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On the equation $\nabla^2\Psi = \kappa^2 \sinh\psi$; Poisson - Boltzmann's equation as called by Chemists.

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In this symposium of non-linear waves, it might be interesting to report on specific applications of some boundary value problems. Particularly, we feel that with the large advances made in non-linear analysis in the past few years, applications to specific physical b.v.p. are needed to ensure a sustained growth of this fascinating field.

The equation (Poisson-Boltzmann)

$$\nabla^2\Psi = \kappa^2 \sinh\Psi \qquad (1)$$

provides such an example if one allows two surfaces S_1, S_2 with $\Psi = 0$ at ∞ , $\Psi = \psi_i$ on S_i $i = 1, 2$.
The origin of this "model" is very simple indeed : the Poisson equation for electrostatics

$$\nabla^2\phi \propto \rho \qquad (2)$$

together with the fact that two bodies of surface potentials ϕ_1 , ϕ_2 are immersed in an 1 - 1 electrolitic solution. Thus the charge density ρ is assumed to have a superposition of positive and negative chargs with a Boltzmann weight or $\rho \propto (\exp(-\beta q\phi) - \exp(\beta q\phi))$ with β being inverse temperature

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and q the electronic charge. Thus equation (2) takes the form (1) for the dimensionless potential ψ, with κ being Debye's inverse length κ. It is worth while to note that in actual systems, κ is very large ($O(\kappa) \sim 10^9$) thus even very small potentials can produce finite Laplacian, which excludes perturbation of Laplace equation in a straightforward manner.

The simplest realization of this model (called also Gouy - Chapman) is the one-dim (parallel plates) linearized version (D.L.V.O. theory). The trivial o.d.e is

$$\psi'' = \kappa^2\psi , \quad \psi(0) = \psi_1, \quad \psi(L) = \psi_2 \tag{3}$$

with the immediate solution

$$\psi = \frac{1}{\sinh(\kappa L)} (\psi_1 \sinh[\kappa(L - x)] + \psi_2 \sinh[\kappa x]) \tag{4}$$

Since the charge densities on the surfaces are proportional to the discontinuities of $d\psi/dx$ we can see that for different separations L, ψ can be monotone or double-layer type (i.e. $d\psi/dx = 0$ at $x = \ell$, $0 < \ell < L$) . In particular, if $\psi_1/\psi_2 > 0$, the system if repulsive or attractive according to its separation. This is a highly non-trivial comment since it deviates from classical electrostatics, and it eluded chemists for nearly a century. This phenomenon persists in the non-linear version as well as in higher dimensional systems. It also produces serious difficulties in numerical evaluations of systems of interest. Thus its aspect must be properly understood in order to usefully utilize the model. The chemists measure "stability parameters" which are integrals of $\exp[E\{\psi(\vec{r})\}]d\vec{r}$. This means that an inaccurate ψ could lead to several orders of magnitude errors, as noted by Sasaki[1] and others.

It is quite illustrative to analyze the system of two unequal sphers [2], utilizing the fact that cylindrical symmetry along the axis of the two sphers reduces the dimensions. More precisely, equation (1) takes the form

$$\left(\frac{\partial^2}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r}\right)\psi = \kappa^2 \sinh\psi \tag{5}$$

with $\psi = \psi_1$ on $z^2 + r^2 = a_1^2$ and $\psi = \psi_2$ on $(z-a_1-a_2-H)^2+r^2=a_2^2$, where suface to surface distance is H and the radii are a_1, a_2 of spheres 1 and 2 respectively. The scale transformation $z = a_1 + \kappa^{-2}Z$, $H = \kappa^{-1}h$, $r = \kappa^{-2}R$ with κ large allows to analyze to leading order in κ^2

$$\frac{\partial^2}{\partial Z^2}\psi \cong \sinh\psi \tag{6}$$

with $\psi(S_1) = \psi_1$, $\psi(S_2) = \psi_2$ and surface-surface separation is given by

$$\Delta Z \cong h + \frac{R^2}{2}\left(\frac{1}{a_1} + \frac{1}{a_2}\right) \tag{7}$$

and S_1, S_L take approximately the shapes of parabolas. Since the first integral is immediate, one obtains

$$\left(\frac{\partial\psi}{\partial Z}\right)^2 \simeq 2\cosh\psi + \Phi(R) \tag{8}$$

and the same question rises can $\partial\psi/\partial Z$ vanish at an interior point $\ell(R)$, $-\frac{R^2}{2a_1} < \ell\,(R) < h + \frac{R^2}{2a_2}$. If vanishing takes place, $\Phi(R) = -2\cosh\{\psi[\ell(R)]\}$ and the second integration is done in two stags to obtain a transcendental equation for $\Phi(R)$. Otherwise, one integrate the R.H.S. from surface to surface and the LHS from ψ_1 to ψ_2 to obtain equation for $\Phi(R)$. This method yields sufficiently good approximation and connect asymptotics, so that improvements can take place on the whole equation (1) by the use of bispherical coordinates[3].

In order to emphasize the importance of symmetry, we address the problem of two parallel cylinders, where the system is two-dimensional in cartezian coordinates.
In this case, scaling is not clear to be as useful.
Thus, we need to assure correct asymptotic behavior, so we take the cylindrically symmetric part, and use the asymptotic expansion of the third Painleve function to obtain our starting solution. By the use of a bipolar coordinate system and the knowledge of their Green's func one iteration (that preserves the correct asymptotics) insures satisfaction of the boundry conditions, and the rest is straightforwards.

Explicitly the two cylinders problem is formulated as follows.

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi = \kappa^2 \sinh\psi \qquad (9)$$

$$\psi = \psi_1 \quad \text{on} \quad x^2 + y^2 = a_1{}^2$$

$$\psi = \psi_2 \quad \text{on} \quad (x-A)^2 + y^2 = a_2{}^2$$

$$\psi \to 0 \quad \text{as} \quad x^2 + y^2 \to \infty$$

$$A = a_1 + a_2 + H$$

with radii a_1 , a_2 and surface to surface distance H .
Asymptotically, ψ is really radially symmetric, therefore

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} \psi \simeq \sinh\psi \qquad (10)$$

with $\rho \equiv \kappa \, (x^2 + y^2)^{1/2}$.

This is the Painleve equation of the third kind that appears in the theory of the Ising model[4]. Let $\psi = \log\eta$, $\eta \simeq 1 + f$; $|f| \ll 1$. Equation (10) takes the form (Modified Bessel's)

$$f'' + \rho^{-1} f' - f \simeq 0 \qquad (11)$$

In other words

$$\eta(x,y) \simeq 1 + C\, K_0(\kappa(x^2+y^2)^{1/2}) \qquad (12)$$

and the constant C is angular dependent. It is convenient to select it as $2/\pi$.

Define

$$\psi_0 = \log(1 + \tfrac{2}{\pi} K_0(\kappa(x^2+y^2)^{1/2})) \qquad (12.a)$$

$$\sinh\psi_0 \simeq \tfrac{2}{\pi} K_0(\kappa(x^2+y^2)^{1/2}) \qquad (12.b)$$

and the iteration

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \psi_{n+1} = \kappa^2 \sinh\psi_n \qquad (13)$$

Define the coordinates μ, ν by

$$x = \frac{a \sinh\mu}{\cosh\mu - \cos\nu}, \quad y = \frac{a \sin\nu}{\cosh\mu - \cos\nu}, \quad \alpha = \frac{a}{\cosh\mu - \cos\nu} \qquad (14)$$

The curve $\mu = \mu_1$ is a circle of radius $a|\mathrm{csch}\mu_1|$ with center at $x = a\coth\mu_1$, $y = 0$, the curve $\eta = \frac{1}{2}\pi$ is a circle of radius a with center at $x = y = 0$, and the curve $\mu = \mu_2$ is a circle of radius $a|\mathrm{csch}\mu_2|$ with center at $x = a\coth\mu_2$, $y = a$.

Equation (13) thus takes the form

$$\alpha^{-3}\left[\frac{\partial}{\partial\mu}\left(\alpha\frac{\partial}{\partial\mu}\right) + \frac{1}{\sin\nu}\frac{\partial}{\partial\nu}\left(\alpha\sin\nu\frac{\partial}{\partial\nu}\right)\right]\psi_{n+1} = \kappa^2\sinh\psi_n \qquad (15)$$

with Green's function G given explicitly in ref.(3) . The rest is straightforward but tedious.

We end this note with the hope that the elegant and powerful soliton theory will yield a better approach to these kind of problems in the near future.

References

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