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An approximate analytic solution of the three-dimensional Poisson–Boltzmann equation

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Abstract
We derive a rational function that is an approximate solution to the three-dimensional Poisson–Boltzmann equation, but show that no rational function can be its exact solution. The approximate solution may be entirely adequate for most purposes because the three-dimensional Poisson–Boltzmann equation represents an unachievable state of equilibrium.

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1. The Poisson–Boltzmann equation

Suppose that ρ is the mass density of a single-component (molecular mass $= m$) isothermal (temperature $= \Theta$) self-gravitating gas. The Poisson equation for the relationship between the gravitational potential Ψ and ρ is

$$\nabla^2\Psi = 4\pi G\rho, \tag{1}$$

where G is the gravitational constant. Let $\Psi = \Psi(r)$ and $\rho = \rho(r)$ be functions only of the coordinate r. The Boltzmann distribution of the gas is then

$$\rho(r) = \rho(0)\exp\left[-\frac{\Psi(r)}{\sigma^2}\right], \tag{2}$$

where $\sigma^2 = k\Theta/m$ and k is the Boltzmann's constant. Combining equations (1) and (2) gives the Poisson–Boltzmann equation, which in n dimensions is

$$\frac{\mathrm{d}^2\Psi_n}{\mathrm{d}r^2} + \frac{n-1}{r}\frac{\mathrm{d}\Psi_n}{\mathrm{d}r} = \Omega^2\exp\left[-\frac{\Psi_n}{\sigma^2}\right], \tag{3}$$

where $\Omega^2 = 4\pi G\rho(0)$. We label the potential and other variables with an n to designate a generic dimension, or with a 1, 2 or 3 to designate a specific dimension. The terms in the

Poisson–Boltzmann equation involve the dimensions of length (L) and time (T); they are Ψ_n (L^2T^{-2}), r (L), Ω (T^{-1}) and σ (LT^{-1}). On substituting the dimensionless variables

$$\check{\Psi}_n = \Psi_n/\sigma^2, \tag{4}$$

$$\zeta = r\Omega/\sigma, \tag{5}$$

the dimensionless form of the Poisson–Boltzmann equation is

$$\frac{\mathrm{d}^2\check{\Psi}_n}{\mathrm{d}\zeta^2} + \frac{n-1}{\zeta}\frac{\mathrm{d}\check{\Psi}_\mathrm{n}}{\mathrm{d}\zeta} = \check{\Psi}_n'' + \frac{n-1}{\zeta}\check{\Psi}_n' = \exp(-\check{\Psi}_n). \tag{6}$$

By defining

$$\check{g}_n = \check{\Psi}_n' \tag{7}$$

and

$$\check{\rho}_n = \exp(-\check{\Psi}_n), \tag{8}$$

the second-order differential equation may be replaced by two first-order differential equations,

$$\check{g}_n' + \frac{n-1}{\zeta}\check{g}_n = \check{\rho}_n \tag{9}$$

and

$$\check{\rho}_n' = -\check{g}_n\check{\rho}_n. \tag{10}$$

The variables are $\check{g}_n$, the relative specific force (acceleration) of the gravity field, and $\check{\rho}_n$, the relative mass density. Their initial conditions are

$$\check{g}_n(0) = 0, \tag{11}$$

$$\lim_{\zeta\to 0}\left[\check{g}_n' + \frac{(n-1)\check{g}_n}{\zeta}\right] = n\check{g}_n'(0) = 1, \tag{12}$$

$$\check{\rho}_n(0) = 1. \tag{13}$$

The analytic solution [1] for $n = 1$ is

$$\check{\rho}_1 = \mathrm{sech}^2(\zeta/\sqrt{2}), \tag{14}$$

$$\check{g}_1 = \sqrt{2}\tanh(\zeta/\sqrt{2}); \tag{15}$$

and the analytic solution [2] for $n = 2$ is the rational function pair

$$\check{\rho}_2 = \frac{64}{(8+\zeta^2)^2}, \tag{16}$$

$$\check{g}_2 = \frac{4\zeta}{8+\zeta^2}. \tag{17}$$

2. An approximate three-dimensional solution

As we shall show in section 3, the solution to the Poisson–Boltzmann equation cannot be a rational function if $n = 3$, but we can find a fairly good rational function approximation. As $\zeta \to \infty$, $\check{\rho}_2 \sim 64/\zeta^4$ (see equation (16)); this disposes us to assume that

$$\check{\rho}_3 \sim c/\zeta^k. \tag{18}$$

Then, by equations (9) and (10),

$$\check{g}_3 \sim k/\zeta, \tag{19}$$

and

$$\check{\rho}_3 \sim k/\zeta^2. \tag{20}$$

The asymptotic relations (18) and (20) are compatible only if $c = k = 2$, that is,

$$\check{\rho}_3 \sim 2/\zeta^2. \tag{21}$$

(For $n = 2$, we must substitute the refined asymptotic relation from equation (17)),

$$\check{g}_2 \sim 4/\zeta - 32/\zeta^3, \tag{22}$$

into equation (9) in order to get $\check{\rho}_2 \sim 64/\zeta^4$.)

The density of a self-gravitating gas is symmetric about its centroid ($\zeta = 0$), so $\check{\rho}_3$ must be an even function of ζ, that is, $\check{\rho}_3(\zeta) = \check{\rho}_3(-\zeta)$. Also, because $\check{\rho}_3(0) = 1$, $\check{\rho}_3 \geqslant 0$ and $\check{\rho}_3(\zeta) \sim 2/\zeta^2$, we choose a $\check{\rho}_3$ approximation that is of the form

$$\check{\rho}_3 \approx \frac{1 + a\zeta^2}{1 + b\zeta^2 + a\zeta^4/2}. \tag{23}$$

Then, taking into account equations (10) and (12), we eliminate b,

$$\check{\rho}_3 \approx \frac{1 + a\zeta^2}{1 + [a + 1/2]\zeta^2 + a\zeta^4/2}. \tag{24}$$

We next expand this expression as a ζ^2 power series which we insert into equation (10), and then the result into equation (9), and arrive at another power series for $\check{\rho}_3$. The two $\check{\rho}_3$ power series have identical ζ^0 (unity) and ζ^2 terms. We finally choose a so that the ζ^4 terms are the same in both series.

The solution is $a = 1/60$, so

$$\check{\rho}_3 \approx \frac{1 + \zeta^2/60}{1 + (11/60)\zeta^2 + (1/120)\zeta^4} = \frac{120 + 2\zeta^2}{(10 + \zeta^2)(12 + \zeta^2)} \tag{25}$$

and

$$\check{g}_3 \approx 2\zeta \left[\frac{1}{10 + \zeta^2} + \frac{1}{12 + \zeta^2} - \frac{1}{60 + \zeta^2}\right] = \frac{2400\zeta + 240\zeta^3 + 2\zeta^5}{(10 + \zeta^2)(12 + \zeta^2)(60 + \zeta^2)}. \tag{26}$$

These rational function approximations (designated by rho and g) of $\check{\rho}_3$ and $\check{g}_3$ are compared graphically with the numerical solutions (designated by rhon and gn) over the range $0 < \zeta \leqslant 100$ in figure 1. The graphs compare the logarithms of the variables. Also shown are the relative differences,

$$\frac{\check{\rho}_3(\text{num}) - \check{\rho}_3(\text{an})}{\check{\rho}_3(\text{num})} = 1 - \frac{\check{\rho}_3(\text{an})}{\check{\rho}_3(\text{num})} \tag{27}$$

and

$$\frac{\check{g}_3(\text{num}) - \check{g}_3(\text{an})}{\check{g}_3(\text{num})} = 1 - \frac{\check{g}_3(\text{an})}{\check{g}_3(\text{num})}. \tag{28}$$

The largest relative difference for $\check{g}_3$ is 7%, and the largest relative difference for $\check{\rho}_3$ is 24%, but that is at $\zeta = 30$ where $\check{\rho}_3 < 0.002$.

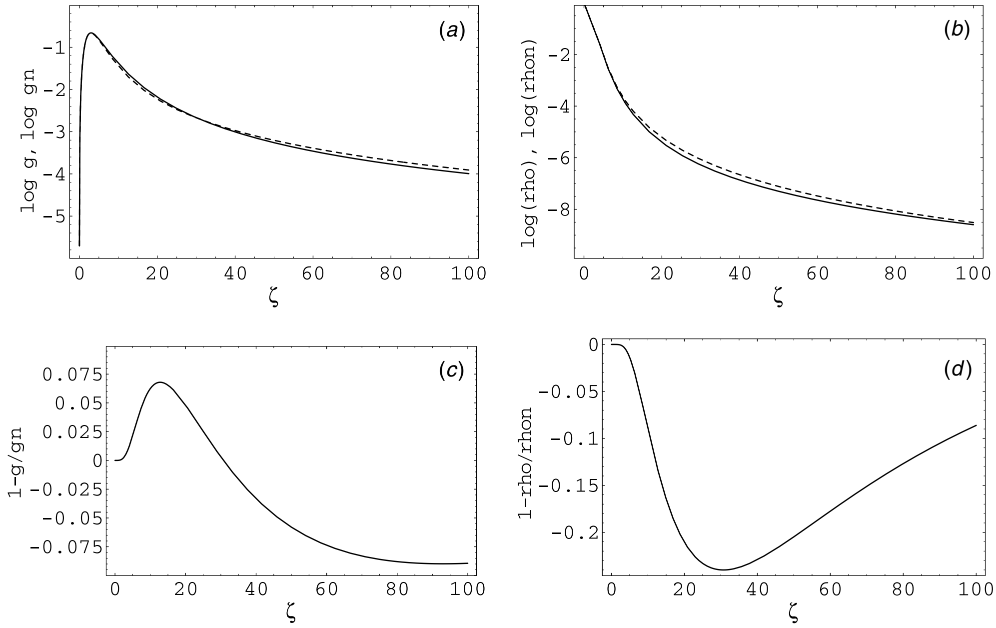

Figure 1. Comparison of the numerical (solid curves) and analytic (dashed curves) solutions of the 3D Poisson–Boltzmann equation and their relative differences.

3. Rational function solution in three dimensions

If we try to improve the approximation by choosing $\check{\rho}_3$ to be of the form

$$\check{\rho}_3 \approx \frac{1 + a\zeta^2 + b\zeta^4}{1 + c\zeta^2 + \mathrm{d}\zeta^4 + b\zeta^6/2}, \tag{29}$$

and solve for the coefficients that equate higher order terms in the $\check{\rho}_3$ power series, we discover that the technique no longer works: some of the coefficients turn out to be complex. Nevertheless, the relatively good fit of the first approximation prompts one to ask whether there can be a rational function that is an exact solution when $n = 3$. The answer is no.

Suppose that $\check{\rho}_3$ is a rational function. Then because $\check{\rho}_3$ is an even function of ζ that is real on the real ζ-axis, and because it peaks at $\check{\rho}_3(0) = 1$, its most general form is

$$\check{\rho}_3 = \prod_{k=1}^{K} [1 + (\zeta/a_k)^2]^{p_k}. \tag{30}$$

If p_k is a positive integer, it is the order of a pair of conjugate zeros at $\pm \mathrm{i}a_k$; and if p_k is a negative integer, it is the order of a pair of conjugate poles at $\pm \mathrm{i}a_k$. Inserting equation (30) into equation (10) gives

$$\check{g}_3 = -\sum_{k=1}^{K} \frac{2p_k\zeta}{\zeta^2 + a_k^2}. \tag{31}$$

Each $\pm \mathrm{i}a_k$ is a first-order pole of $\check{g}_n$. Then, inserting equation (31) into equation (9) gives

$$\check{\rho}_3 = -\sum_{k=1}^{K} \frac{2p_k\left(3a_k^2 + \zeta^2\right)}{\left(\zeta^2 + a_k^2\right)^2}. \tag{32}$$

The relative densities $\check{\rho}_3$ in equations (30) and (32) must be identical. But all zeros and poles in equation (30) are second-order poles in equation (32). Since a point cannot be both a zero and a pole, $\check{\rho}_3$ can have no zeros. Also, all the poles of $\check{\rho}_3$ must be of second order, that is, $p_k = -2$, so

$$\check{\rho}_3 = \prod_{k=1}^{K} \frac{1}{[1+(\zeta/a_k)^2]^2} = 4\sum_{k=1}^{K} \frac{3a_k^2+\zeta^2}{\left(a_k^2+\zeta^2\right)^2}. \tag{33}$$

As $\zeta \to \infty$, the first term on the RHS of this expression falls off as $1/\zeta^{4K}$, $K \geqslant 1$, while the second term falls off as $1/\zeta^2$. These are incompatible, so the exact solution for $\check{\rho}_3$ cannot be a rational function.

4. Physical implications

If $\check{\rho}_n = 0$, the solution to equation (9) is $\check{g}_n \propto \zeta^{1-n}$, so in the far field where $\check{\rho}_n \approx 0$, $\check{\Psi}_1 \propto \zeta$, $\check{\Psi}_2 \propto \log\zeta$ and $\check{\Psi}_3 \propto -1/\zeta$. The depths of the potential wells for $n \leqslant 2$ are infinite, whereas the depth of the potential well for $n = 3$ is finite; and so the escape velocity for $n \leqslant 2$ is infinite, whereas the escape velocity for $n = 3$ is finite. But there is no upper limit to the molecular velocities of an isothermal gas which has a Maxwell distribution. The probability densities of the high velocities in the far wings of the Maxwell distribution are small, but non zero. Thus for $n = 3$, there is a leakage of gas that precludes long-term stability, even if the leakage is negligible; there is no stable self-gravitating hydrostatic spherical model with finite mass. This means, for example, that the Boltzmann distribution will not accurately model the structure of an isothermal star. The solution to the Poisson–Boltzmann equation will give, at best, a maximum envolope for $\check{\rho}_3(r)$. For this purpose, the numerical solution of Chandrasekhar and Wares [3] appears to have no advantage over our approximate solution.

With the substitutions $\theta = -\Psi_n/\sigma^2$, $z = r/\sigma$, $k = n-1$ and $\delta = -\Omega^2$, equation (3) takes the form introduced by Chambré [2] and adopted by Zwillinger [4]:

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}z^2} + \frac{k}{z}\frac{\mathrm{d}\theta}{\mathrm{d}z} = -\delta\exp(\theta). \tag{34}$$

Chambré used this equation to model thermal explosions in closed cylindrical ($k = 1, n = 2$) and spherical ($k = 2, n = 3$) containers. Because the containers are closed, Chambré's numerical solution [3] for $n = 3$ is stable. The far field ($\zeta \gg 1$) is not of concern for these models, so a series solution appears appropriate. For a spherical container, we expand $\check{\Psi}_3$ into the form

$$\check{\Psi}_3 = \sum_{k=1}^{K} b_{2k}\zeta^{2k}, \tag{35}$$

and then evaluate the series for $\check{\rho}_3$ using equation (8) and, independently (see equation (9)), using

$$\check{\rho}_3 = \check{\Psi}_3'' + 2\check{\Psi}_3'/\zeta. \tag{36}$$

We solve for the b_{2k} coefficients by equating the two $\check{\rho}_3$ power series, and find

$$\check{\Psi}_3 = \frac{\zeta^2}{8} - \frac{\zeta^4}{120} + \frac{\zeta^6}{1890} - \frac{61\zeta^8}{1632\,960} + \cdots \tag{37}$$

$$\check{\rho}_3 = 1 - \frac{\zeta^2}{8} + \frac{31\zeta^4}{1920} - \frac{367\zeta^6}{193\,536} + \frac{892\,477\zeta^8}{4180\,377\,600} + \cdots \tag{38}$$

$$\breve{g}_3 = \frac{\zeta}{4} - \frac{\zeta^3}{30} + \frac{\zeta^5}{315} - \frac{61\zeta^7}{204\,120} + \cdots. \tag{39}$$

These series converge slowly (if at all), but they may be adequate for modeling thermal explosions in spherical containers. Nevertheless, the rational function approximation is also accurate within the near field, and it is simpler to evaluate; so the series solution is of nugatory interest except to signal the overall advantage of the rational function approximation.

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