The cylindrical Poisson–Boltzmann equation. I. Transformations and general solutions

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In this paper the cylindrical Poisson–Boltzmann equation in reduced coordinates is transformed into an algebraically nonlinear second order ordinary differential equation, which is a particular case of Painlevé's third equation. The only singularities of solutions to this equation are movable poles of second order. Series expansions are developed which express the general solution locally about points of analyticity and about a pole. Back transformation yields local solutions to the cylindrical Poisson–Boltzmann equation. The solutions throughout an interval generally require analytic continuation of these local expressions. In addition to developing exact solutions, asymptotic properties are analyzed for the case of an isolated cylindrical polyelectrolyte. Further, an alternative technique of solution is sketched in which the cylindrical Poisson–Boltzmann equation is transformed into the sine-Gordon equation, which may then be solved by standard methods to give a one parameter family of solutions. A bibliography of references to the third Painlevé equation is presented. The application of these results to the analysis of the theoretical behavior of cylindrical polyelectrolytes in ionic solutions will be presented in a subsequent contribution.

I. INTRODUCTION

The Poisson–Boltzmann equation of electrostatics, given in reduced variables by[1]

$$\nabla^2 y = \sinh y \ , \tag{1}$$

describes the equilibrium distribution of counter- and coions about a charged polyelectrolyte. Three important special cases occur when the polyelectrolyte has specific symmetry properties. These are given by

$$\left(\frac{1}{x}\right)^n \frac{d}{dx}\left(x^n \frac{dy}{dx}\right) = \sinh y \ . \tag{2}$$

If $n=0$, one has the one-dimensional case of a planar polyelectrolyte of uniform charge density. The analytic solution of the one-dimensional equation is well known.[2] The Poisson–Boltzmann equation for a uniformly charged spherical polyelectrolyte is given by Eq. (2) with $n=2$. Historically this case has been of greatest interest to physical chemists, as it treats equilibrium distributions around spherically symmetric ions in solution.[3] Finally, the case where the polyelectrolyte is cylindrical with uniform charge density is described by the Poisson–Boltzmann equation (2) with $n=1$.[4] Interest in this case has been greatly stimulated by the study of the properties of DNA in solution, many of which show important variations with ionic strength.

The general solution of the spherical equation is not presently known. In this paper we give local expressions for the general solution of the cylindrical Poisson-Boltzmann equation. This approach also may be used in cases where the presence of coions is neglected, so that the hyperbolic sine term is replaced by an exponential.

II. EXISTENCE OF SOLUTIONS

The equations of present interest may be most effectively treated using the powerful methods of complex analysis. To this end we must regard the quantities x and y of Eq. (2) as complex variables. Then the physically significant range of the independent variable x is an interval (possibly semi-infinite) on the real axis which excludes the origin. In this interval our solution y will be real, provided the initial conditions are.

Evaluation of the derivatives in Eq. (2) above yield

$$\frac{d^2y}{dx^2} + \frac{n}{x}\frac{dy}{dx} = \sinh y \ . \tag{3}$$

The substitution $w = dy/dx$ displays this second order equation as a system of two first order equations:

$$\frac{dy}{dx} = w = f_1(x, y, w) \ , \tag{4a}$$

$$\frac{dw}{dx} = -\frac{n}{x}w + \sinh y = f_2(x, y, w) \ . \tag{4b}$$

At any point (x_0, y_0, w_0) with $x_0 \neq 0$ the functions f_1 and f_2 in this system are analytic in all three variables x, y, w. It follows from the fundamental existence theorem that there is a unique analytic solution to this system of equations near the point (x_0, y_0, w_0), whose radius of convergence may be explicitly evaluated.[5]

III. ASYMPTOTIC PROPERTIES OF SOLUTIONS

Before developing general solutions we treat the behavior of the generalized potential y at large distances from an isolated polyelectrolyte. As the solution to the one-dimensional case has been previously determined exactly, this asymptotic analysis is only useful for the cylindrical and spherical cases. When the radial distance increases without limit, the potential y approaches zero.

First we consider the spherical equation

$$\ddot{y} + \frac{2\dot{y}}{x} = \sinh y \ , \tag{5}$$

into which we substitute $z = xy$. This gives the expression

$$\ddot{z} = x \sinh\left(\frac{z}{x}\right) = z + \frac{z^3}{3!\,x^2} + \frac{z^5}{5!\,x^4} + \cdots + \frac{z^{2n+1}}{(2n+1)!\,x^{2n}} + \cdots \ .$$

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If $|z|$ remains bounded then the solution to this equation is asymptotic to $\ddot{z}=z$ when $x\to\infty$, as the other terms on the right-hand side approach zero. The general solution of $\ddot{z}=z$ is given by

$$z=A\,e^{x}+B\,e^{-x}\ .$$

For $|z|$ to remain bounded one must have $A=0$. Thus the solution to the spherical Poisson–Boltzmann equation is asymptotic to

$$y\approx(B\,e^{-x}/x)\ .$$

This is the well-known Debye–Hückel solution to the linearized spherical Poisson–Boltzmann equation.[6]

The solution to the cylindrical equation is also asymptotic to a function which decomposes into a term which grows with x and another which decays. Starting with

$$\ddot{y}+(\dot{y}/x)=\sinh y\ , \tag{6}$$

and assuming $y\to 0$ as $x\to\infty$, we may keep only the lowest order term in y. That is, our solution is asymptotic to the solution of

$$\ddot{y}+(\dot{y}/x)=y\ .$$

Multiplying by x^2, this equation becomes

$$x^2\ddot{y}+x\dot{y}-x^2y=0\ ,$$

which is the modified Bessel's equation of order zero.[7] This differential equation has general solution

$$y=c_1I_0(x)+c_2K_0(x)\ .$$

The terms in this expression have asymptotic series expansions for large x which are given by[8]

$$I_0(x)\approx\frac{e^{x}}{(2\pi x)^{1/2}}\left[1+\frac{1^2}{1!\,(8x)}+\frac{1^2\cdot 3^2}{2!\,(8x)^2}+\cdots\right]\ ,$$

$$K_0(x)\approx\left(\frac{\pi}{2x}\right)^{1/2}e^{-x}\left[1-\frac{1^2}{1!\,(8x)}+\frac{1^2\cdot 3^2}{2!\,(8x)^2}-\cdots\right]\ .$$

As $I_0(x)$ grows with x, we must have $c_1=0$, so the solution to the Poisson–Boltzmann equation for an isolated cylindrical polyelectrolyte asymptotically satisfies $y\approx c_2K_0(x)$. Or, keeping only the term which dominates at large x, we have

$$y\approx C\,e^{-x}/x^{1/2}\ .$$

IV. TRANSFORMATIONS OF THE CYLINDRICAL EQUATION

The cylindrical Poisson–Boltzmann equation (6) has two properties which complicate the search for solutions. First, the presence of the term $\sinh y$ renders the equation transcendentally nonlinear. In addition, the point $x=0$ is a singular point. This singularity is not fundamental to the problem at hand, but instead is a consequence of the coordinate system involved. (Note that points with $r=0$ do not have unique coordinate expressions in either cylindrical or spherical coordinates, which are the cases where a singular point occurs in the corresponding Poisson–Boltzmann equation. The one-dimensional equation, being expressed in well-behaved coordinates, does not have singular points.)

We perform coordinate transformations which eliminate these difficulties. First, we substitute $w=\exp(y)$. This transforms the transcendentally nonlinear differential equation into an algebraically nonlinear one in which the dependent variable w is related to the counterion concentration. The resulting expression is

$$\frac{d^2w}{dx^2}=\frac{1}{w}\left(\frac{dw}{dx}\right)^2-\frac{1}{x}\frac{dw}{dx}+\frac{w^2-1}{2}\ .$$

Next we remove the singular point to infinity by performing the logarithmic transformation $t=2\ln x-3\ln 2$. The physically relevant domain of definition of our problem, which is an interval within the positive x axis, is transformed to an interval on the t axis. Within this domain the physical solutions $w=\exp(y)$ have no zeros. The differential equation which results from applying this sequence of transformations to the cylindrical Poisson–Boltzmann equation is

$$\frac{d^2w}{dt^2}=\frac{1}{w}\left(\frac{dw}{dt}\right)^2+e^{t}(w^2-1)\ . \tag{7}$$

An alternative useful form of this equation is achieved by the substitution $z=\exp(t)$:

$$\frac{d^2w}{dz^2}=\frac{1}{w}\left(\frac{dw}{dz}\right)^2-\frac{1}{z}\left(\frac{dw}{dz}-w^2+1\right)\ . \tag{8}$$

This differential equation first appears in mathematics in the work of Painlevé,[9] who was attempting to classify those second order algebraically nonlinear ordinary differential equations having critical points (i.e., branch points and essential singularities) which occur at fixed points for all values of the initial conditions. This line of research ultimately lead to an exhaustive list of 50 equations, in which expression (8) appears as a special case of number (XIII):

$$\frac{d^2w}{dz^2}=\frac{1}{w}\left(\frac{dw}{dz}\right)^2-\frac{1}{z}\frac{dw}{dz}+\frac{1}{z}(\alpha w^2+\beta)+\gamma w^3+\frac{\delta}{w}\ . \tag{XIII}$$

(A summary in English of this research with an enumeration of the resulting list is given in the book by Ince.[5]) It has been shown that exactly six of these equations have solutions involving transcendental functions which are new to mathematics. These are called the six Painlevé transcendents (although the last three were actually found by Gambier[10]). Equation (XIII) above is the third of these; hence, it is also known as the third Painlevé equation. This equation is the subject of much current interest in mathematics. Before treating exact solutions we summarize the relevant information, both about our particular case [Eqs. (7) and (8) above] and about the general expression (XIII). A fairly complete bibliography relating to the third Painlevé equation is presented in the references below.[9–25]

Painlevé[9] showed that the solutions to (XIII) have no branch points or essential singularities, but instead are meromorphic and uniform throughout the finite z plane. Therefore all solutions may be expressed as the ratio of two entire functions, $w=u_1/u_2$, which in turn satisfy the system of equations

$$\left(\frac{u_2'}{u_2}\right)'=-\frac{1}{z}\frac{u_2'}{u_2}-\frac{\alpha u_1}{zu_2}-\gamma\frac{u_1^2}{u_2^2}\,, \tag{9a}$$

$$\left(\frac{u_1'}{u_1}\right)'=-\frac{1}{z}\left(\frac{u_1'}{u_1}\right)+\frac{\beta u_2}{zu_1}+\delta\frac{u_2^2}{u_1^2}\,. \tag{9b}$$

Because the solutions w are uniform, all analytic continuations of w to a given point will agree. The only possible singularities of w in the finite plane are poles, of which there may be a finite or an infinite number.

We now specialize to the particular case of present interest, Eq. (8) above, which has $\gamma = \delta = 0$, $\alpha = 1$, and $\beta = -1$. Direct calculation establishes that the reciprocal $(1/w)$ of a solution (w) to this equation is itself a solution. [This conclusion is equivalent to the observation that if y is a solution to the cylindrical Poisson–Boltzmann equation (6), then $-y$ is also a solution.] Airault[18] has determined conditions under which certain Painlevé equations have rational solutions. Using his methods one can show that the solutions in the case of present interest are never rational functions. Indeed, when expressed as a ratio of entire functions $w = u_1/u_2$, neither u_1 nor u_2 will have finite degree. That is, the power series which represent them never truncate. Finally, the poles (if any) of solutions to Eq. (8) are all of second order. This result is established by inserting a Laurent series expansion whose lowest degree term is z^{-n}, then solving for n to find that $n = 2$.

V. EXACT SOLUTIONS

In this section we develop series representations for the general solution to our transformed version [Eq. (7)] of the cylindrical Poisson–Boltzmann equation. As these solutions are meromorphic in the whole plane, we develop separate expressions for their expansions about a pole and at a point of analyticity. Only the latter expansions are relevant to the chemical problem, however, as there will be no singularities of the solutions within the physically relevant domain.

First, suppose t_0 to be a point of analyticity of the solution to Eq. (7). We may transform t_0 to the origin by a substitution of the form $v = t - t_0$, yielding the differential equation

$$w \frac{d^2 w}{dv^2} = \left(\frac{dw}{dv}\right)^2 + k\, e^{v}\, w(w^2 - 1) ,$$

where $k = e^{t_0}$. As w is analytic near $v = 0$, it is given by a power series expansion of the form

$$w = \sum_{n=0}^{\infty} a_n v^n .$$

If one substitutes this expression into the differential equation one finds the recursion relation for the coefficients a_n to be $a_2 = [a_1^2 + k a_0(a_0^2 - 1)]/2a_0$,

$$a_{n+2} = \frac{1}{(n+2)(n+1)a_0} \left\{ \sum_{i=0}^{n} \left[(i+1)(n-i+1) a_{i+1} a_{n-i+1} - \frac{k a_{n-i}}{i!} + k \left(\sum_{j=0}^{i} a_j a_{i-j} \right) \left(\sum_{j=0}^{n-i} \frac{a_{n-i-j}}{j!} \right) \right] - \sum_{i=0}^{n-1} (i+2)(i+1) a_{i+2} a_{n-i} \right\} \quad n > 0 .$$

As this expression contains two arbitrary constants a_0 and a_1, it represents the general solution in the neighborhood of a point of analyticity. The resulting power series will have radius of convergence equal to the distance from the point of expansion t_0 to the nearest pole. Although the chemically relevant solutions will all be analytic everywhere throughout their domain D of definition (which is an interval on the real axis), the circle of convergence about a point $t_0 \in D$ may not be large enough to contain the whole of D. If this situation occurs, the solution throughout the domain may be constructed by analytic continuation, starting with a series solution near any point.

The series solution derived above may be transformed back to the original dependent variable y if desired. Given the power series for the function w, the associated series for $y = \ln w$ is[26]

$$y = \sum_{n=0}^{\infty} c_n v^n ,$$

where

$$c_0 = \ln a_0 ,$$

$$c_1 = a_1/a_0 ,$$

$$c_i = \frac{a_i}{a_0} - \sum_{j=1}^{i-1} \frac{j a_{n-j} c_j}{i a_0} .$$

It is instructive to compute the Laurent series expansion for solutions near poles. Let a pole occur at a point $t = t_0$, and assume a solution of the form

$$w = \sum_{n=-i}^{\infty} c_n (t - t_0)^n .$$

Substituting this expression into the differential equation (7) and equating powers of the lowest order term yields $-2i - 2 = -3i$, or $i = 2$. The resulting equation in terms of series is

$$\sum_{m=-6}^{\infty} \left(\sum_{j=-4}^{m+2} (j+2)(j+1) c_{j+2} c_{m-j} \right) (t - t_0)^m = \sum_{m=-6}^{\infty} \left(\sum_{j=-3}^{m+3} (j+1)(m-j+1) c_{j+1} c_{m-j+1} \right) (t - t_0)^m + e^{t_0} \left[\sum_{m=-2}^{\infty} \left(\sum_{j=-2}^{m} \frac{c_j}{(m-j)!} \right) (t - t_0)^m \right] \left[-1 + \sum_{m=-4}^{\infty} \left(\sum_{j=-2}^{m+2} c_j c_{m-j} \right) (t - t_0)^m \right] .$$

One evaluates the coefficients c_n by equating terms having like powers of $(t - t_0)$. This procedure yields

$$c_{-2} = 2/\exp(t_0) , \quad c_{-1} = -c_{-2} , \quad c_0 \text{ is arbitrary} , \quad c_1 = -c_0 + \frac{c_{-2}}{3} ,$$

while the recursion relationship for c_{m+4} $(m \geq -2)$ is

$$c_{m+4}=\frac{\exp(t_0)}{2(m+7)(m+2)}\left\{\sum_{j=-2}^{m+2}(j+1)(m-j+1)c_{j+1}\,c_{m-j+1}-\sum_{j=-3}^{m+1}(j+2)(j+1)c_{j+2}\,c_{m-j}\right.$$
$$\left.+\exp(t_0)\left[\sum_{j=-2}^{m+3}\frac{c_{-2}^2\,c_j}{(m+4-j)!}+\sum_{j=-1}^{m+3}c_{-2}\,c_j\,c_{m+2-j}+\sum_{j=-3}^{m+1}\left[\sum_{i=-2}^{j+2}c_i\,c_{j-i}\right]\left[\sum_{i=-2}^{m-j}\frac{c_i}{(m-j-i)!}\right]-\sum_{j=-2}^{m+2}\frac{c_j}{(m-j)!}\right]\right\}.$$

This expression gives the general solution near a pole. It contains two arbitrary constants, which are c_0 and the location t_0 of the pole itself. This result illustrates an important property of solutions of nonlinear equations, the occurrence of moveable poles. It follows that the radius of convergence about a point of analyticity will generally vary with the initial conditions imposed. Thus the procedure for analytic continuation of a given solution cannot be generally prescribed, but instead will vary with the particular solution being treated.

The solutions presented here may be trivially modified to handle cases where the coion distribution is ignored. The cylindrical Poisson–Boltzmann equation in these situations contains the term $\exp(-y)$ instead of $\sinh(y)$. We do not pursue this because exact solutions in this case are already known.[27,28]

VI. ALTERNATIVE TECHNIQUES OF SOLUTION

In this paper we have transformed the cylindrical Poisson–Boltzmann equation into a particular case of the third Painlevé equation, and presented local expressions for its general solution. Because these solutions have moveable poles, their extension throughout the physically significant interval of the real axis will generally require analytic continuation.

Alternative methods suggest themselves for analyzing solutions of our associated third Painlevé equation. For example, solutions may be expressed as the ratio of entire functions satisfying Eqs. (9a) and (9b) above. Development of these entire functions in terms of power series would express the solution as a ratio of series, each of which has infinite radius of convergence. Although this method obviates the need for analytic continuation, we do not pursue it further because another technique is more useful.

The substitutions $w=\exp(y)$ and $z=x^2/4$ transform the cylindrical Poisson–Boltzmann equation (6) into the expression

$$\frac{d^2w}{dz^2}=\frac{1}{w}\left(\frac{dw}{dz}\right)^2-\frac{1}{z}\frac{dw}{dz}+\frac{w^2-1}{2z}\,. \tag{10}$$

This particular version of Painlevé's third equation is known[25] to be transformable into the sine-Gordon equation using $z=xt$, $w(z)=\exp[iu(x,t)]$. The resulting equation, which now involves partial derivatives, is

$$u_{xt}=\sin u\,.$$

The self-similar solutions of this equation may be found by standard bilinear techniques,[29] from which solutions of Eq. (10) above may be found.[25] Briefly, the substitution

$$u=-2i\ln[(f+ig)/(f-ig)]$$

transform the sine-Gordon equation into the bilinear form

$$D_xD_t\,g\cdot f=gf\,,$$
$$D_xD_t(f\cdot f-g\cdot g)=0\,.$$

Let $h_1(z)=f(x,t)$ and $h_2(z)=g(x,t)$. Direct calculation shows that

$$w(z)=[h_1(z)+ih_2(z)]^2/[h_1(z)-ih_2(z)]^2$$

satisfies the above Painlevé equation. This fact was used by Oishi to develop one-parameter solutions for Eq. (10) above. His results may be back-transformed to yield the following solution to the original cylindrical Poisson–Boltzmann equation:

$$y=2\{\ln[h_1(x^2/4)+ih_2(x^2/4)]-\ln[h_1(x^2/4)-ih_2(x^2/4)]\}\,.$$

Unfortunately, this approach gives only a one-parameter family of solutions, not the general solution.

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