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New types of polarisation following from the non-linear spherical radial Poisson–Boltzmann equation

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Abstract. All possible types of solutions of the non-linear spherical radial Poisson-Boltzmann equation, describing the spatial distribution of the particles in a classical two-component Coulomb gas, are investigated analytically and numerically. The obtained solutions show that every particle of the system and its screening cloud forms an atom- or ion-like structure and reveals a tendency towards condensation in the Coulomb gas.

In this paper the non-linear spherical radial Poisson-Boltzmann (PB) equation is investigated. This equation describes the spatial distribution of the particles in a classical Coulomb gas. In thermal equilibrium an average electrostatic potential φ can be introduced into the system. This potential is determined by the spatial distribution of the particles, which in turn is controlled by that potential.

In thermal equilibrium the spatial distribution of the charged particles follows the Boltzmann law in the self-consistent field φ. Consequently, for the concentrations of the positive and negative particles, n_+ and n_-, respectively, we obtain

$$n_+ = n_0 \exp(-e\varphi/kT) \qquad n_- = n_0 \exp(e\varphi/kT). \tag{1}$$

Here n_0 is the average concentration of the particles, e is the absolute value of the electron charge, T is the absolute temperature and k is the Boltzmann constant.

In this case for the space-charge density we obtain

$$\rho = -2en_0 \sinh(e\varphi/kT). \tag{2}$$

Setting ρ into the Poisson equation we obtain the self-consistent non-linear Poisson-Boltzmann equation (Debye and Hückel 1923)

$$\Delta\left(\frac{e\varphi}{kT}\right) = \left(\frac{8\pi n_0 e^2}{\varepsilon kT}\right) \sinh\left(\frac{e\varphi}{kT}\right). \tag{3}$$

If $e\varphi/kT = \psi$, $X = fx$, $Y = fy$ and $Z = fz$, equation (3) has the form

$$\Delta\psi = \sinh \psi. \tag{4}$$

Here $f = (8\pi n_0 e^2/\varepsilon kT)^{1/2}$ is the reciprocal Debye length, which is the characteristic space parameter of the Coulomb gas.

In spherical symmetry, equation (4) has the form

$$\psi'' + (2/R)\psi' = \sinh \psi \qquad R^2 = X^2 + Y^2 + Z^2. \tag{5}$$

The physical situation described by the Poisson-Boltzmann equation in this symmetry is the following: at $R = 0$ it can be regarded as the existence of a motionless positively charged particle. The spatial distribution of the charged particles of the Coulomb system is determined by the solutions of the non-linear equation (5). A similar formulation of the self-consistent problem is first given by Debye and Hückel (1923) in their linear theory of electrolytes. In this theory the PB equation is linearised

$$\psi'' + (2/R)\psi' = \psi \tag{6}$$

and has a solution

$$\psi = (A/R)\,\mathrm{e}^{-R} \tag{7}$$

which is vanishing at infinity. In the linear theory the concentration of the particles is a monotonously decreasing function of R and the singularity at $R=0$ is related to the point charge of the central particle.

The non-linear PB equation (5) also possesses a monotonously decreasing (ψ_{L}) solution (Lampert and Crandall 1979, 1980)—a generalised non-linear Debye-Hückel-type solution.

The non-linear PB equation (5) also possesses two different types of solutions, which are not monotonously vanishing. In figure 1 we present all three types of solutions of equation (5) for the self-consistent potential. The realisation of a certain type of these solutions is determined by the initial conditions (Couche boundary conditions) for ψ and its derivative ψ' at $R=R_0$.

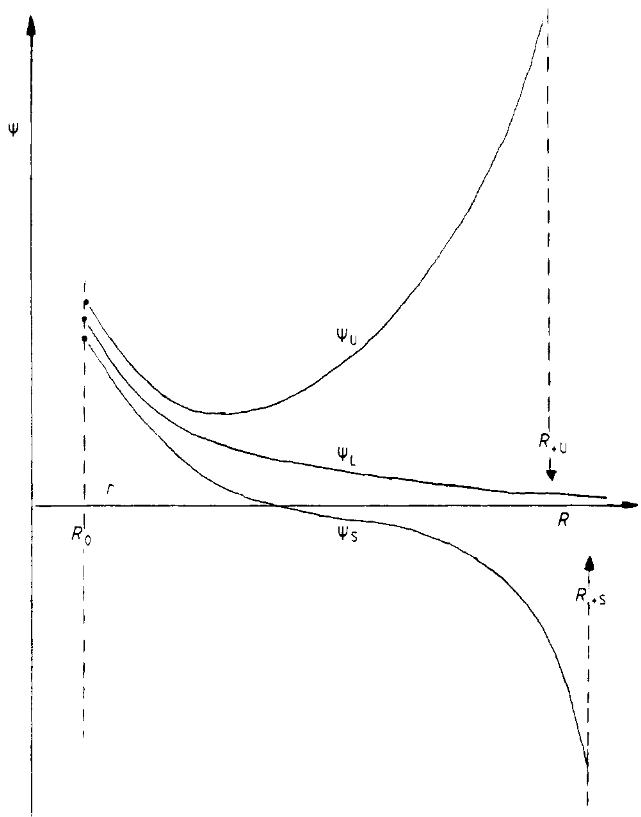

Figure 1. Exemplary spatial variation of the three possible types of solutions of the non-linear PB equation ($\psi_{\mathrm{S}}, \psi_{\mathrm{L}}, \psi_{\mathrm{U}}$).

From here on we suppose that $R>0$ and R_+ denotes the right boundary of the maximum interval in which a given solution ψ still exists. (In principle R_+ could be ∞.)

Lemma 1. If $\psi(\bar{R})>0$ at some $\bar{R}$, then the solution does not have a local maximum at $\bar{R}$. If $\psi(\bar{R})<0$ at the point $\bar{R}$, then $\psi(R)$ does not have a local minimum at $\bar{R}$.

Let ψ have a local maximum at $\bar{R}$ and $\psi'(\bar{R})=0$. From (5) it follows that $\psi''(\bar{R})>0$, which is impossible. By analogy, one can prove the second part of lemma 1.

Corollary 1. From lemma 1 it follows that if $\psi(\bar{R})>0$ and $\psi'(\bar{R})>0$, then $\psi(R)$ is an increasing function in the interval $(\bar{R}, R_+)$.

Corollary 2. By analogy, if at some $\bar{R}$, $\psi(\bar{R})<0$ and $\psi'(\bar{R})<0$, then $\psi(R)$ is a decreasing function in the interval $(\bar{R}, R_+)$.

Lemma 2. If for some $\bar{R}$, $\psi(\bar{R})>0$ and $\psi'(\bar{R})>0$, then $\lim_{R\to R_+}\psi(R)=\infty$.

Let us assume that R_+ is finite and $\lim_{R\to R_+}\psi(R)=C$, $0<C<\infty$. Then if $\lim_{R\to R_+}\psi'(R)<\infty$, R_+ is not the maximal interval of existence of the solution, as follows from the theorem of Picar-Lindelov (Hartman 1964).

If $\lim_{R\to R_+}\psi'(R)=\infty$, then from (5) it follows that $\lim_{R\to R_+}\psi''(R)=-\infty$. This is impossible, because $\lim_{R\to R_+}\psi'(R)=\psi'(\bar{R})+\int_{\bar{R}}^{R_+}\psi''(R)\,\mathrm{d}R<+\infty$. Now let $R_+=\infty$. Then obviously $\lim_{R\to\infty}\mathrm{d}\psi/\mathrm{d}R=0$, hence $\lim_{R\to\infty}\psi''>0$ which is impossible, because in this case we have

$$\lim_{R\to\infty}\psi'(R)=\psi(\bar{R})+\int_{\bar{R}}^{\infty}\psi''\,\mathrm{d}R=\infty.$$

Lemma 3. If for some $\bar{R}$, $\psi(\bar{R})<0$ and $\psi'(\bar{R})<0$, then $\lim_{R\to R_+}\psi(R)=-\infty$. The proof is analogous to the proof of lemma 2.

Lemma 4. If ψ is a solution of equation (5) and at some $\bar{R}$, $\psi(\bar{R})>0$ and $\psi'(\bar{R})>0$, then R_+ is finite.

As follows from lemma 1, ψ is a reversible function in the interval $[\bar{R}, R\infty)$. The reverse function $R(\psi)$ is defined in the interval $[a,\infty)$, where $0<a=\psi(\bar{R})$. For the function we obtain

$$(\mathrm{d}\psi/\mathrm{d}R)=(\mathrm{d}R/\mathrm{d}\psi)^{-1}$$
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}R^2}=\frac{\mathrm{d}}{\mathrm{d}R}\left(\frac{\mathrm{d}\psi}{\mathrm{d}R}\right)=\frac{\mathrm{d}}{\mathrm{d}R}\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^{-1}=\frac{\mathrm{d}\psi}{\mathrm{d}R}\frac{\mathrm{d}}{\mathrm{d}\psi}\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^{-1}=-\frac{\mathrm{d}\psi}{\mathrm{d}R}\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^{-2}\frac{\mathrm{d}^2R}{\mathrm{d}\psi^2} \tag{8}$$
$$=-\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^{-3}\frac{\mathrm{d}^2R}{\mathrm{d}\psi^2}.$$

From (5) we obtain

$$\frac{\mathrm{d}^2R}{\mathrm{d}\psi^2}=-\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^3\sinh\psi+\frac{2}{R(\psi)}\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^2. \tag{9}$$

From lemma 1, it follows that $R(\psi)$ is a strictly increasing and positive function.

Consequently for its asymptotic behaviour there exist three possibilities:

(i) $\lim_{\psi\to\infty} \mathrm{d}R/\mathrm{d}\psi = d \qquad 0<d<\infty$

(ii) $\lim_{\psi\to\infty} \mathrm{d}R/\mathrm{d}\psi = \infty$

(iii) $\lim_{\psi\to\infty} \mathrm{d}R/\mathrm{d}\psi = 0.$

In case (i), from equation (9) it follows that $\lim_{\psi\to\infty} \mathrm{d}^2R/\mathrm{d}\psi^2 = -\infty$. Consequently for some ψ, we obtain $(\mathrm{d}R/\mathrm{d}\psi < 0)$, which is impossible.

In case (ii) we also obtain from (9) that $\lim_{\psi\to\infty} \mathrm{d}^2R/\mathrm{d}\psi^2 = -\infty$ because $\sinh\psi$ is an increasing function and $(R(\psi))^{-1}$ is a limited decreasing function. As was shown above, this is a contradiction. Consequently $\lim_{\psi\to\infty} \mathrm{d}R/\mathrm{d}\psi = 0$.

We shall further prove: $\lim_{\psi\to\infty}(\mathrm{d}R/\mathrm{d}\psi)^3 \sinh\psi = 0$.

Let us assume the contrary:

(A) $\lim_{\psi\to\infty} (\mathrm{d}R/\mathrm{d}\psi)^3 \sinh\psi = \infty$

(B) $\lim_{\psi\to\infty} (\mathrm{d}R/\mathrm{d}\psi)^3 \sinh\psi = \mathscr{C} \qquad 0<\mathscr{C}<\infty.$

In case A we also obtain $\lim_{\psi\to\infty} \mathrm{d}^2R/\mathrm{d}\psi^2 = -\infty$ which, as was shown, is impossible. In case B we obtain from equation (9) $\lim_{\psi\to\infty} \mathrm{d}^2R/\mathrm{d}\psi^2 = -\mathscr{C}$. Let us take $\varepsilon > 0$, such that $\varepsilon - \mathscr{C} < 0$ and $\mathrm{d}^2R/\mathrm{d}\psi^2 < \varepsilon - \mathscr{C}$ for some $\infty > \tilde{\psi} > a$; then

$$\lim_{\psi\to\infty} \frac{\mathrm{d}R}{\mathrm{d}\psi} = \int_a^{\tilde{\psi}} \frac{\mathrm{d}^2R}{\mathrm{d}\psi^2}\,\mathrm{d}\psi + \int_{\tilde{\psi}}^{\infty} \frac{\mathrm{d}^2R}{\mathrm{d}\psi^2}\,\mathrm{d}\psi \tag{10}$$

and

$$\int_{\tilde{\psi}}^{\infty} \frac{\mathrm{d}^2R}{\mathrm{d}\psi^2}\,\mathrm{d}\psi < \int_{\tilde{\psi}}^{\infty} (\varepsilon - \mathscr{C})\,\mathrm{d}\psi = -\infty \tag{11}$$

hence $\lim_{\psi\to\infty} \mathrm{d}R/\mathrm{d}\psi = -\infty$, which is impossible.

From the proven property $\lim_{\psi\to\infty}(\mathrm{d}R/\mathrm{d}\psi)^3 \sinh\psi$, it follows that there always exists a function ψ^*, such that $\psi > \psi^*$ is fulfilled;

$$\left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)^3 \sinh\psi < \varepsilon^3 \qquad 0 < \frac{\mathrm{d}R}{\mathrm{d}\psi} < \frac{\varepsilon}{(\sinh\psi)^{1/3}}. \tag{12}$$

Now let

$$R_+ = \lim_{\psi\to\infty} R(\psi) = \int_a^{\infty} \left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)\mathrm{d}\psi + \bar{R} = \int_a^{\psi^*} \left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)\mathrm{d}\psi + \int_{\psi^*}^{\infty} \left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)\mathrm{d}\psi + \bar{R} \tag{13}$$

but

$$\int_{\psi^*}^{\infty} \left(\frac{\mathrm{d}R}{\mathrm{d}\psi}\right)\mathrm{d}\psi < \int_{\psi^*}^{\infty} \frac{\varepsilon}{(\sinh\psi)^{1/3}}\,\mathrm{d}\psi < \infty. \tag{14}$$

Consequently R_+ has a finite value.

In the above proofs we only used the following two properties of the function $f(\psi) = \sinh\psi$:

(i) $f(\psi)$ is a strictly increasing function,

(ii) $\int_{\psi^*}^{\infty} (f(\psi))^{-1/3}\,\mathrm{d}\psi < \infty$.

Therefore, some results are strictly applicable for any Poisson equation with the right-hand function $f(\psi)$ which has the above-mentioned properties.

These results show that besides the monotonously decreasing solution ψ_L (Lampert and Crandall 1979, 1980) the non-linear spherical PB equation also possesses other solutions. These solutions tend to $+\infty$ (U type) or to $-\infty$ (S type) at finite R_+.

The non-linear PB equation in the plane symmetry case also possesses similar solutions, as was shown by Georgiev *et al* (1980) and Martinov *et al* (1984), in solving this equation analytically.

We carried out a computer integration of the non-linear PB equation (5) using the Runge–Kutta method. The obtained U- and S-type solutions are shown in figure 2. These numerical calculations confirm our analytical results.

The type of the solution depends of course on the boundary conditions, which, as we shall show, depend on the parameters of the Coulomb gas of temperature and concentration. Let us assume that a U-type solution occurs in the system.

For every solution of this type there exists a point $\tilde{R}$ in which the electrostatic field $\psi'(\tilde{R})$ is equal to 0. If we apply the Gauss theorem for a sphere with radius R we shall find that the charge inside this sphere is also zero. Inside the sphere we have the charge of the central positive particle e and the charge of the screening cloud Q

$$Q = \frac{1}{f^3}\int_{R_0}^{\tilde{R}} \rho(R) 4\pi R^2 \, dR = -\int_{R_0}^{\tilde{R}} \frac{8\pi n_0 e}{f^3} \sinh \psi R^2 \, dR. \tag{15}$$

Using (5) we obtain for Q

$$Q = -\frac{8\pi n_0}{f^3} (\psi' R^2)\big|_{R_0}^{\tilde{R}} \tag{16}$$

where R_0 is an initial point, chosen such that the interval $[0, R_0]$ is less than the average distance between the particles of the system.

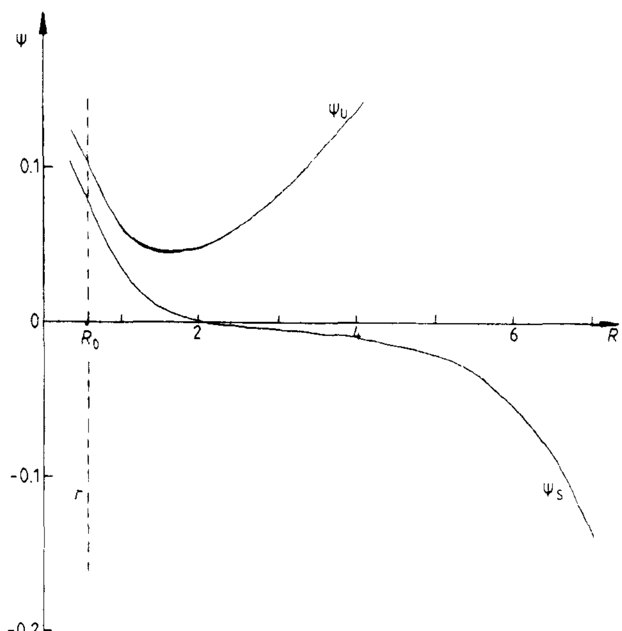

Figure 2. U- and S-type solutions of the non-linear PB equation numerically obtained by the following initial conditions; $R_0 = 0.57$, $\psi_{0S} = \psi_S(R_0) = 0.074$, $\psi_{0U} = \psi_U(R_0) = 0.100$, $\psi_0'(S, U) = \psi'(R_0) = -0.211$.

Consequently the point R_0 is very near the central particle, where there are no screening particles.

From the electroneutrality condition $Q=-e$, the system is a central particle with a polarised Coulomb gas around it and from (16) it follows that

$$\psi'(R=R_0)=\psi_0'=-e^2/\theta f r_0^2\varepsilon \qquad r_0=R_0/f. \tag{17}$$

The corresponding initial value of the electrostatic field $d\varphi/dr$ is

$$(d\varphi/dr)r=r_0=-e/\varepsilon r_0^2 \tag{18}$$

or exactly the Coulomb field of a point particle. This gives us grounds for assuming that the potential at the point r_0 is also a Coulomb potential

$$\psi_0=e^2/\varepsilon r_0\theta. \tag{19}$$

Equation (17) is also valid in the case $\tilde{R}=\infty$. The conclusion, which follows from this fact, is that the solution of the non-linear PB equation tends to 0 at infinity faster than the Coulomb potential. As shown by Lampert and Crandall (1980) the solution decreasing monotonically to 0 at ∞ of the non-linear PB equation tends to 0 even faster than solution (7) of the linear PB equation. This gives us grounds for setting $\psi'R^2=0$ at ∞. The case $\tilde{R}=\infty$ is a limiting case between U- and S-type solutions. Changing the boundary conditions (18) and (19), which can be performed by changing the temperature and the concentration of the Coulomb gas, the position of the point R can be changed, and then only in a particular case $\tilde{R}=\infty$. Further change of the conditions (18) and (19) will convert the type of the solution from U to S.

Similar U- and S-type solutions arise in the atomic model of Thomas-Fermi, which is analogous to the model of Debye-Hückel, but treats a degenerate Coulomb gas. The physical meaning of these solutions was clarified by Flüge (1971). The U- and S-type solutions obtained by us can be interpreted in a similar way. A U-type solution means that the central particle is completely screened by the surrounding particles forming something like an atom with finite radius $\tilde{R}$. If the temperature or the concentration changes in such a way that the solution turns into an S type, it can be said that the positive central particle 'pierces' the screening and gives rise to a localisation of particles of opposite sign at finite distance R_+ (the point at which the potential is tending to $-\infty$).

Here it should be underlined that the interval $[0, R_+]$ is finite as follows from lemma 4 and this is a sequence arising from the non-linearity of the PB equation. The case of S solutions reveals a tendency for condensation in the classical Coulomb system, due to the non-linearity of the equation for the self-consistent potential.

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