(\frac{p^2}{2m} + q\phi(r) \right)}$$

$$= \frac{4\pi}{\lambda^3} \int_R^\infty r^2 e^{-\beta q\phi(r)} dr$$

The r integral in the calculation of Z_{1S} is over the cavity surface, and $A = 4\pi R^2$ is the area of that surface; the r integral in the calculation of Z_{1B} is over the volume of the solvent; and

$$\lambda = \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2} \qquad (20)$$

is the thermal wavelength. Inserting into (19), we find

$$\frac{N_S}{N} = A\lambda \cdot \frac{e^{-\beta q\phi(R)}}{4\pi \int_R^\infty r^2 e^{-\beta q\phi(r)} dr}. \qquad (21)$$

To proceed it is convenient to introduce a fictitious outer boundary for the solvent at $r = R_c$, in terms of which the solvent has finite volume $V = 4\pi(R_c^3 - R^3)/3$. Then we may rewrite (21) in terms of the surface and bulk concentrations $n_S = N_S/A$ and $n = N/V$:

$$n_S = n\lambda \cdot \Gamma \tag{22}$$

where the dimensionless Γ factor is

$$\Gamma = \frac{e^{-\beta q\phi(R)}}{\frac{4\pi}{V} \int_R^{R_c} r^2 e^{-\beta q\phi(r)} dr}$$

$$= \frac{e^{-\beta q\phi(R)}}{1 - \frac{3}{R_c^3} \int_R^{R_c} r^2 \left[1 - e^{-\beta q\phi(r)}\right] dr}$$

In going to the last line we approximated $R_c^3 - R^3 \approx R_c^3$.

To get an estimate of some of the numbers here, let's consider a 0.01 M aqueous solution of NaCl, corresponding to an ion density (of each type of ion) of about $6 \cdot 10^{-4}$ Å^{-3}. If the charge Q is positive, we need only consider the contribution to the surface charge layer from Cl$^-$ ions. These have a mass of about 35 nucleon masses or roughly $35 \cdot 10^9$ eV/c^2 so, from (20),

$$\lambda = \left(\frac{(2\pi)(6.6 \cdot 10^{-16} \text{ ev s})^2 (9 \cdot 10^{16} \text{ m s}^{-1})}{(35)(10^9 \text{ ev})(0.026 \text{ ev})}\right)^{1/2} \approx 0.16 \text{ Å}$$

at room temperature. Then (22) says the charge density on the cavity surface should be

$$\sigma = en_S \approx 10^{-3} e\Gamma \text{ Å}^{-2},$$

i.e. only a thousandth of an electron charge per square Angstrom, times the Γ factor. So unless the dimensionless Γ factor gets pretty significantly large, we are justified in neglecting the surface charge σ_R.

3.2   Point Charge Near Planar Air–Solution Boundary

Somewhat disillusioned and demoralized by the null result of the previous subsection, I think I will go home and watch movies now instead of bothering to work out this case.

4   Charged Sheets In Electrolytic Solutions

Just for fun let's consider a few problems in which sheets of fixed surface charge are inserted into electrolytic solutions.
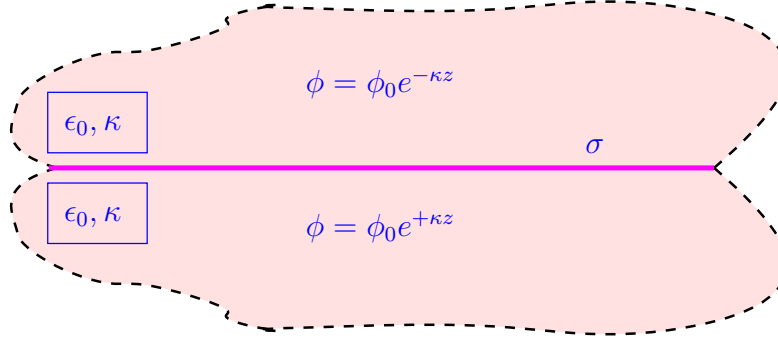
Figure 4: Charged sheet inserted into uniform electrolytic solution.

4.1 Charged Sheet In A Uniform Solution

As a first example of problems involving solutions, let's consider the case of an infinite sheet carrying fixed surface charge σ inserted into a uniform Debye-Hückel electrolyte.[2]

For simplicity we will assume the surrounding solution is nonpolarizable, i.e. $\epsilon_r = 1$. What relation holds between the fields above and below the sheet?

Taking the sheet to exist at $z = 0$, the solutions to (1) in the regions above and below the sheet are

$$\phi(z) = \begin{cases} \phi_0 e^{-\kappa z}, & z > 0 \\ \phi_0 e^{+\kappa z}, & z < 0, \end{cases} \tag{23}$$

where ϕ_0 is the potential at the sheet. Then applying (5) yields

$$2\kappa\phi_0 = \frac{\sigma}{\epsilon_0}$$

or

$$\phi_0 = \frac{\sigma}{2\kappa\epsilon_0} \tag{24}$$

Inserting into (23) and taking derivatives, the electric field is

$$E_z(z) = \begin{cases} \frac{\sigma}{2\epsilon_0} e^{-\kappa z}, & z > 0 \\ -\frac{\sigma}{2\epsilon_0} e^{+\kappa z}, & z < 0. \end{cases} \tag{25}$$

The field is just that of the infinite plane sheet, damped exponentially by the screening effects of the ions in the solution.

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[2]If you don't like the idea of a sheet with a predetermined bound surface charge, think instead of the sheet as being a conductor which we hold at some fixed potential ϕ_0. Mathematically the problem is the same, with the only difference being whether we solve for ϕ_0 in terms of σ or for σ in terms of ϕ_0. In either case we obtain the relation (24).

It is useful to investigate how (25) comes about from the distribution of ionic charges in the solution. For this purpose we note that the charge distribution in the solution is

$$\rho(z) = -\epsilon_0 \nabla^2 \phi_0$$

$$= \begin{cases} -\frac{\kappa\sigma}{2}e^{-\kappa z}, & z > 0, \\ -\frac{\kappa\sigma}{2}e^{+\kappa z}, & z > 0. \end{cases} \tag{26}$$

The electric field at any point is the field of the charge sheet plus the field of the charge distribution (26). The former is just $\sigma/2\epsilon_0$, while to calculate the latter we think of it as an infinite stack of sheets of infinitesimal thickness dz and surface charge $\sigma(z) = \rho(z)dz$. All sheets below the observation point contribute to the field in one direction, whereas sheets above contribute in the opposite direction. If we are a distance z above the sheet, then the field we see is

$$E_z = \frac{\sigma}{2\epsilon_0} + \int_{-\infty}^{z} \frac{\rho(z')dz'}{2\epsilon_0} - \int_{z}^{\infty} \frac{\rho(z')dz'}{2\epsilon_0}$$

$$= \frac{\sigma}{2\epsilon_0}\left\{ 1 - \frac{\kappa}{2}\int_{-\infty}^{0} e^{+\kappa z'}dz' - \frac{\kappa}{2}\int_{0}^{z} e^{-\kappa z'}dz' + \frac{\kappa}{2}\int_{z}^{\infty} e^{-\kappa z'}dz' \right\}$$

$$= \frac{\sigma}{2\epsilon_0}\left\{ 1 - \frac{1}{2} + \frac{1}{2}\left(e^{-\kappa z} - 1\right) + \frac{1}{2}e^{-\kappa z} \right\}$$

$$= \frac{\sigma}{2\epsilon_0}e^{-\kappa z}$$

confirming the result of (25). So this all seems quite reasonable.

4.2   Charged Sheet At Solution–Air Interface: Infinite Area

What happens if we evacuate the solution from the region above the sheet, leaving only empty space? As shown in Figure 5, the solution to the Helmholtz equation in the lower region is again

$$\phi = \phi_0 e^{\kappa z}, \qquad E_z = -\kappa\phi_0 e^{\kappa z} \qquad (z < 0) \tag{27}$$

while the general solution to the Laplace equation above the sheet is

$$\phi = \phi_0 + Bz, \qquad E_z = -B \qquad (z > 0). \tag{28}$$

Equation (5) then tells us that

$$-B + \kappa\phi_0 = \frac{\sigma}{\epsilon_0}$$

or

$$-B = \frac{\sigma}{\epsilon_0} - \kappa\phi_0. \tag{29}$$

However, this is only one equation for the two unknowns B and ϕ_0. To get

$$\phi = \phi_0 + Bz$$

ϵ_0

σ

ϵ_0, κ

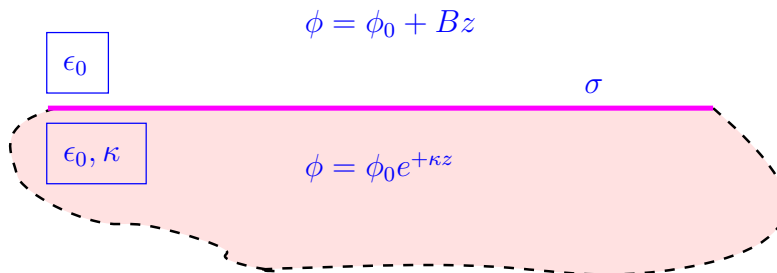$$\phi = \phi_0 e^{+\kappa z}$$

Figure 5: Charged sheet inserted between an electrolytic solution and empty space.

another equation, let's proceed as we did in the previous section by explicitly summing the contributions of all the ionic charges. The charge density in the solution is

$$\rho(z) = -\epsilon_0 \nabla^2 \phi$$
$$= -\epsilon_0 \kappa^2 \phi_0 e^{\kappa z}. \tag{30}$$

If we are a distance z above the interface (i.e. in the empty-space region) then we feel the field of the charged sheet plus the field of the charge distribution (30), which we again think of as an infinite stack of charged sheets:

$$E_z(z) = \frac{\sigma}{2\epsilon_0} - \frac{\kappa^2 \phi_0}{2} \int_{-\infty}^{0} e^{\kappa z} dz$$
$$= -\frac{\sigma}{2\epsilon_0} - \frac{\kappa \phi_0}{2}.$$

From (28) this must just be equal to $-B$:

$$-B = \frac{\sigma}{2\epsilon_0} - \frac{\kappa \phi_0}{2}. \tag{31}$$

But (29) and (31) then say that B equals half of itself, so it must be zero. *There is no electric field above the charged sheet,* and we find

$$\phi_0 = \frac{\sigma}{\kappa \epsilon_0}.$$

The potential at the charged sheet, and the prefactor in the screening charge density, are twice as large as they were when upper region was filled with solution instead of air.

Huh? The electric field above a region of solution simply *vanishes*? This doesn't seem to make any sense. Maybe the weirdness arises because we took our system to have infinite size in the lateral dimensions. Let's investigate a finite-size case to see if the pathology remains.
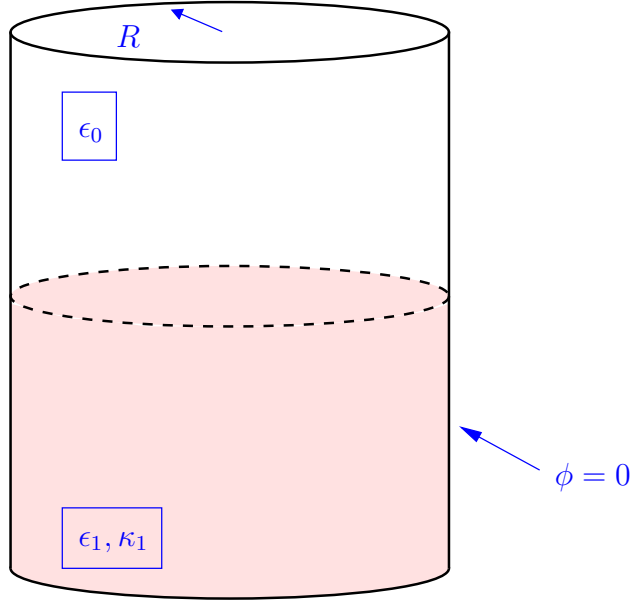
Figure 6: Solution–air interface in a grounded conducting cylinder.

4.3   Charged Sheet At Solution–Air Interface: Finite Area

To eliminate the artifice of the infinite-area interface, we imagine confining our system to the interior of a grounded metallic cylinder of radius R, as shown in Figure 6.

In the region $z > 0$, the general solution of Laplace's equation that vanishes at $\rho = R$ is

$$\phi(\rho, z) = \sum C_n J_0(q_n \rho) e^{-q_n z}, \qquad q_n = \frac{x_n}{R} \tag{32}$$

where x_n is the nth zero of J_0, the Bessel function for $\nu = 0$. For $z < 0$ we can write a similar expansion for the general solution of the Helmholtz equation:

$$\phi(\rho, z) = \sum D_n J_0(q_n \rho) e^{+q_n' z}, \qquad q_n' = \sqrt{q_n^2 + \kappa^2}. \tag{33}$$

The continuity of ϕ at $z = 0$ requires

$$C_n = D_n,$$

while condition (5) requires

$$\sum C_n (q_n + q_n') J_0(q_n \rho) = \frac{\sigma}{\epsilon_0}.$$

Multiply both sides by $\rho J_0(q_m \rho)$, integrate from $\rho = 0$ to $\rho = R$, and use the

relations

$$\int_0^R \rho J_0\left(x_n\frac{\rho}{R}\right) J_0\left(x_m\frac{\rho}{R}\right) d\rho = \frac{1}{2}R^2 J_1^2(x_n)\delta_{mn}, \qquad \int_0^R \rho J_0\left(x_n\frac{\rho}{R}\right) d\rho = \frac{R^2}{x_n}J_1(x_n).$$

to obtain the result

$$C_n = \frac{\sigma}{\epsilon_0}\left(\frac{2}{q_n + q_n'}\right)\left(\frac{1}{x_n J_1(x_n)}\right). \tag{34}$$

To separate out dimensional factors it is convenient to write (34) as

$$C_n = \frac{2R\sigma}{\epsilon_0}\frac{1}{x_n(x_n + x_n')J_1(x_n)}$$

where

$$x_n' = \sqrt{x_n^2 + (\kappa R)^2}.$$

Then the expansions of the potential and the electric field are

$$\phi(\rho, z) = \begin{cases} \dfrac{2R\sigma}{\epsilon_0}\displaystyle\sum \dfrac{J_0(q_n\rho)e^{-q_n z}}{x_n(x_n + x_n')J_1(x_n)}, & z > 0 \\[4mm] \dfrac{2R\sigma}{\epsilon_0}\displaystyle\sum \dfrac{J_0(q_n\rho)e^{+q_n' z}}{x_n(x_n + x_n')J_1(x_n)}, & z < 0 \end{cases} \tag{35}$$

$$E_z(\rho, z) = \begin{cases} \dfrac{2\sigma}{\epsilon_0}\displaystyle\sum \dfrac{J_0(q_n\rho)e^{-q_n z}}{(x_n + x_n')J_1(x_n)}, & z > 0 \\[4mm] -\dfrac{2\sigma}{\epsilon_0}\displaystyle\sum \dfrac{x_n' J_0(q_n\rho)e^{+q_n' z}}{x_n(x_n + x_n')J_1(x_n)}, & z < 0. \end{cases} \tag{36}$$

Before going any further let's stop to confirm that this makes sense: If $\kappa = 0$ (empty space above and below the charged sheet) then for points near the center of the plate the fields both above and below must reduce to the standard result $E = \sigma/2\epsilon_0$. Do they? Taking $\kappa = 0$ in (36) gives $x_n' = x_n$ and

$$E_z\left(\rho = 0, z = 0^+\right) = -E_z\left(\rho = 0, z = 0^-\right) = \frac{\sigma}{\epsilon_0}\sum \frac{1}{x_n J_1(x_n)}.$$

We have verified numerically that the sum does indeed converge to the correct answer, i.e.

$$\sum_{n=1}^\infty \frac{1}{x_n J_1(x_n)} = \frac{1}{2}.$$

So there's a nice little Bessel function identity that was probably known to the classical European analysts and can perhaps even be found somewhere in Whittaker and Watson, but which was news to me.

The electric fields above and below the cylinder are plotted for various values of κ in Figure 7. We note that

- For $\kappa = 0$, the fields above and below are equal to $\sigma/2\epsilon_0$ and slowly varying.

- For R large on the scale of the Debye length, the field above the center of the plate is damped out, as we found in the case of the infinite planar interface.
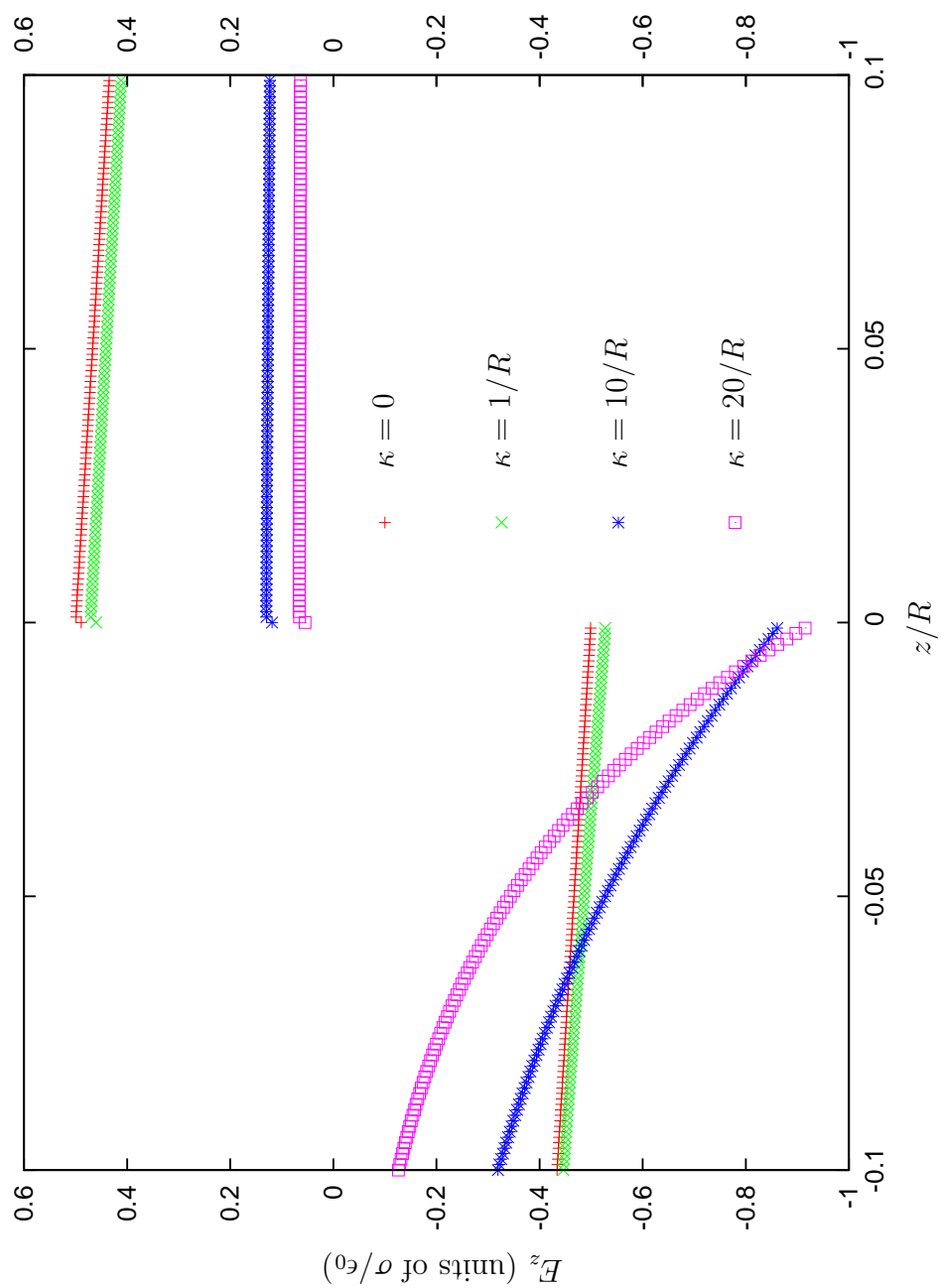
Figure 7: Electric field above and below the charged plate in Figure 6.