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Gauss law constraints on Debye–Hückel screening

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Abstract. We demand that the Gauss law at the edge must be obeyed by the electric potential $\phi(r)$ generated within a neutral plasma/electrolyte of strictly finite size by the introduction of a test charge q_b. Our proposal has the nice features that total ionic numbers are conserved, the point-Coulomb behaviour of $\phi(r)$ is guaranteed at short-distance, and accumulation of induced charges near the centre and the surface can be demonstrated rigorously. In contrast, the standard Debye–Hückel potential $\phi_{\mathrm{D}}(r)$ applicable to unbounded plasma has the strange features that the Gauss law cannot be obeyed at the plasma's edge, total ionic numbers themselves are altered, the short-distance Coulomb behaviour has to be imposed by hand, and induced charge appearance at the surface cannot be built-in.

Keywords. Plasma/colloid; Boltzmann density; Poisson equation; Gauss law.

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1. Introduction

The celebrated concept of static (time-independent) or dynamic (time-dependent) Debye–Hückel (DH) shielding has been extensively used by research workers in many areas of theoretical as well as experimental physics/chemistry. These areas include classical electrodynamics [1], equilibrium statistical mechanics [2,3], nonequilibrium transport processes [4], plasma physics [5–7], relativistic heavy-ion collisions [8–10] and chemical electrolytes/colloids [11–14].

All such investigations can be broadly classified into two types: (i) The self-screening type [1,2,11] where the charge of every ion already present in a neutral plasma gets inherently screened due to its neighbours. This topic will not be discussed further in the present work. (ii) The induced screening type [4,5,10] where the effect of an externally-introduced test charge on an originally neutral plasma is considered. The present paper will address some very subtle mathematical issues confronting this topic only. The physics of the induced-screening problem is well-known. If an externally-created test charge named b is placed inside an otherwise homogeneous and isotropic neutral plasma, the medium gets somewhat polarized, a nonzero local charge density appears in space, the Poisson equation becomes nontrivial, and the electric potential due to the test charge gets screened compared to the point Coulomb value.

The Boltzmann distribution-based theory of Debye shielding is assumed to be standard (see §2 for a quick recap in the static case) and hence used by all researchers without further scrutiny. The aim of the present paper is three-fold: (i) to point out in §2 some peculiarities of the standard DH theory as applied to unbounded plasmas related to the individual ionic numbers, total charge of the system, electrostatic Gauss law, short-distance behaviour of the potential etc.; (ii) to demonstrate in §3 how the said peculiarities can be overcome through a proper normalization of ionic numbers as applied to a plasma of strictly finite size, and (iii) to give in §4 a pointwise comparison between the salient features of the two approaches. Algebraic details of analysing the strong shielding problem are relegated to the Appendix. Although our emphasis will be on conceptual/algebraic aspects, it is hoped that practitioners can apply the ideas also to numerical data fitting.

2. Debye–Hückel theory for unbounded plasmas recapitulated [1,2,5,11]

Customary ionic densities and Poisson equation

The standard treatment begins with an unperturbed equilibrium plasma in which ions of the ath variety have charge q_a esu and uniform number density n_a^0 obeying the charge neutrality relation $\sum_a q_a n_a^0 = 0$. Upon introducing the test particle b, a polarization potential $\phi_{\rm D}(r)$ is created around b (taken as the origin) and equilibrium is re-established assuming chemical reactions to be absent. Employing the unnormalized Boltzmann barometric formula and linearizing it, one writes the perturbed number density as

$$n_{a\rm D}(r) = n_a^0 \exp\left\{-\frac{q_a \phi_{\rm D}(r)}{kT}\right\} \approx n_a^0 \left\{1 - \frac{q_a \phi_{\rm D}(r)}{kT} + \cdots\right\}, \tag{1}$$

where k is the Boltzmann's constant, T is the absolute temperature, and $n_{a\rm D}(r)$ is assumed to coincide with n_a^0 as $r \to \infty$. The polarization-induced local charge density reads as

$$\left.\begin{aligned} &\rho_{\rm D}(r) = q_b \delta(\vec{r}) + \sum_a q_a n_{a\rm D}(r) = -\mu^2 \phi_{\rm D}(r)/4\pi; \quad r > 0 \\ &\mu^2 = 4\pi \sum_a q_a^2 n_a^0/kT; \quad \lambda = \mu^{-1} \end{aligned}\right\} \tag{2}$$

with μ being the Debye parameter and λ the screening length. The conventional Poisson equation $\nabla^2 \phi_{\rm D} = -4\pi\rho_{\rm D} = \mu^2 \phi_{\rm D}$ has the famous Debye solution

$$\phi_{\rm D}(r) = \left\{A_{\rm D} {\rm e}^{\mu r} + B_{\rm D} {\rm e}^{-\mu r}\right\}/r = q_b {\rm e}^{-\mu r}/r, \tag{3}$$

where one sets by hand $A_{\rm D} = 0$ to avoid exponential growth at $r/\lambda \gg 1$ and $B_{\rm D} = q_b$ to retrieve the point Coulomb behaviour at $r/\lambda \ll 1$. The linearization of the exponential in (1) remains valid even near the origin provided

$$\left|\frac{q_a \phi_{\rm D}(r)}{kT}\right| \sim \left|\frac{q_a q_b}{kTr}\right| \ll 1 \quad \text{if} \quad r \gg \frac{q_0^2}{kT}, \tag{4}$$

where q_0 esu is the fundamental electronic charge. In all problems of shielding the phrase '$r \to 0$ behaviour' is to be understood under the restriction (4).

Peculiarities

Although the above derivation is very elegant and formula (3) has widespread applications in physics/chemistry, the following conceptual difficulties do arise if the plasma has a *finite* (though large) physical size R occupying a volume $V = 4\pi R^3/3$ such that the phrase 'unbounded plasma' has to be understood as the limit $R/\lambda \to \infty$.

(a) The test particle together with the overall neutral plasma have net charge q_b. Assuming spherical symmetry and Gauss's theorem the unknown exact potential $\phi(r)$ and its derivative $\phi'(r)$ must become pure Coulombic for all $r \geq R$. In particular, one must have

$$\phi(R) = q_b/R, \quad \phi'(R) = -q_b/R^2 \tag{5}$$

even if polarization-induced surface charges appear at R. Unfortunately, the Debye expression (3) gets rapidly damped for $r > \lambda$ and, hence, it fails to satisfy the requirements (5).

(b) Of course, it is possible to construct a different, rather peculiar solution $\phi_{\rm P}(r)$ of the customary Poisson equation $\nabla^2\phi_{\rm P} = \mu^2\phi_{\rm P}$ via

$$\phi_{\rm P}(r) = q_b r^{-1} \cosh\mu(R-r); \quad 0 < r \leq R. \tag{6}$$

It has the proper boundary conditions at the edge since $\phi_{\rm P}(R) = q_b/R, \phi'_{\rm P}(R) = -q_b/R^2$ but its bahaviour near the origin becomes bad, namely $\phi_{\rm P}(r) \xrightarrow[r\to 0]{} q_b(\cosh\mu R)/r$.

(c) Before perturbation the total number of ions of type a was $N_a^0 = \int_V {\rm d}^3 s n_a^0 = n_a^0 V$ where ${\rm d}^3 s$ is the integration measure at the dummy position $\vec{s}$. After introduction of the test charge the number becomes, in view of (1),

$$\begin{aligned} N_{a{\rm D}} &= \int_V {\rm d}^3 s n_a^0 \left\{1 - \frac{q_a q_b}{kT}\frac{{\rm e}^{-\mu s}}{s}\right\} \\ &= N_a^0 - 4\pi n_a^0 q_a q_b/(kT\mu^2). \end{aligned} \tag{7}$$

In the absence of chemical reactions, the fact that $N_{a{\rm D}} - N_a^0 \neq 0$ is alarming. Hence one is compelled to abandon the conventional demand $n_{a{\rm D}}(r) \xrightarrow[r\to\infty]{} n_a^0$ which was in-built in writing (1).

3. Our formulation applied to strictly bounded plasma

The formalism developed below applies to a plasma/colloid of finite size R such that the ratio R/λ is arbitrary.

Modified ionic densities and Poisson equation

We demand that, after introduction of the test charge, the perturbed number density $n_a(r)$ must be proportional to the usual Boltzmann factor but subject to a normalization condition $\int \mathrm{d}^3 s n_a(s) = N_a^0$ = unperturbed number. Explicitly

$$n_a(r) = \frac{N_a^0 \exp\{-q_a \phi(r)/kT\}}{\int \mathrm{d}^3 \vec{s} \exp\{-q_a \phi(s)/kT\}} \approx n_a^0 \left[1 - \frac{q_a\{\phi(r) - \langle\phi\rangle\}}{kT}\right]; \quad \langle\phi\rangle \equiv \frac{\int \mathrm{d}^3 s \phi(s)}{V}, \tag{8}$$

where the exponentials have again been linearized and $\langle\phi\rangle$ represents the unknown spatial average of the desired potential $\phi(s)$. Clearly, the contrast between the Debye density (1) and our density (8) arises from $\langle\phi\rangle$. The corresponding charge density and Poisson equation read

$$\left.\begin{aligned} \rho(r) &= q_b \delta(\vec{r}) + \sum_a q_a n_a(r) = -\mu^2 \xi(r)/4\pi; \quad \xi(r) \equiv \phi(r) - \langle\phi\rangle \\ \nabla^2 \phi &= \nabla^2 \xi = \mu^2 \xi; \quad 0 < r \le R \\ &= 0; \quad R < r < \infty \end{aligned}\right\} \tag{9}$$

whose contrast with the Debye prescription (2) should be noted. Solution of this differential equation has the general form

$$\left.\begin{aligned} \phi(r) &\equiv \xi(r) + \langle\phi\rangle = \{A\mathrm{e}^{\mu r} + B\mathrm{e}^{-\mu r}\}/r + \langle\phi\rangle; \quad 0 < r \le R \\ &= q_b/r; \quad R \le r < \infty \end{aligned}\right\}, \tag{10}$$

where the unknown constants $A, B, \langle\phi\rangle$ can be determined by imposing three conditions, namely

$$\left.\begin{aligned} \phi(R) &\equiv \{A\mathrm{e}^{\mu R} + B\mathrm{e}^{-\mu R}\}/R + \langle\phi\rangle = q_b/R \\ \phi'(R) &\equiv \{A(\mu R - 1)\mathrm{e}^{\mu R} - B(\mu R + 1)\mathrm{e}^{-\mu R}\}/R^2 = -q_b/R^2 \\ \int_V \mathrm{d}^3 s \xi(s) &\equiv 4\pi[A\{(\mu R - 1)\mathrm{e}^{\mu R} + 1\} + B\{-(\mu R + 1)\mathrm{e}^{-\mu R} + 1\}]/\mu^2 = 0 \end{aligned}\right\}. \tag{11}$$

After a little algebra the set of simultaneous equations (11) can be solved exactly as

$$A = \frac{q_b}{\eta}\left\{(\mu R + 1)\mathrm{e}^{-\mu R} - 1\right\}; \quad B = \frac{q_b}{\eta}\left\{(\mu R - 1)\mathrm{e}^{\mu R} + 1\right\}$$

$$\langle\phi\rangle = \frac{\mu q_b}{\eta}\left\{\mathrm{e}^{\mu R} + \mathrm{e}^{-\mu R} - 2\right\}; \quad \eta \equiv (\mu R - 1)\mathrm{e}^{\mu R} + (\mu R + 1)\mathrm{e}^{-\mu R}. \tag{12}$$

Equations (10), (12) constitute the main algebraic results of the present paper. Since their structure looks complicated we examine below some limiting situations depending on the parameter μR and variable μr.

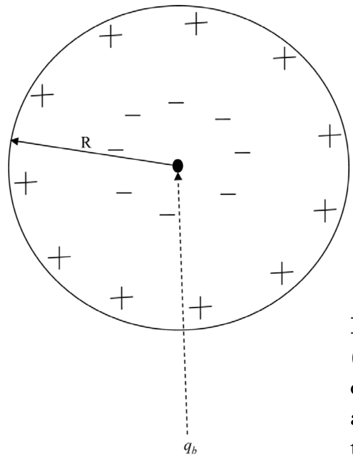

Figure 1. Schematic diagram showing a test charge q_b (assumed positive) inserted at the centre of a spherical quasi-neutral plasma. The accumulation of induced negative charges around the centre and positive charges at the surface layer are marked.

Limiting situations

Keeping in mind the relation $A+B = q_b$, and doing elementary Taylor or asymptotic expansions, we report the following cases:
(a) *Short distance behaviour.* Let

$$\left.\begin{array}{l}\mu R \equiv R/\lambda = \text{ fixed;} \quad \mu r \equiv r/\lambda \ll 1 \\ \phi(r) \xrightarrow[r/\lambda \to 0]{} r^{-1} q_b \left[1 + O(r/\lambda)\right]\end{array}\right\} \tag{13}$$

showing that the point Coulomb value in close vicinity of the test charge is satisfied automatically in our theory.
(b) *Strong shielding.* Next, consider

$$\left.\begin{array}{l}0 < r = \text{fixed} \ < \ R; \quad \mu R \equiv R/\lambda \gg 1 \\ \phi(r) \xrightarrow[R/\lambda \to \infty]{} \dfrac{q_b}{r}\,\mathrm{e}^{-\mu r} + \dfrac{q_b}{R}\end{array}\right\} \tag{14}$$

implying that the celebrated Debye–Hückel result (3) (along with a constant correction term q_b/R) also follows as a special case from our formalism if $\lambda \ll R$.

Actually, in the present case, one can ask mathematically much deeper and physically very interesting question: 'Suppose a positive charge q_b is added at the centre of a spherical quasi-neutral plasma of radius R as shown in figure 1. The electrons will then rush around q_b and shield it. However, at the surface of the plasma a net induced +ve charge (of value q_b) should develop distributed uniformly. How can our theory describe such charge polarization?' A detailed satisfactory answer to this question is worked out in the Appendix by pin-pointing the role of every term occurring in our general potential (10) and plotting the results in figure 2.
(c) *Weak screening.* Next, let

$$\begin{array}{l}\mu r \equiv r/\lambda \ll 1 \text{ at fixed } r; \quad \mu R \equiv R/\lambda \ll 1 \\ \phi(r) \xrightarrow[R/\lambda \to 0]{} r^{-1} q_b [1 + O(R/\lambda)^2]\end{array} \tag{15}$$

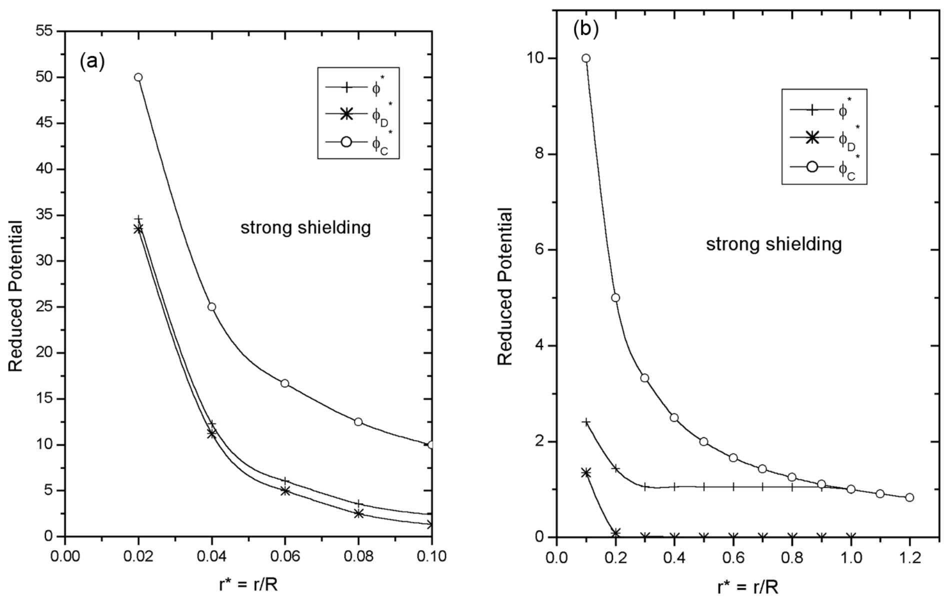

Figure 2. Plots of the reduced Coulomb potential $\phi_{\mathrm{C}}^* = 1/r^*$, reduced Debye potential $\phi_{\mathrm{D}}^* \equiv R\phi_{\mathrm{D}}/q_b = \mathrm{e}^{-\mu^* r^*}/r^*$, and our reduced potential $\phi^* \equiv R\phi/q_b$ with the dimensionless distance $r^* \equiv r/R$ for the strong screening case $\mu R \equiv R/\lambda = 20$ (**a**) over the narrow span $0 < r^* \leq 0.1$ and (**b**) over the wide span $0.1 \leq r^* \leq 1.0$. Of course, at $r^* > 1$ only ϕ_{C}^* is relevant.

demonstrating that for $\lambda \gg R$ our potential goes into the unscreened Coulomb form as expected.

(d) *Intermediate shielding.* Finally, the case $\mu R \sim 1, \lambda \sim R$ is of considerable interest to theoretical physicists even if not easily achievable in the experimental laboratory. For explicit illustration we take

$$\mu R = 1; \quad \lambda = R; \quad r^* = r/R; \quad 0 < r^* \leq 1$$
$$\phi_{\mathrm{C}}^* \equiv \frac{1}{r^*}; \quad \phi_{\mathrm{D}}^* \equiv \frac{\phi_{\mathrm{D}}}{\mu q_b} \equiv \frac{\mathrm{e}^{-r^*}}{r^*}; \quad \phi^* \equiv \frac{R\phi}{q_b}, \tag{16}$$

where $\phi_{\mathrm{C}}^*, \phi_{\mathrm{D}}^*$, and ϕ^* are the reduced Coulomb potential, reduced Debye potential and our reduced potential respectively, When their numerical values are plotted in figure 3 noticeable differences between ϕ_{D}^* and ϕ^* are observed.

4. Conclusions

Table 1 summarizes some salient features of the Debye theory *vis-à-vis* our approach. Researchers should notice four important points: (a) a small difference between the ionic number densities (1) and (8) causes substantial difference between the two treatments, (b) imposition of the Gauss law boundary conditions in

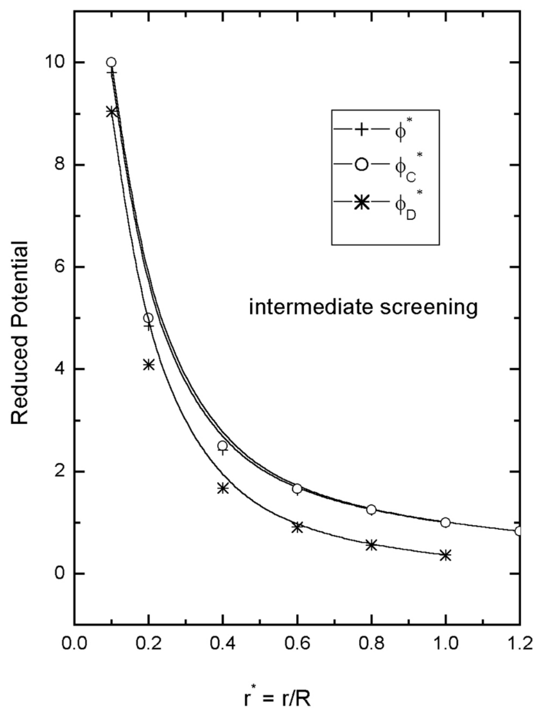

Figure 3. Same as in figure 2 except that the case corresponds to intermediate shielding with $\mu R = R/\lambda = 1$ as given in eq. (16).

(11) is enough to generate a consistent solution $\phi(r)$ throughout the wide region $0 < r \le R$, (c) various terms present in our solution (A1), (A2) can explain satisfactorily the charge polarization occurring in the medium, (d) the famous Debye term follows as a special case of our expression (14) for strong shielding $\mu \gg R^{-1}$, and (e) since laboratory-produced plasmas/colloids often belong to the case $\lambda \ll R$ the usual Debye potential (1) gives good numerical fit to experimental data (in spite of the conceptual ambiguities mentioned in §2).

Before ending it may be added that this paper is not concerned with entirely different treatments of the screening problem, e.g. Bogolyubov's handling [3] of the static two-body correlation function and the dynamic linear-response analysis [4] of the collisionless Vlasov equation. The question of whether normalization of the species number can be crucial in these approaches also will be discussed in a future communication.

Appendix: Our detailed analysis of the strong screening case of figure 1

Genaral solution and charge density. Now we shall address the important question posed below eq. (14) of the text by rewriting the general solution (10) and charge density (9) inside the plasma as

Table 1. Salient features of Debye's theory and our approach to the problem of static plasma/colloid screening.

Debye theory	Our approach
(i) *Ionic density.* It is demanded that $n_{a\mathrm{D}}(r)$ in eq. (1) coincides with the unperturbed n_a^0 as $r \to \infty$.	We demand that the unperturbed and perturbed ionic numbers must have the same value N_a^0 in eq. (8).
(ii) *Charge density.* At $r > 0$, the $\rho_{\mathrm{D}}(r)$ of eq. (2) is proportional to the unknown potential $\phi_{\mathrm{D}}(r)$ itself.	At $r > 0$ our $\rho(r)$ in eq. (9) is proportional to the difference $\phi(r) - \langle\phi\rangle$ with $\langle\phi\rangle$ being the spatial average of the unknown potential.
(iii) *Gauss law.* At sufficiently large distance R from the test charge it is not possible to impose the Gauss law conditions on $\phi_{\mathrm{D}}(R)$ and $\phi'_{\mathrm{D}}(R)$ in eq. (3). Any such attempt leads to a peculiar solution $\phi_{\mathrm{P}}(r)$ in eq. (6) having bad behaviour near the origin.	The Gauss law boundary conditions on $\phi\,(R)$ and $\phi'(R)$ can be readily imposed on our solution (10) so as to fix uniquely the unknown constants A, B in eq. (12). This logic remains valid even if polarization-induced surface charges appear at R.
(iv) *Rigidity of Poisson equation.* It is usually believed that the shielded formula (3) describes the potential within a distance of order λ around the test charge. But in Debye–Poisson equation $\nabla^2\phi_{\mathrm{D}} = \mu^2\phi_{\mathrm{D}}$ there is no more freedom to generate any other dependence of $\phi_{a\mathrm{D}}(r)$ at larger distances.	The structure of our Poisson equation $\nabla^2\phi = \mu^2(\phi - \langle\phi\rangle)$, though again unique, has additional freedom due to the appearance of the parameter $\langle\phi\rangle$. Consequently, our solution $\phi(r)$ in (10), (12) describes the potential throughout the wide region $0 < r \leq R$, without any restriction from λ.
(v) *Short distance behaviour* (subject to the restriction (4)). The requirement $\phi_{\mathrm{D}}(r) \xrightarrow[r\to 0]{} q_b/r$ is imposed by hand on the Debye solution (3) to fix the unknown constant B_{D} as q_b.	Our constants A and B in eq. (12) always satisfy $A + B = q_b$. Hence the property $\phi(r) \xrightarrow[r\to 0]{} q_b/r$ is automatically obeyed by our solution as seen from (13).
(vi) *Shielding strength.* The celebrated form (3) of $\phi_{\mathrm{D}}(r)$ is supposed to hold for all values of the screening parameter $\mu \equiv \lambda^{-1}$ defined by (2).	We find that the Debye functional form (3) follows as a special case of our theory in eq. (14) only for strong screening $\mu R \equiv R/\lambda \gg 1$. The two theories, however, become quite different for intermediate screening $\mu R \sim 1$ as sketched in figure 3.
(vii) *Polarization pattern.* The $q_b\mathrm{e}^{-\mu r}/r$ term in (2), (3) accounts for the shielding effect around the centre but disregards the induced charge development at the surface.	The Appendix shows that the $B\mathrm{e}^{-\mu r}/r$ and $A\mathrm{e}^{\mu r}/r$ terms in (10), (A2) correctly describe the charge polarization around the centre and within the surface layer. Of course, both ϕ and $\mathrm{d}\phi/\mathrm{d}r$ remain single-valuedly continuous across R.

$$\begin{aligned}\phi(r) &= \xi_{\rm B}(r) + \langle\phi\rangle + \xi_{\rm S}(r),\\ \rho(r) &= -\mu^2\xi(r)/4\pi = \rho_{\rm B}(r) + \rho_{\rm S}(r),\end{aligned}\quad 0 < r \le R \tag{A1}$$

where the new functions are

$$\begin{aligned}\xi_{\rm B}(r) &\equiv \frac{B{\rm e}^{-\mu r}}{r}; \quad \xi_{\rm S}(r) \equiv \frac{A{\rm e}^{\mu r}}{r};\\ \rho_{\rm B}(r) &\equiv \frac{-\mu^2}{4\pi}\xi_{\rm B}(r); \quad \rho_{\rm S}(r) \equiv \frac{-\mu^2}{4\pi}\xi_{\rm S}(r).\end{aligned} \tag{A2}$$

For reasons to become clear later the suffixes B and S will label the bulk and surface regions of the plasma, respectively. Next, attention will be focused on the strong coupling limit of eq. (12), namely

$$\left.\begin{aligned}&R \gg \lambda; \quad \mu^* = \mu R \gg 1; \quad \eta \approx \mu R{\rm e}^{\mu R}\\ &B \approx q_b; \quad \langle\phi\rangle \approx q_b/R; \quad A \approx -q_b{\rm e}^{-\mu R}/\mu R\end{aligned}\right\}. \tag{A3}$$

The bulk region ($0 < r \le R - 5\lambda$, *say*). Suppose the point r of measurement is located several Debye lengths away from the edge R. Then (A2), (A3) yield

$$\left.\begin{aligned}&\xi_{\rm B}(r) \approx q_b{\rm e}^{-\mu r}/r \approx \phi_{\rm D}(r); \quad \xi_{\rm S}(r) \approx 0\\ &\phi(r) \approx \phi_{\rm D}(r) + q_b/R; \quad \phi'(r) \approx \phi'_{\rm D}(r)\\ &\rho_{\rm B}(r) \approx -\mu^2 q_b{\rm e}^{-\mu r}/(4\pi r) \approx q_b\delta'(r)/(4\pi r)\end{aligned}\right\}, \tag{A4}$$

where $\phi_{\rm D}(r)$ is the standard Debye term and $\delta'(r) \underset{\mu^*\gg 1}{=} -\mu^2{\rm e}^{-\mu r}$ is a useful representation [15] of the derivative Dirac delta. Thus, our theory (A4) nicely reproduces the DH potential $\phi_{\rm D}(r)$ (plus a constant correction term) together with the DH electric field $-\phi'_{\rm D}(r)$ throughout the bulk region. Of course, the dominant influence of the DH functions is felt only over distances of $O(\lambda)$ around the origin owing to the damping factor ${\rm e}^{-\mu r}$. Also, the net charge residing in the DH cloud must be $-q_b$ because, from (A4),

$$Q_{\rm B} \equiv \int_V {\rm d}^3 r\rho_{\rm B}(r) \approx \int_0^R {\rm d}r r^2 4\pi\left\{\frac{q_b\delta'(r)}{4\pi r}\right\} \approx -q_b \tag{A5}$$

by partial integration. Hence, the electronic charge accumulation around the centre in figure 1 is explained correctly.

The surface layer ($R - 5\lambda$ (*say*) $\le r \le R$). Next, suppose the point of observation r is situated near the edge within a layer of thickness of a few Debye lengths. Then, dropping terms of relative order $1/\mu R$ and ${\rm e}^{-\mu R}$ our results (A2), (A3) give

$$\left.\begin{aligned}&\xi_{\rm B}(r) \approx 0; \quad \xi_{\rm S}(r) \approx -q_b{\rm e}^{-\mu(R-r)}/(\mu R r)\\ &\phi(r) \approx \tfrac{q_b}{R}\left[1 - \tfrac{{\rm e}^{-\mu(R-r)}}{\mu r}\right]; \quad \phi'(r) \approx \tfrac{-q_b{\rm e}^{-\mu(R-r)}}{Rr}\\ &\rho_{\rm S}(r) \approx \tfrac{q_b\mu{\rm e}^{-\mu(R-r)}}{4\pi R r} \approx \tfrac{q_b\delta(R-r)}{4\pi R^2}\end{aligned}\right\}, \tag{A6}$$

where the Debye contribution $\xi_{\rm B}(r)$ has become negligible and $\delta(R-r) \underset{\mu^*\gg 1}{=} \mu{\rm e}^{-\mu(R-r)}$ is a convenient representation [15] of the Dirac delta. The adjective

'surface layer' is appropriate because the function $\mathrm{e}^{-\mu(R-r)}$ is 1 at the edge R but drops to e^{-5} at the lower tip $R-5\lambda$.
Variation with distance. In (A6) the distance difference $R-r$ may be scanned either by a fine length scale $\lambda/5$ (say) or course length scale 5λ (say). More specifically let us consider the edge R, a vicinity point R_-, and the distant tip point R_t together with the corresponding physical observables defined by

$$\left.\begin{array}{l} R \gg \lambda; \quad \phi(R) \approx q_b/R; \quad \phi'(R) \approx -q_b/R^2 \\ R_- \equiv R-\lambda/5; \quad \phi(R_-) \approx \phi(R)[1+\cdots]; \quad \phi'(R_-) \approx \phi'(R)[1+\cdots] \\ R_\mathrm{t} \equiv R-5\lambda; \quad \phi(R_\mathrm{t}) \approx \phi(R)[1+\cdots]; \quad \phi'(R_\mathrm{t}) \approx \phi'(R)\cdot \mathrm{e}^{-5} \approx -0 \end{array}\right\}, \tag{A7}$$

where the dots $\cdots$ denote neglected terms of relative order $1/\mu R$. Clearly, our potential $\phi(r)$ varies continuously throughout the boundary layer without suffering any jump while going from the edge R up to the tip R_t. The derivative $\phi'(r)$ also remains continuous at the vicinity point since $\phi'(R_-)-\phi'(R) \approx 0$ but it suffers a finite jump while going up to the tip because $\phi'(R_\mathrm{t})-\phi'(R) \approx q_b/R^2$. The induced charge, residing within the thin boundary layer or (almost equivalently) smeared over the spherical surface, has the net value computed from (A6) as

$$Q_\mathrm{S} \equiv \int \mathrm{d}^3 r \rho_\mathrm{S}(r) = \int_0^R \mathrm{d}r r^2 4\pi \left\{\frac{q_b \delta(R-r)}{4\pi R^2}\right\} \approx q_b. \tag{A8}$$

Hence the $A\mathrm{e}^{\mu r}/r$ term correctly explains the positive charge accumulation at the edge in figure 1.
A calculus-based remark. One may also obtain the physical quantities near the surface by directly solving the Poisson equation

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\{r^2\phi'(r)\} \underset{r\to R}{\approx} \frac{-q_b \mathrm{e}^{-\mu(R-r)}}{Rr} \approx \frac{-q_b\delta(R-r)}{R^2} \tag{A9}$$

subject to the externally-imposed Gauss boundary conditions $\phi(R) = q_b(R)$ and $\phi'(R) = -q_b/R^2$. The mathematically precise method is to exploit the presence of an inherent length scale $\lambda \equiv \mu^{-1}$ in the problem, consider a vicinity point $R_- \equiv R-\lambda/5$ along with the distant tip point $R_\mathrm{t} \equiv R-5\lambda$, integrate twice the exponential in (A9) over the corresponding ranges, and thereby obtain

$$\left.\begin{array}{l} \phi'(R_-)-\phi'(R) \approx 0; \quad \phi'(R_\mathrm{t})-\phi'(R) \approx q_b/R^2 \\ \phi(R_-)-\phi(R) \approx 0; \quad \phi(R_\mathrm{t})-\phi(R) \approx 0 \end{array}\right\}. \tag{A10}$$

This proves once again that ϕ' suffers a jump between R_t and R (not between R_- and R) while ϕ remains continuous throughout the boundary layer. A mathematically vague method is to treat $\delta(R-r)$ in (A9) as a strict delta function of calculus (having no inherent length scale) and integrate twice over the range $R-\varepsilon$ to R for obtaining

$$\phi'(R-\varepsilon)-\phi'(R) = q_b/R^2; \quad \phi(R-\varepsilon)-\phi(R) = 0, \tag{A11}$$

where the 'infinitesimal ε' is still vague but the potential ϕ remains jump-free here too.

Numerical illustration. Figures 2a and 2b plot the Coulomb, Debye, and our reduced potentials as functions of the dimensionless distance $r^* \equiv r/R$ for the choice $\mu^* \equiv \mu R = 20$. Figure 2a clearly shows how DH ϕ^*_{D} falls from a big value to almost zero over the narrow span $0 < r^* \lesssim 0.1$. On the other hand, figure 2b depicts how our ϕ^* remains essentially constant over the wide span $0.2 \lesssim r^* \leq 1.0$. Of course, outside the edge, i.e., for $r^* > 1.0$ only the Coulomb form $\phi^*_{\mathrm{C}} = 1/r^*$ is relevant.

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