Fate of the Coulomb singularity in nonlinear Poisson-Boltzmann theory: The point charge as an electrically invisible object

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An absolute upper bound of Debye-Hückel form, $U(r_s)e^{-r}/r$, is derived for solutions to the nonlinear, spherical, radial Poisson-Boltzmann equation for the problem of an isolated charged sphere, dimensionless radius r_s, in an infinite volume of electrolyte. For $r_s \ll 1$, $U(r_s) \propto r_s \ln(1/r_s)$. Thus, as $r_s \to 0$, $U(r_s) \to 0$ and the shielding cloud around a point charge shrinks to zero radius. From any finite distance away, however small, the point charge is electrically invisible.

It seems that the simple, nonlinear Poisson-Boltzmann (PB) equation harbors within itself, unbeknownst to its users for many decades now, the remarkable implication that a point charge is electrically invisible. We prove this by deriving an absolute upper bound to the radial potential distribution generated by an isolated, uniformly charged sphere, dimensionless radius r_s, in an infinite volume of electrolyte, and then observing that, at any fixed dimensionless $r > r_s$, the upper bound vanishes as $r_s \ln(1/r_s)$ as $r_s \to 0$. The Coulomb singularity characteristic of the Debye-Hückel (DH) solution to the linearized equation is simply wiped out by the nonlinearity in the PB equation.

Poisson-Boltzmann theory is defined by the relations $\vec{F} = -\text{grad}\Psi$, the Poisson equation $\epsilon\, \text{div}\vec{F} = e[P(\vec{R}) - N(\vec{R})]$, and the dissociation equilibrium relation $P(\vec{R})N(\vec{R}) = P_0 N_0 = P_0^2$ for the ions in solution. Here $\vec{F}$ is the electric field, Ψ the potential, ϵ the dielectric constant of the solvent, e the magnitude of electronic charge, $P(\vec{R})$ and $N(\vec{R})$ the local concentrations of positive and negative ions, and P_0 and $N_0 = P_0$ the corresponding concentrations in the neutral electrolyte at infinity. Taking Ψ at infinity as the reference potential $\Psi(\infty) = 0$, we can write $P(\vec{R}) = P_0\, e^{(-e\Psi(\vec{R})/kT)}$ and $N(\vec{R}) = P_0\, e^{\, e\Psi(\vec{R})/kT}$, where we have assumed a simple 1:1 electrolyte. These various relations, taken together, yield the PB equation:

$$\nabla^2\Psi = (e/\epsilon)P_0(e^{e\Psi/kT} - e^{-e\Psi/kT}) \ . \qquad (1)$$

Here and throughout we use mks units.

For an isolated uniformly charged sphere of radius R_s in an infinite volume of electrolyte, all quantities vary only in the radial coordinate R. The appropriate boundary conditions (BC) are $\Psi = 0$ at $R = \infty$ and $d\Psi/dR = -e\Sigma/\epsilon$ at $R = R_s$, where $e\Sigma$ is the surface concentration of charge, assumed positive, on the sphere. Convenient dimensionless variables are $\psi = \Psi/V_T$ and $r = R/L_D$, where the units of potential and length are, respectively, $V_T = kT/e$ and $L_D = (\epsilon kT/2e^2P_0)^{1/2}$, the well-known Debye length. The dimensionless form of Eq. (1) is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \sinh\psi \ . \qquad (2)$$

The corresponding BC are $\psi = 0$ at $r = \infty$ and $d\psi/dr = -e\Sigma/(2\epsilon kTP_0)^{1/2}$ at $r = r_s$, the sphere radius. Henceforth we shall refer to a solution of Eq. (2), satisfying appropriate boundary conditions, as a "PB solution."

Intractability of the PB Eq. (2) led Debye and Hückel (DH) to consider its linearized version

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_{\text{DH}}}{dr}\right) = \psi_{\text{DH}} \ , \qquad (3)$$

which has as its solution satisfying $\psi_{\text{DH}} = 0$ at $r = \infty$ the Debye-Hückel function

$$\psi_{\text{DH}}(r) = f(r_s, \psi_s)e^{-r}/r, \quad f(r_s, \psi_s) = \psi_s r_s e^{r_s} \ , \qquad (4)$$

where the subscript s prescribes evaluation at the surface of the sphere. More generally, the DH function which takes on a preassigned value ψ_1 at $r = r_1$ can be written as $\psi_{\text{DH}}(r) = f(r_1, \psi_1)\, e^{-r}/r$, with $f(r_1, \psi_1) = \psi_1 r_1\, e^{r_1}$.

It is readily checked that $\psi_{\text{DH},s} \propto (d\psi_{\text{DH}}/dr)_s$, that is, that the sphere potential varies linearly with the charge on the sphere. Thus, at fixed r_s, as $\Sigma \to \infty$ also $\psi_{\text{DH},s} \to \infty$. Hence from Eq. (4), the linearized DH solutions do not possess a bound as the charge on a sphere goes to infinity. On the other hand, the linearized Eq. (3) obviously cannot hold up as a good approximation to the nonlinear

Eq. (2) for indefinitely large ψ. At sufficiently large ψ, the PB solution $\psi(r)$ near the sphere behaves in every respect like a planar solution, as is shown strikingly by the last column in Table I, discussed below. This observation suggests that a close examination of solutions to the planar PB equation can be turned to advantage in our quest for a useful bound. Consider, then, a uniformly charged isolated plate, of infinite lateral extent, immersed in an infinite volume of electrolyte, located at $Z=0$. All quantities vary only in the Z coordinate normal to the plate. In the dimensionless variables Eq. (2) is replaced by

$$\frac{d^2\psi}{dz^2}=\sinh\psi. \tag{5}$$

Integration[1] of Eq. (5) gives, for the limiting case of infinite charge density on the plate, the solution

$$\psi=\psi_\infty(z)=2\ln(1+e^{-z})/(1-e^{-z}) \; , \tag{6}$$

satisfying $-(d\psi/dz)=\infty$ and $\psi=\infty$ at $z=0$, and $\psi=0$ at $z=\infty$.

Note that $\psi_\infty(z)$ does for the plate what we have set out to do for the sphere, namely, it provides an absolute upper bound, at every z, for *all* other planar solutions to the PB equation. Note further that, despite the infinite surface charge concentration on the plate, the induced potential $\psi_\infty(z)$ is everywhere finite, except right at the plate, where $z=0$, and that, for $z>1$, $\psi_\infty(z)$ rapidly approaches $4e^{-z}$ asymptotically.

It is quite easily seen that an infinitely charged plate also provides an absolute upper bound, at every $r>r_s$, for *all* PB solutions to Eq. (2) for the charged sphere of radius r_s. In order to see this, compare the following two situations. In the first, we have the sphere generating the PB potential $\psi(r_1)$ at any chosen $r=r_1>r_s$. In the second, we imagine the sphere replaced by an infinitely charged plate tangent to the sphere and perpendicular to the radial line joining $r=0$ and $r=r_1$. Because, looked at from r_1, all of the sphere is behind the plate, and because the plate has infinite charge density, the potential $\psi_\infty(r_1-r_s)$ at r_1 due to the plate must obviously be greater than the PB potential $\psi(r_1)$ at r_1, whatever the charge density on the sphere. This physically plausible argument can be buttressed with a formal mathematical proof. The proof is given in Appendix B.

The problem with the upper bound provided by the planar solution $\psi_\infty(r-r_s)$ is that it is simply not good enough to yield interesting information about the PB solution for a sphere. Nonetheless, this planar upper bound is indispensable for finding an upper bound that is useful. In fact, the strategy that works uses the planar absolute upper bound $\psi_\infty(r_1-r_s)$ *at a single point*, $r_1>r_s$, but near r_s then, for all $r>r_1$, takes for the upper bound that DH function $\psi_{\rm DH}(r)$ for which $\psi_{\rm DH}(r_1)=\psi_\infty(r_1-r_s)$. The remainder of this paper is devoted to the proof that this procedure indeed yields an absolute upper bound.

As a preliminary, it is necessary to establish certain analytic and geometric properties of PB solutions $\psi(r)$ and DH functions $\psi_{\rm DH}(r)$. First, integration of Eq. (2) over the domain $r_1\leqslant r\leqslant r_2$ gives

$$r_1^2\left|\frac{d\psi}{dr}\right|_1-r_2^2\left|\frac{d\psi}{dr}\right|_2=\int_{r_1}^{r_2} r^2\sinh\psi\, dr, \tag{7}$$

where we have used explicitly the monotonically decreasing behavior of $\psi(r)$ for $r_s\leqslant r\leqslant\infty$, which is established formally in Appendix A. The corresponding integral of Eq. (3) is

$$r_1^2\left|\frac{d\psi_{\rm DH}}{dr}\right|_1-r_2^2\left|\frac{d\psi_{\rm DH}}{dr}\right|_2=\int_{r_1}^{r_2} r^2\psi_{\rm DH}\, dr. \tag{8}$$

Now $d\psi_{\rm DH}/dr$ varies as e^{-r} for all r, from Eq. (4), and $d\psi/dr$ likewise for sufficiently large r, where $\psi\ll 1$. This behavior enables the following simplification of Eqs. (7) and (8), respectively, in the limit $r_2=\infty$:

$$r_1^2\left|\frac{d\psi}{dr}\right|_1=\int_{r_1}^{\infty} r^2\sinh\psi\, dr \tag{9}$$

and

$$r_1^2\left|\frac{d\psi_{\rm DH}}{dr}\right|_1=\int_{r_1}^{\infty} r^2\psi_{\rm DH}\, dr\; . \tag{10}$$

With the help of Eqs. (7)–(10) we now prove the following:

If a DH function $\psi_{\rm DH}(r)$ and a PB solution $\psi(r)$ coincide at some radius r_1, $\psi_{\rm DH}(r_1)=\psi(r_1)$, then $\psi_{\rm DH}(r)$ is an upper bound to $\psi(r)$ for all $r>r_1$ [proposition (11)].

The proof is by contradiction. Assume there exists an $\bar r>r_1$ at which $\psi(\bar r)>\psi_{\rm DH}(\bar r)$. There are now two possibilities. One is that $\psi(r)\geqslant\psi_{\rm DH}(r)$ for all $r>r_1$, as illustrated in Fig. 1(a). By inspection, we see that this is possible only if $|d\psi/dr|_1\leqslant|d\psi_{\rm DH}/dr|_1$, keeping in mind the monotonicity of both functions. Thus the left-hand side (LHS) of Eq. (9) cannot exceed the LHS of Eq. (10). But the right-hand side (RHS) of Eq. (9) must exceed the RHS of Eq. (10) since, for all $r>r_1$, $\sinh\psi(r)>\psi(r)\geqslant\psi_{\rm DH}(r)$. This is an evident contradiction. Thus the situation depicted in Fig. 1(a) cannot arise.

The second possibility is that $\psi(r)$ crosses $\psi_{\rm DH}(r)$ at some finite $r>\bar r$. Let r_2 be the first such

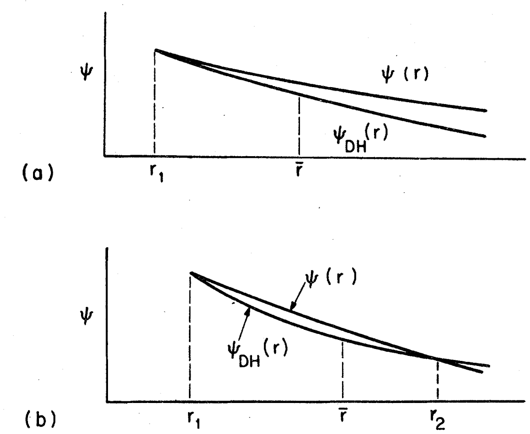

FIG. 1. Impossible forms of behavior for a PB solution $\psi(r)$.

crossing point to the right of $\bar{r}$. Likewise, proceeding leftward from $\bar{r}$ there must also be a first crossing point, which might as well be that at r_1. Thus, everywhere in the range $r_1 \leq r \leq r_2$, $\psi(r) \geq \psi_{DH}(r)$ and the situation is as illustrated in Fig. 1(b). As before, the crossing at r_1 requires that $|d\psi/dr|_1 \leq |d\psi_{DH}/dr|_1$. However, the crossing at r_2 requires the opposite inequality, $|d\psi/dr|_2 \geq |d\psi_{DH}/dr|_2$. These two inequalities together imply that the LHS of Eq. (7) cannot exceed the LHS of Eq. (8). But the RHS of Eq. (7) must exceed the RHS of Eq. (8), since everywhere in the common interval of integration, $r_1 \leq r \leq r_2$, $\sinh\psi(r) > \psi(r) \geq \psi_{DH}(r)$. Again a contradiction has been achieved, and (11) is proven.

It is now simple to prove the basic result of this note, namely, Boundedness Theorem [proposition (12)]: For any r_s and any $r_1 > r_s$, for all $r \geq r_1$, an absolute upper bound to the solution $\psi(r)$ to the PB Eq. (2), for any charge density $\in \Sigma$ on the sphere, up to infinite charge density, is $\psi_{DH}(r) = f(r_1, \psi_1)\, e^{-r}/r$, with $\psi_1 = \psi_\infty(r_1 - r_s)$, where ψ_∞ is given by Eq. (6) and $f(r_1, \psi_1)$ by Eq. (4).

We have proven above that this $\psi_{DH}(r_1) > \psi(r_1)$. Let $\bar{\psi}_{DH}(r)$ be a second DH function, as defined in Eq. (4), with $\bar{\psi}_{DH}(r_1) = \psi(r_1)$. From (4), $\psi_{DH}(r)$ bounds $\bar{\psi}_{DH}(r)$ for all r, and from (11), $\bar{\psi}_{DH}(r)$ bounds $\psi(r)$ for all $r > r_1$. The Boundedness Theorem is proven.

Letting $r_1 - r_s = \alpha r_s$, and using Eqs. (4) and (6), we give the absolute bound function specified by the Boundedness Theorem, written as $\psi_{DH,UB}(r)$, as

$$\begin{aligned} \psi_{DH,UB}(r) &= U(r_s, \alpha) e^{-r}/r, \\ U(r_s, \alpha) &= 2(1+\alpha) r_s e^{(1+\alpha)r_s} \\ &\quad \times \ln\frac{(1+e^{-\alpha r_s})}{(1-e^{-\alpha r_s})}, \end{aligned} \tag{13}$$

valid for $r \geq (1+\alpha) r_s$.

For r_s and αr_s small, expansion of the exponentials in Eq. (13) yields the simpler expression

$$\begin{aligned} \psi_{DH,UB}(r) &= U(r_s, \alpha) e^{-r}/r, \\ U(r_s, \alpha) &= 2(1+\alpha) r_s \ln(2/\alpha r_s), \end{aligned} \tag{14}$$

valid for $r_s \ll 1$, $\alpha r_s \ll 1$, and $r \geq (1+\alpha) r_s$.

Up to this point α is arbitrary. We now choose $\alpha = \alpha_{min}$ so as to minimize $U(r_s, \alpha)$. Setting $dU(r_s, \alpha)/d\alpha = 0$ gives, for α_{min}, the equation $(1+\alpha_{min})/\alpha_{min} = \ln(2/\alpha_{min} r_s)$, which is readily solved by an iterative procedure.

Table I lists, for $10^{-1} \geq r_s \geq 10^{-4}$, corresponding values of α_{min} and $U(r_s, \alpha_{min})$. The quantity labeled $A(r_s)$ in Table I is obtained from a computer solution to the PB Eq. (2) for a high value of field at the sphere, namely $-(d\psi/dr)_s = e^{12}$. This value of field corresponds in the planar problem, Eq. (5) to a plate potential $\psi_{pl} = 24$. For each r_s, $A(r_s)$ is determined as the large-r limit of $r\psi(r)e^r$. In the last column of Table I are listed the computer-determined values for ψ_s. It is seen that, for $r_s \geq 0.0005$, ψ_s is close to $\psi_{pl} = 24$. This indicates that, near the sphere surface, the potential has platelike behavior. Concomitantly, for $r_s > 0.005$, $A(r_s)$ is fairly close to $U(r_s, \alpha_{min})$, though always below, as it must be. As expected, ψ_s is always below ψ_{pl} for the same $-(d\psi/dr)_s$. At $r_s = 0.0001$, ψ_s is well below $\psi_{pl} = 24$. This indicates that the PB solution for ψ is DH-like right up to the sphere, which is verified by comparison with the DH values for $\psi_{DH,s}$ and $A_{DH}(r_s)$ in the last row of Table I. Accordingly, the computed $A(r_s)$ deviates more noticeably from $U(r_s, \alpha_{min})$. That a DH-like behavior should be found for all

TABLE I. Bound constant $U(r_s, \alpha_{min})$ compared to computed constant $A(r_s)$.[a] All computations made for $-(d\psi/dr)_s = e^{12}$, corresponding to the flat-plate potential $\psi_{pl} = 24$; ψ_s is the corresponding sphere potential. $U(r_s, \alpha_{min})$ is given by Eq. (14), with $\alpha = \alpha_{min}$.

r_s	α_{min}	$U(r_s, \alpha_{min})$	$A(r_s)$	ψ_s
10^{-1}	0.318 478	1.091 7	1.025 0	23.999 5038
5×10^{-2}	0.243 913	0.634 37	0.575 1	23.999 0141
10^{-2}	0.163 722	0.165 43	0.153 6	23.995 0000
5×10^{-3}	0.144 365	0.090 71	0.085 15	23.989 7914
10^{-3}	0.113 992	0.021 77	0.020 57	23.938 0782
5×10^{-4}	0.104 705	0.011 65	0.010 93	23.841 385
2×10^{-4}	0.094 624	0.005 07	0.004 54	23.168 68
10^{-4}	0.088 253	0.002 68	0.001 63	16.269 5
			0.001 63 [b]	16.275 5 [c]

[a] $A(r_s)$ is the large-r limit of $\psi(r)re^r$.

[b] This is $A_{DH}(r_s)$, the DH value for the asymptotic constant, calculated from $A_{DH}(r_s) = \psi_s r_s e^{r_s}$.

[c] This is $\psi_{DH,s}$, the DH value for the sphere potential, calculated from $\psi_{DH,s} = -[r_s/(1+r_s)]\,(d\psi/dr)_s$.

$r > r_s$, even though $\psi_s \gg 1$, is an apparent paradox, which is analyzed elsewhere.[2]

The unexpected outcome of this work lies in the small-r_s limit of $U(r_s, \alpha_{\min})$: $U(r_s, \alpha = 1) = 4r_s \ln(2/r_s) > U(r_s, \alpha_{\min})$ and $U(r_s, \alpha = 1) \to 0$ as $r_s \to 0$. Since these bounds are absolute, independent of the charge on the sphere, this means that a point charge is structureless, that is, has a shielding cloud around it of zero radius. The point charge is, in effect, a δ function encapsulated and compensated by a δ function of counterions. From any finite distance away, however small, the point charge is electrically invisible. The nonlinearity residing in $\sinh\psi$ has completely overridden and wiped out the $1/r$ Coulomb singularity which is characteristic of the linearized DH solution. Although this result is of theoretical interest, it should be kept in mind that in real electrolytes the PB model for screening must break down at the level of a few angstroms because of the finite size of solvent molecules and ions in solution.

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APPENDIX A: MONOTONICITY OF A PB SOLUTION $\psi(r)$

The proof of the monotonicity of $\psi(r)$ rests on the integral of Eq. (2) over the domain $r_1 \leq r \leq r_2$, namely,

$$r_2^2\left(\frac{d\psi}{dr}\right)_2 - r_1^2\left(\frac{d\psi}{dr}\right)_1 = \int_{r_1}^{r_2} r^2 \sinh\psi\, dr, \tag{A1}$$

which is Eq. (7) *without* the assumption of monotonicity.

Monotonicity is now proven by the method of contradiction. If $\psi(r)$ does not monotonically decrease with r, then $\psi(r)$ must have a minimum somewhere in the domain $r_s < r < \infty$, either at positive ψ as in curve A or at negative ψ as in curve B in Fig. 2(a). First consider curve A with a minimum at $r = r_a$. Beyond r_a there must be a maximum at some $r = r_b$, in order that $\psi \to 0$ as $r \to \infty$. Taking $r_1 = r_a$ and $r_2 = r_b$ in Eq. (A1), we see that the LHS is zero, because both $(d\psi/dr)_a$ and $(d\psi/dr)_b = 0$. But the RHS of Eq. (A1) must be positive, since everywhere in $r_a < r \leq r_b$, $\sinh\psi > \psi > 0$. (Note that if $\psi_a = 0$, the proof is unaltered.) Thus, curve A is not a possible behavior for $\psi(r)$. Next consider curve B with a minimum at $r = r_d$. En route from $\psi_s > 0$ to $\psi_d < 0$, $\psi(r)$ must cross the r axis, say at $r = r_c$. Taking $r_1 = r_c$ and $r_2 = r_d$ in Eq. (A1), we see that the LHS is positive, because $(d\psi/dr)_d = 0$ and $(d\psi/dr)_c$ must be negative. But the RHS of Eq. (A1) must be negative, since everywhere in $r_c < r \leq r_d$, $\sinh\psi < \psi < 0$. Thus curve B is also not a possible behavior for $\psi(r)$, and the monotonic behavior of $\psi(r)$ is established. It follows that everywhere in $r_s \leq r < \infty$, $(d\psi/dr) < 0$, thereby justifying the replacement of Eq. (A1) by Eq. (7).

APPENDIX B: THE POTENTIAL DUE TO AN INFINITELY CHARGED TANGENT PLANE BOUNDS ABSOLUTELY THE POTENTIAL DUE TO A FINITELY CHARGED SPHERE

The finitely charged sphere is of radius r_s, and the infinitely charged plane is located at $r = r_s$. The proof of the boundedness relation rests on four relations:

$$\left|\frac{d\psi}{dr}\right|_1 = \int_{r_1}^{\infty} \left(\frac{r}{r_1}\right)^2 \sinh\psi\, dr, \tag{B1}$$

$$\left|\frac{d\psi_{\rm pl}}{dr}\right|_1 = \int_{r_1}^{\infty} \sinh\psi_{\rm pl}\, dr\ , \tag{B2}$$

and, for $r_1 < r_2 < \infty$,

$$\left|\frac{d\psi}{dr}\right|_1 - \left(\frac{r_2}{r_1}\right)^2 \left|\frac{d\psi}{dr}\right|_2 = \int_{r_1}^{r_2} \left(\frac{r}{r_1}\right)^2 \sinh\psi\, dr, \tag{B3}$$

$$\left|\frac{d\psi_{\rm pl}}{dr}\right|_1 - \left|\frac{d\psi_{\rm pl}}{dr}\right|_2 = \int_{r_1}^{r_2} \sinh\psi_{\rm pl}\, dr\ . \tag{B4}$$

In these equations ψ denotes the potential due to

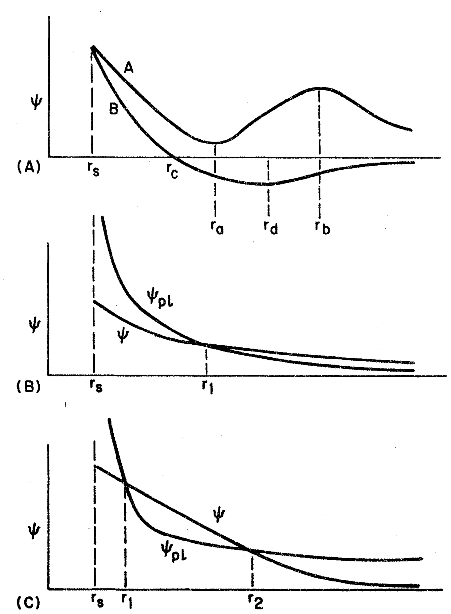

FIG. 2. (a) Impossible forms of behavior for a PB solution $\psi(r)$; (b) and (c) impossible crossings of $\psi(r)$ and $\psi_{\rm pl}(r)$.

the finitely charged sphere, and ψ_{pl} that due to the infinitely charged tangent plate. Note that Eq. (B1) is Eq. (9) divided through by r_1^2, and Eq. (B3) is Eq. (7) divided through by r_1^2. The monotonicity of ψ proved in Appendix A has been used in writing Eqs. (B1) and (B3), i.e., Eqs. (9) and (7). Equation (B4) is simply the integral of the planar PB equation, $(d^2\psi_{pl}/dr^2) = \sinh\psi$, and (B4) reduces to (B2) as $r_2 \to \infty$. Here too the monotonicity of ψ_{pl} has been used, and this property of ψ_{pl} is readily checked from the explicit solution for ψ_{pl}, namely Eq. (6).

The boundedness of ψ_{pl} over any ψ is proven by the method of contradiction. First we note that a single crossing situation such as depicted in Fig. 2(b) is impossible. If such a crossing did take place, say at $r = r_1$, then compare Eqs. (B1) and (B2). Since $\psi \geq \psi_{pl}$ for all r in the domain of integration, $r_1 \leq r < \infty$, and also $r/r_1 \geq 1$ everywhere in this domain, the RHS of Eq. (B1) must exceed the RHS of Eq. (B2). But because of the monotonicity of both ψ_{pl} and ψ the crossing at $r = r_1$ requires that the LHS of Eq. (B1) be less than the LHS of Eq. (B2). A contradiction has been obtained and a single crossing, as in Fig. 2(b), is therefore not possible.

Using the same method of contradiction we next prove that a pair of crossings of ψ and ψ_{pl} such as that depicted in Fig. 2(c) is also impossible. If such a pair of crossings did take place, say at $r = r_1$ and $r = r_2 > r_1$, then compare Eqs. (B3) and (B4). Again, since $\psi \geq \psi_{pl}$ everywhere in $r_1 \leq r \leq r_2$, the RHS of Eq. (B3) must exceed the RHS of Eq. (B4). But the monotonicity of both ψ and ψ_{pl} and the nature of the crossings require that $|d\psi/dr|_1 < |d\psi_{pl}/dr|_1$ and $|d\psi/dr|_2 > |d\psi_{pl}/dr|_2$; hence $(r_2/r_1)^2 \, |d\psi/dr|_2 > |d\psi_{pl}/dr|_2$. Hence the LHS of Eq. (3) is less than the LHS of Eq. (B4). A contradiction has been obtained, and consequently a pair of crossings, such as that shown in Fig. 2(c) is also impossible. The only remaining alternative is that ψ_{pl} everywhere bounds ψ, in $r_s \leq r < \infty$, as expected on physical grounds.

Note that in the above discussion we have taken ψ_s as finite, whereas $\psi_{pl,s}$ is infinite: ψ_s is finite because $-(d\psi/dr)_s \propto \Sigma$ is finite, the latter being a boundary condition. If ψ_s were infinite with $-(d\psi/dr)_s$ finite we would immediately run into a contradiction with Eq. (B3), taking $r_1 = r_s$ and r_2 a nearby point (the LHS finite, the RHS infinite).

[1]E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[2]M. A. Lampert and R. S. Crandall, Chem. Phys. Lett. (to be published).