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Localisation of charges according to the non-linear self-consistent electrostatic (Poisson–Boltzmann) theory

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Abstract. Using the periodic solutions of the non-linear Poisson-Boltzmann equation it is shown that in a many-particle Coulomb system a periodic localisation of charges may occur. The value of the charge density at which localisation commences is found. This density and the spacing of the localised charges are shown to be characteristic properties of the system under investigation. Their values characterise the self-organisation of the system. The results depend on the non-linearity of the Poisson-Boltzmann equation and are not found if the linearised form is used.

In this paper we will show that the non-linear Poisson-Boltzmann equation (NPBE) leads to some new physical effects. The NPBE describes classical Coulomb systems and is obtained by the combination of two basic physical laws—the Poisson equation and the Boltzmann energy distribution (together with an assumption that the statistical mechanics of the system can be treated via a potential of mean-force type method) (Debye and Hückel 1923). Because the basic elements of this theoretical picture are so simple and universal, the NPBE may be successfully applied in many fields of physics. Examples are the system of point defects in an ionic crystal (Kliewer and Koehler 1965), a system of electrons and holes in a non-degenerate semiconductor (Many *et al* 1965), some of the properties of polyelectrolytes (Lampert and Grandal 1980), some of the properties of a classical gaseous plasma (Balescu 1975) and some effects in biological systems (Melanglin *et al* 1971).

It must be emphasised that the physical effects which are discussed here follow directly from the NPBE and the specific properties of its solutions. Accordingly it is to be expected that some of these physical effects will be realised in some of the above mentioned systems.

The NPBE for a two-component Coulomb system consisting of equally charged particles has the form

$$\nabla^2\psi = \sinh\psi \tag{1}$$

where $\psi = e\beta(\varphi - \varphi_\infty)$ is the reduced average electrostatic potential and φ is the self-consistent electrostatic potential with reference value φ_∞; the Laplacian is taken using the scaled position coordinates $(X, Y, Z) = f(x, y, z)$ where $f = (8\pi n_0 e^2\beta/\varepsilon)^{1/2}$ is the inverse Debye length and (x, y, z) are unscaled position coordinates and $\beta = 1/kT$. Here n_0 is the average particle concentration, k is Boltzmann's constant, T is the absolute temperature and ε is the static dielectric constant of the medium.

If ψ depends only on X then the first integral of equation (1) is

$$(\mathrm{d}\psi/\mathrm{d}X)^2 = 2\cosh\psi + C$$

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where C is the constant of integration. Martinov *et al* (1984) showed that when the system has a plane symmetry (in the Y and Z directions) equation (1) possesses the following three types of solutions.

I For

$$C > 2 \qquad \psi_{\mathrm{I}} = 2\tanh^{-1}[\mathrm{sn}(X/k', k)] \tag{2}$$

where $k^2 = (C-2)/(C+2)$, $T_x = 4K(k)k'/f$ and $k' = (1-k^2)^{1/2}$.

II For

$$2 \geqslant C \geqslant -2 \qquad \psi_{\mathrm{II}} = 2\tanh^{-1}[\mathrm{cn}(X, k)] \tag{3}$$

where here $k^2 = (2-C)/4$, $T_x = 4K(k)/f$.

III For $-2 > C$

$$\psi_{\mathrm{III}} = 2\tanh^{-1}[\mathrm{dn}(X/k', k)] \tag{4}$$

where $k^2 = 4/(2-C)$, $T_x = 2K(k)k/f$ and $k' = (1-k^2)^{1/2}$. In these expressions $\mathrm{sn}(X, k)$, $\mathrm{cn}(X, k)$ and $\mathrm{dn}(X, k)$ are the standard Jacobi elliptic functions and T_x is the period of the periodic solutions displayed here. The functions $K(k)$ are the complete elliptic integrals of the first kind. It can be seen from these equations and the properties of the relevant elliptic equations that in general these solutions are periodic in X. Only at $C = -2$ is the solution non-periodic, reducing then to the form

$$\psi = \ln[\coth^2(X/2)] \tag{5}$$

which is non-periodic.

Solutions of the type given by equation (5) were used by Kliewer and Koehler (1965) and Many *et al* (1965) to describe the space-charge layer which occurs close to a charged surface of a 'thick crystal'. Solutions of the form of equation (4) have been used in an investigation of the spatial distribution of Schottky defects in an ionic crystal (Kliewer 1965). The first application of solutions of the form of equations (2) and (3) was in the work of Georgiev *et al* (1980) and Martinov *et al* (1984). These solutions with their periodicity were used to predict periodic structures in the classical Coulomb lattice gas.

That study met some particular problems associated with the fact that the solutions presented in equations (2)–(4) possess divergent singularities at those points at which the argument of the inverse hyperbolic tangent is equal to ± 1. For these solutions the singular points are

(i) $X = nK(k)k'$, $n = 0, 1, 2, 3, \ldots$,

(ii) $X = (2n+1)K(k)$, $n = 0, 1, 2, 3, \ldots$ and

(iii) $X = 2nK(k)$, $n = 0, 1, 2, 3, \ldots$.

In this context it is important to mention that the non-periodic solution in equation (5) also possesses a singularity at the point $X = 0$. The presence of these singularities makes physical interpretation of the solutions more complicated. If the cross sectional area of the y, z plane involved in the sample is S, then the Boltzmann distribution inherent in the NPBE shows that every period of the solutions contains

$$N(+) = n_0 S \int_0^{T_x} \exp(-\psi(X))\,\mathrm{d}x$$

and

$$N(-) = n_0 S \int_0^{T_x} \exp(\psi(X))\,\mathrm{d}x \tag{6}$$

positive and negative particles. If we look at the solution of equation (3) we see the problem which now occurs in a simple form. Near $X = 0$, the cn function may be approximated by $1 - aX$ for some a. We then have $\psi \approx \ln X$ for X close to zero and so one of the integrals in (6) does not exist. We may also see a similar difficulty with solutions of the linearised NPBE (otherwise known as the Debye-Hückel approximation). The solution of the linearised equation (1) is

$$\psi = \exp(-X) \tag{7}$$

and this solution has a non-integrable solution at $X = -\infty$. The non-integrability of these solutions appears to be inherent in the self-consistent Poisson-Boltzmann theory (and must, of course, be viewed as a defect of that theory).

Usually such divergences are cancelled out by using a 'cutoff' procedure at the surface of a spherical particle or by imposing boundary conditions connected with the existence of a charged surface at $x = 0$ or at $x = 0$ and $x = L$, if we have a system bounded by two surfaces. These procedures remove the singularities from the region where equation (1) holds. Thus we use a part of the periodic solution and require that the function achieves the values ψ_0 and ψ_L at $x = 0$ and $x = L$. This situation is illustrated in figure 1. The values of ψ_0 and ψ_L used here depend on the concrete physical problem. Such a procedure is quite normal in electrostatics; we quite happily change the solution to the Poisson equation when the boundary conditions change and we thereby avoid $1/r$ singularities in many solutions. In our case the problem is rather more delicate because we have a self-consistent equation. The potential created by the charged particles of the system is determined by the potentials on the charged surface or surfaces, but also contributes to those potentials.

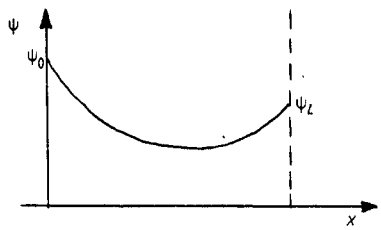

Figure 1. Sketch graph of the potential in a system in which a particle core cutoff is used.

The problem which arises when such a boundary condition procedure is used is that the total numbers of particles $N(+)$ and $N(-)$ per unit area of system change their values from the ones they have at $\psi = 0$, the case of homogeneous particle density. This result can be seen clearly by using equations (6) to give

$$N(+) + N(-) = 2n_0 \int_0^L \cosh \psi \, dx \geq 2n_0 L \tag{8}$$

where L is the size of the system in the x direction. We obtain an equality only when $\psi = 0$. Thus we may conclude that any redistribution of the particles in the system is connected with a change in their total number. This effect is of course also to be seen with the linearised Poisson-Boltzmann equation, which implies an inequality similar to equation (8).

When problems in solid state physics are analysed using the Poisson-Boltzmann theory, the analysis assumes that the surfaces are sinks or sources of charged particles

(Kliewer and Koehler 1965). An example is the formation and spatial distribution of Schottky defects in an ionic crystal. Another is the so called MOS (metal-oxide-semiconductor) structures, where the metal is a source of electrons (Many *et al* 1965).

The problem which we shall discuss here is how the particles are distributed in the system and what the boundary conditions must be if no sinks or sources exist. This is in fact the problem of self-organisation of a classical Coulomb system. As a first step we shall do this for a system with planar symmetry because in that case all the calculations can be performed analytically and estimates of the new effects can be obtained. The ideas presented here can also be applied in systems with lower symmetry using the solutions obtained in this case as a basis. Structures in more than one dimension are found (Martinov and Ouroushev 1986).

In this analysis we restrict our attention to the NPBE. We shall show that the singularities in a solution of this equation can be interpreted as localised charges. These localised charges exhibit an inherent property of the self-consistent system under investigation and so must not be ignored. However, if we want to include these singularities in our analysis, we must first clarify the meaning of an infinite boundary condition. We should remember that such conditions do occur in ordinary electrostatics: the potentials of point charges, lines of charge and infinite charged planes contain infinite divergences. Further, in the original paper of Debye and Hückel (1923), the singularity in the solution obtained for the Poisson–Boltzmann equation is interpreted as a central particle around which a screening cloud of charged particles is distributed.

We assume now that we have a system of width L in the x direction. The average density of positive and negative particles is n_0. The cross sectional area of the system in the yz plane is S. There are no sinks or sources of particles and consequently the numbers of positive and negative particles are $N(+) = n_0LS$ and $N(-) = n_0LS$. We shall apply the NPBE to this system assuming that a redistribution of the particles occurs only in the x direction. We shall assume that the self-consistent potential in the system is given by one of the solutions (2)–(5). For the periodic solutions we shall assume that there are m periods in the system (with $m = 1, 2, 3, \ldots$).

We include the singularities in our analysis and we shall give them a meaning. To clarify the idea we start with the case described by equation (4) and sketched in figure 2. In this case the singularities are at the points $X = 2nK(k)k$, where the potential diverges to $+\infty$. These singularities are in fact integrable. The number of positive

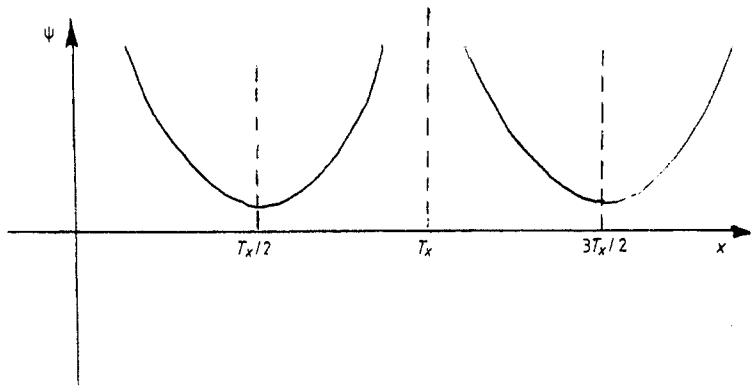

Figure 2. Sketch of the potentials described by equation (4).

particles distributed spatially in one period is, from equations (4) and (6),

$$N(+) = n_0 S \int_0^{T_x} \exp\{-2\tanh^{-1}[\mathrm{dn}(X/k, k)]\}\,\mathrm{d}x. \tag{9}$$

The integral here may be evaluated to give

$$N(+) = 2n_0 S[K(k)(1+k'^2) - 2E(k)]/kf \tag{10}$$

where now $E(k)$ is the complete elliptic integral of the second kind. Since the period of the solution is $T = 2K(k)k/f$, the total number of particles in one period of the solution is

$$N_{\mathrm{hom}} = n_0 S(2K(k)k/f). \tag{11}$$

Comparing equations (10) and (11) we see that

$$N(+) < N_{\mathrm{hom}}.$$

Thus the number of spatially distributed positive particles given by equation (9) is less than the total number of positive particles. We propose that the other positive particles must be seen as localised at the singularity points. There they form a charged surface with zero thickness. The surface charge density can be easily calculated if we assume that the surface charges are uniformly distributed on the singularity surfaces. This surface charge is given by

$$Q_{\mathrm{loc}} = (4n_0 eS/f)[E(k) - K(k)k'^2]/k. \tag{12}$$

Equation (12) shows that in this case the amount of localised surface charge varies increasingly through the range

$$0 \leqslant Q_{\mathrm{loc}} \leqslant 4n_0 eS/f \tag{13}$$

as the period of the solution (4) varies from 0 to ∞.

Similar calculations can be performed using solutions (2) or (3) in place of (4), since those solutions have similar structure. The form of the potential over a part of the x axis is schematically plotted in figure 3. The calculation of the number $N(+; \mathrm{A}, \mathrm{B})$ of spatially distributed positive particles for the solution (2) in the first part of the period between the points A and B reduces after integration to

$$N(+; \mathrm{A}, \mathrm{B}) = 2n_0\{k'^2 K(k) - 2E(k) + 2\}/fk'. \tag{14}$$

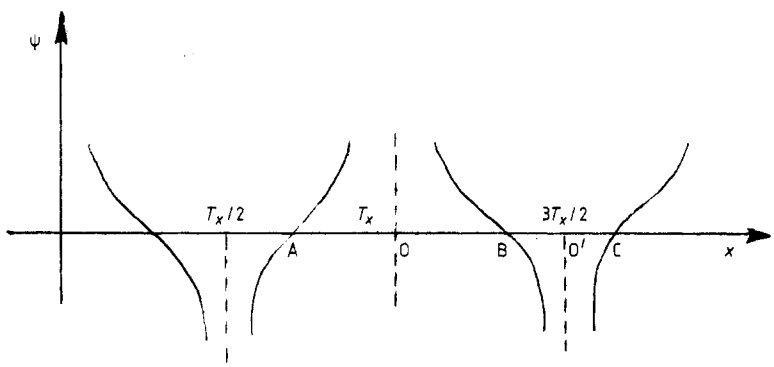

Figure 3. Sketch of the potentials described by equations (2) and (3).

The next problem is to evaluate the corresponding integral in the second part of the period between the points B and C. The singularity here is not integrable. However, the number of spatially distributed positive particles may be evaluated using Gauss's theorem. It must be emphasised here that the procedure we are about to perform is only possible in the non-linear problem for only there does a solution with finite period exist. The linearised problem does not admit such an analysis. We may conclude that investigation of self-organisation in classical Coulomb systems requires that the full non-linear equation be used.

The symmetry of the potential in the interval A to C implies

$$N(+;\,\mathrm{A},\,\mathrm{B}) = N(-;\,\mathrm{B},\,\mathrm{C}) \tag{15}$$

where $N(-;\,\mathrm{B},\,\mathrm{C})$ is the number of spatially distributed negative particles in the interval B to C.

Because we know that the electric field at B and C has the x-component value

$$E = -f(2+C)^{1/2}/\beta e \tag{16}$$

we can calculate the total charge in the region BC easily using Gauss's theorem. From equation (16), the total charge in the interval BC is then

$$Q(\mathrm{B},\,\mathrm{C}) = -fS(2+C)^{1/2}/2\pi\beta e. \tag{17}$$

Using equations (15) and (17) we can then find

$$N(+;\,\mathrm{A},\,\mathrm{C}) = 4n_0S\{k'^2K(k) - 2E(k)\}/f_{K'} + 2Q_{\mathrm{loc}}/e \tag{18}$$

where Q_{loc} is the negative surface charge localised on the plane at the point O. The symmetry of the problem gives us reason to assume that the localised positive charge at the point O′ has the same value and thus

$$Q_{\mathrm{loc}} = 4n_0eSE(k)/fk'. \tag{19}$$

When we use equation (3) for a solution, the total number of particles with one sign in a period is

$$N(+;\,\mathrm{A},\,\mathrm{C}) = 4n_0\{K(k) - 2E(k)\} + 2Q_{\mathrm{loc}}/e. \tag{20}$$

Combining our results again we find that in this case the localised charge at the points O or O′ is

$$Q_{\mathrm{loc}} = 4n_0eSE(k)/f. \tag{21}$$

The value of the function $E(k)$ varies between $\pi/2$ and 1.

Since the localised positive charge is less than the total positive charge, substituting (21) in (20) gives

$$Q_{\mathrm{loc}} = 4n_0eSE(k)/f \leqslant 4n_0eSK(k)/f = eN(+;\,\mathrm{A},\,\mathrm{C}). \tag{22}$$

This inequality holds for all $k > 0$. At $k = 0$ we have an equality which means that all particles in the system are localised. This is an extremely interesting limiting case because it suggests that at $k = 0$ (or $C = +2$) a form of condensation occurs in the system.

For the solution (2) a similar comparison can be made resulting in an inequality like that of equation (22), namely

$$Q_{\mathrm{loc}} = 4n_0SeE(k)/k'f \geqslant 4n_0Sek'K(k)/f = n_0eST_x \tag{23}$$

which uses the fact that the complete elliptic integrals obey the inequality $E(k) \geqslant k'^2 K(k)$ (Janke *et al* 1960). The inequality between Q_{loc} and $n_0 T_x$ is the wrong way round. This implies that from the point of view used in this paper solutions of type (2) do not have physical meaning. The inequality (23) would imply that the number of localised positive particles is larger than the total number of positive particles in the system.

We have used the NPBE to describe some new self-organisation effects in classical Coulomb systems. The effects are not present in the linear form of this equation, which has to include a cutoff due to finite particle size. Such a procedure always means that the description of systems using the linearised Poisson-Boltzmann equation involves including particle sources and sinks in the description. This inclusion means that the total number of particles in the system changes as the boundary conditions change. This change occurs because the theoretical description is self-consistent. Within the NPBE we are able to describe systems with fixed particle number. The system then displays self-organisation effects which are connected with the use of infinite boundary conditions. Our interpretation of these infinite boundary conditions is that they correspond to the appearance of two-dimensional charge densities arranged on planes in the system. The solutions of class (3) which we discussed give periodically distributed localised charge layers with periods between $2\pi/f$ and ∞.

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