# Solving the Poisson−Boltzmann Equation for Two Parallel Cylinders

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The electrostatic interaction between two parallel charged cylinders of arbitrary diameters $a_1$ and $a_2$ is studied by solving numerically the nonlinear Poisson−Boltzmann equation. A limit of particular interest is that of a charged cylinder interacting with a charged plane ($a_1 \rightarrow \infty$). The interaction free energy is calculated, as a function of the separation distance between the cylinders, for either fixed charge density or mixed (fixed charge, fixed potential) boundary conditions.

## I. Introduction

The electrostatic interaction between colloidal particles and macromolecules often plays a crucial role in the stability of these systems.[1] Albeit, while the cases of two charged interacting planes and spheres have been extensively studied,[1−7] the case of two rods has gained less attention. Thus, our goal in the present study is to present a numerical method for calculating the electrostatic interaction either between two (infinitely long) parallel charged rods or between a rod and a charged planar surface, in a solution containing added salt.

Evaluating the electrostatic force between these model particles, even within the framework of Poisson−Boltzmann (PB) theory, is a formidable task. A growing motivation to further study the electrostatic interaction between two cylinders, and between cylinders and planes, comes from recent experiments probing the complexes formed when (negatively charged) DNA molecules are mixed with positively charged membranes (liposomes).[8,9] To a good approximation, the interaction between two double-stranded DNA molecules can be modeled as that between infinite cylinders, since DNA is a rigid polyelectrolyte, with a typical persistence length of 50 nm, much larger than the (axial) separation between neighboring charges (~0.17 nm). In a similar fashion, lipid bilayers may be modeled as infinite planes or slightly curved surfaces.

Several studies of the interaction between charged rodlike particles have been presented in the past.[10−14] Some of these rely on the use of the linearized version of the PB equation (in the case that the cylinders are immersed in a salt solution).[11,12] This is an appropriate approximation in cases of low surface charge densities. However, when dealing with particles of high surface charge density, and a radius comparable to the Debye length (e.g. DNA molecules), this approximation is no longer valid. In the limit where the interparticle distance is much smaller than their radii, the Derjaguin approximation may be employed.[1] However, no *single* approximation is expected to hold true for the whole range of interparticle separations.

Another, alternative approach to studying the interaction between charged rods is provided by the "counterion condensation" (CC) theory.[14] Using this theory, an attractive force was found between two interacting line charges (though the force was not evaluated continuously for the whole range of interparticle distances). This is in contrast to the expected result from PB theory, where two equally charged rods should always repel (see section III). We note, however, that it has been suggested that CC theory is not a preferable approximation to PB theory.[15]

In the case that no salt is added, an exact analytical solution exists for the force between two rods using PB theory.[10] In a recent study, the force between two charged rods with no added salt was evaluated using Brownian-dynamics simulations.[13] Inter-rod attraction was found in the case corresponding to DNA in a solution of divalent counterions.

In the past few years, several numerical procedures have been devised for calculating the double-layer forces and free energies between *spherical* particles.[3−7] Usually these studies involve using bispherical coordinates to transform the problem into one solvable in a closed domain and with convenient boundary conditions. Prominent among these methods is the procedure first introduced by Carnie et al.,[3] which was later extended to the treatment of two spheres of arbitrary radii. In the limiting case where one radius is infinite, this corresponds to the interaction of a sphere and a plane. This numerical

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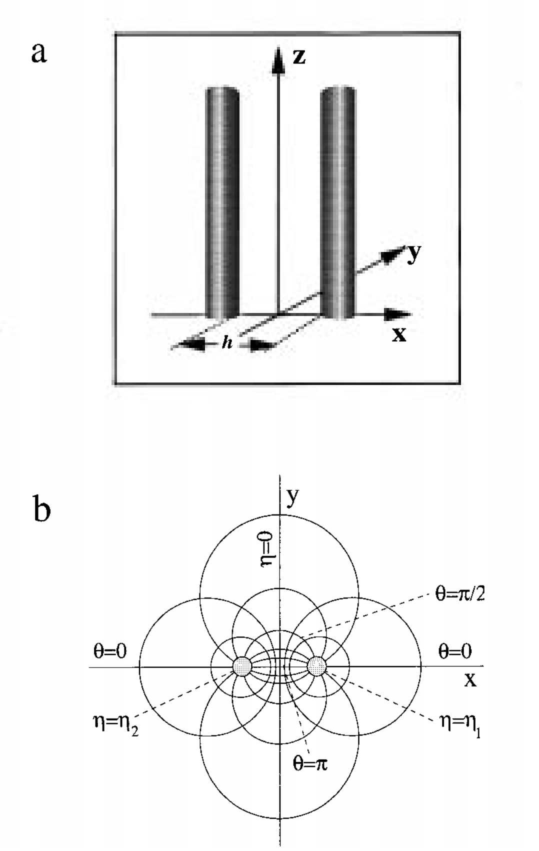

**Figure 1.** (a) System of two interacting charged parallel rods. (b) Traces of constant $\eta$ and $\theta$ curves in the bicylinder coordinate system. The shaded areas correspond to the volume interior to the two interacting cylinders in the model system.

algorithm, which uses a spline collocation scheme to solve the full PB equation, will be extended in the present study to the treatment of cylindrical particles. The method presented here is most general and can be used to treat, for example, the interaction of various types of colloidal particles. However, the numerical examples presented below are mainly relevant to systems containing DNA and lipid bilayers. In particular, it will be shown that the interaction between equally charged rods is always repulsive, whereas when the rods are not equally charged, an attraction may appear. Results for the case of an interacting cylinder with a wall are also presented. We find that the surface charge density modulation on the plane of constant potential may show either an accumulation or depletion of counter charges near the cylinder (depending on the ratio between the surface charge densities on the plane and cylinder).

## II. Method of Solution

The model consists of two infinitely long cylinders of radii $a_1$ and $a_2$, immersed in a solution of 1:1 electrolyte of bulk concentration $n_0$. The two cylinders are separated by a surface to surface distance $h$ (see Figure 1a). In all cases considered, it is assumed that inside the particles the dielectric constant is zero. This is a common approximation when dealing with low dielectric particles, eliminating the need to solve for the potential within them.

All lengths in the system will henceforth be expressed in terms of the Debye length, $\kappa^{-1} = (\epsilon_0\epsilon_r k_B T/2n_0e^2)^{1/2}$, where $\epsilon_r$ is the dielectric constant of the solution, $\epsilon_0$ is the permittivity of vacuum, $e$ is the electronic charge, $k_B$ is Boltzmann's constant, and $T$ is the absolute temperature. The PB equation for the scaled electrostatic potential $\psi = e\phi/k_BT$ everywhere outside the cylinders is

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

In a similar manner, reduced units will be used to scale the surface charge density ($\sigma^* = \sigma l_B/e\kappa$), the force per unit length ($f^* = fl_B/k_BT\kappa$), and the free energy per unit length ($F^* = Fl_B/k_BT$), where $l_B = e^2/\epsilon_0\epsilon_r k_BT$ is the Bjerrum length.

The boundary conditions for this system can be conveniently expressed in terms of bicylinder coordinates ($\eta$, $\theta$, $z$).[16] The traces of the coordinate surface on the $xy$ plane are shown in Figure 1b. The coordinate surfaces are obtained by translating these curves along the $z$ axis. Coordinate surfaces of constant $\eta$ form nested, nonconcentric cylinders whose centers lie on the $x$ axis. The $\eta = 0$ ($x = 0$) surface corresponds to the infinite midplane with an infinite radius. The bicylinder coordinates relate to the rectangular ones by

$$y = \frac{b\sin\theta}{\cosh\eta - \cos\theta}$$

$$x = \frac{b\sinh\eta}{\cosh\eta - \cos\theta}$$

$$z = z \tag{2}$$

Thus in bicylinder coordinates, the region outside the two cylinders corresponds to a rectangular domain with $0 \le \theta \le 2\pi$ and $\eta_2 \le \eta \le \eta_1$, where $\eta_1$ and $\eta_2$ correspond to the surface of the two cylinders; $\eta_1$, $\eta_2$ and $b$ are related to $\kappa a_1$, $\kappa a_2$, and $\kappa h$ through

$$\frac{b}{\sinh\eta_1} = \kappa a_1$$

$$-\frac{b}{\sinh\eta_2} = \kappa a_2$$

$$\frac{b}{\tanh\eta_1} - \frac{b}{\tanh\eta_2} = \kappa a_1 + \kappa a_1 + \kappa h \tag{3}$$

The use of this coordinate system is similar to the use of bispherical coordinates to study the two-sphere interaction problem.[3-7] The difference can be expressed in terms of the scale factors: two in one set have the same form as the corresponding two in the other set, while the third differs.[16]

Noting the $z$-invariance of the potential, the PB equation (eq 1) assumes the form

$$\frac{(\cosh\eta - \cos\theta)^2}{b^2}\left(\frac{\partial^2\psi}{\partial\eta^2} + \frac{\partial^2\psi}{\partial\theta^2}\right) = \sinh\psi \tag{4}$$

Following Carnie et al.,[3] we solve this equation using Newton–Raphson (NR) iteration and collocation with bicubic Hermite basis functions. All calculations of the potential were performed using a 29 × 29 grid. The maximum absolute difference between the final values of the potential in succeeding iterations in the NR scheme was less than $5 \times 10^{-4}$. The boundary condition corresponding to interaction under constant surface potential is $\psi = \psi_0$ on the surface of the cylinder. For interaction under constant charge density, the boundary condition will be $-\nabla\psi\cdot\hat{\mathbf{n}} = \sigma^*$, on the surface of the cylinder (of

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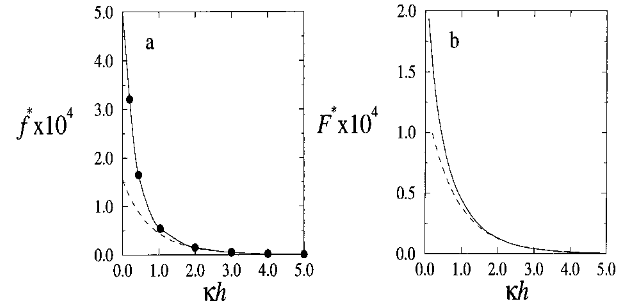

**Figure 2.** (a) Reduced force per unit length for two interacting cylinders as a function of separation distance, for equal radii $\kappa a = 1$ and an equal constant charge density $\sigma^* = 0.001$. The full and dashed lines correspond to the numerical and approximate calculations, respectively. The dots represent the points evaluated numerically. (b) Free energy $F^*$ as a function of separation distance for the same system as in part a.

constant $\eta$), where $\hat{\mathbf{n}}$ is the unit normal directed toward the particle. In cases where the surface charge density is not constant, the local charge density can be evaluated using this relation. Two additional boundary conditions arise from the symmetry of the system and correspond to $\partial\psi/\partial\theta = 0$, on surfaces of $\theta = 0$ and $\theta = \pi$ (see Figure 1).

As was previously shown,[7] the dimensionless force (per unit length) $f^*$ acting on one of the particles can be found by integrating the stress tensor over a closed surface enveloping that particle. In the present case, we can choose to integrate over a closed surface consisting of a cylinder with constant $\eta < \eta_1$, and of unit (Debye) length, capped by two planer circles. We can thus find the force per unit length acting on one of the cylinders. The contribution to the integral from the end caps vanishes, and hence

$$f^* = \frac{2}{b}\int_0^{\pi}\left\{\left[\frac{b^2(\cosh\psi - 1)}{(\cosh\eta - \cos\theta)^2} + \frac{1}{2}\left(\left(\frac{\partial\psi}{\partial\theta}\right)^2 - \left(\frac{\partial\psi}{\partial\eta}\right)^2\right)\right] \times (1 - \cosh\eta\cos\theta) + \frac{\partial\psi}{\partial\theta}\frac{\partial\psi}{\partial\eta}\sinh\eta\sin\theta\right\} d\theta \quad (5)$$

For two cylinders of equal radii, it is convenient to integrate over the plane $\eta = 0$. For cylinder–plane interaction, the integration was carried out over the cylinder of $\eta = \eta_1/2$. The free energy of two interacting cylinders with respect to a state of infinite separation $F^*$ was then evaluated by integrating the force over the separation distance $\kappa h$. We note that the free energy may also be evaluated using a spatial integration, but this was found in previous studies to be less accurate numerically in the corresponding case of interacting spheres.[3]

## III. Results and Discussion

For the sake of comparison with previous approximate solutions of the PB equation, we first consider a system of two *weakly* charged rods of equal radii. In this limit the electrostatic potential is everywhere small ($\psi \ll 1$) and the use of the linearized PB equation is valid for the single cylinder case. As previously shown by Brenner et al.,[11,12] if $h > \kappa^{-1}$, the interaction free energy between two cylinders can be evaluated on the basis of the linearized PB equation and using the superposition approximation. One then finds $F(\kappa R) = CK_0(\kappa R)$, where $R = h + 2a$ is the interaxial distance, $K_0$ is the zero-order modified Bessel function of the second kind, and $C$ is a constant related to the charge densities on the cylinders. In Figure 2 we compare the force and interaction free energy between two weakly charged cylinders ($\kappa a_1 = \kappa a_2 = 1$, $\sigma^* = 0.001$, $n_0 \simeq 0.065$ M), as calculated by the approximate solution above, with the full numerical calculation of eq 5, treating $C$ as an adjustable parameter to be optimized. As expected, deviations are observed at small intercylinder separations, $\kappa h$, in which regime the superposition approximation used by Brenner et al.[11,12] is no longer valid.

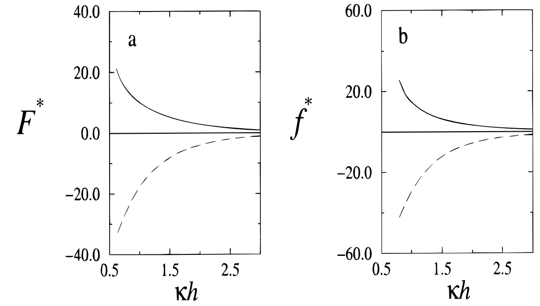

**Figure 3.** (a) Free energy $F^*$ for two interacting cylinders as a function of separation distance, for equal radii of $\kappa a = 1$ and equal (full line) and opposite (dashed line) constant charge densities of $\sigma^* = \pm 8.4$. (b) Reduced force per unit length as a function of separation distance for the same systems as in part a.

We now turn to the numerical solution of the nonlinear PB equation for the interaction between two charged cylinders of equal radii and *high* charge densities. The forces were calculated using eq 5 and the free energy by integrating the force. The interaction between *two cylinders of equal radii and equal constant surface charge densities* was calculated for $\sigma^* = -8.4$, and $\kappa a = 1$ (see Figure 3). For $a \simeq 1.2$ nm, corresponding to the radius of B-DNA, the latter condition implies $n_0 \simeq 0.065$ M. Also shown in Figure 3 are results for the interaction between two *oppositely charged* cylinders with $\sigma^* = \pm 8.4$. We find that in the first case the interaction is always repulsive, whereas in the second it is always attractive. Note however that the repulsion (for a given $h$) is always weaker than the attraction.

These results can be explained as follows. When integrating the stress tensor over the plane of $\eta = 0$ the integrand assumes a simple form. It can be shown, using symmetry considerations alone, that the force between equally charged cylinders of equal radii (for which $\partial\psi/\partial\eta = 0$ at the midplane) will always be repulsive.[2,3,10] Similarly, for two cylinders of equal radii but opposite charge density (for which $\partial\psi/\partial\theta = 0$ and $\psi = 0$ at the midplane) it will always be attractive within the PB formulation. In the specific case studied, the difference between the repulsion and attraction forces reflects the influence of the added salt. For the equally charged cylinders,[10] the volume between the two cylinders will contain a high concentration of ions of the opposite charge, while for the oppositely charged cylinders this volume will be low in ionic concentration for ions of both charges. This "counterion release"—the release of counterions from the confined volume between cylinders due to the mutual charge compensation of the two cylinders—is entropically favorable, contributing to the attraction. In turn, this will also result in a stronger direct interaction between the oppositely charged, unmasked rods. However, in general it might also be found in other cases that confining the ions to the intercylinder volume in the equally charged cylinders' case will result in a strong repulsion at small distances.

We note that for very large charge densities or surface potentials (exceeding $\sigma^* \sim 7.0$ in the systems considered), in particular for small separation distances (say $\kappa h < 0.4$), a well-converged result for the potential was not always

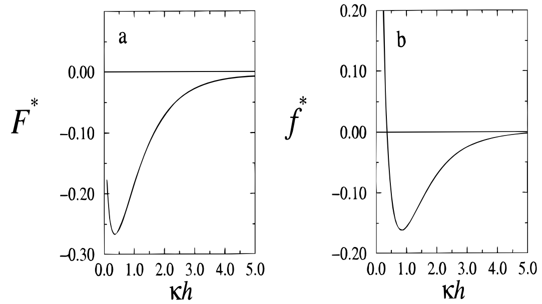

**Figure 4.** (a) Free energy $F^*$ per unit length for two interacting cylinders as a function of separation distance, for equal radii of $\kappa a = 1$ and constant charge densities $\sigma^*_1 = 1$ and $\sigma^*_2 = -2$. (b) Reduced force as a function of separation distance for the same systems as in part a.

achieved. The problem may be overcome, at least in some cases, by increasing the number of grid points (also making the calculations lengthier in time), supplying a better initial approximate guess for the potential, or solving the PB equation for the potential difference between an initial guess and the true potential (instead of solving for the potential itself).

When the two cylinders are *oppositely charged, but not with the same surface charge density*, a minimum in both the force and free energy may appear (as is also the case with charged spheres).[3,4] This can be seen in Figure 4, where the cylinders (each with the same unit radius as before) have surface charge densities of $\sigma^*_1 = 1$ and $\sigma^*_2 = -2$, respectively. Previous calculations pertaining to the interaction between *spheres* show that a similar minimum was found mainly due to an entropic contribution.[4] In the present case, this may be explained as follows. At large enough distances, the approach of the two oppositely charged cylinders enables counterion release, which is entropically favorable. When the distance becomes small enough, the nonequal surface charge densities require that some of the counterions remain in the intercylinder volume, resulting in an entropically unfavorable compression of counterions which ultimately leads to repulsion.

We have also calculated the interaction free energy as a function of the distance between *a charged cylinder and an oppositely charged plane* ($\eta = 0$). In Figure 5a we show the interaction free energy between a cylinder of charge density $\sigma_c^* = -6$ and a planar surface of a constant electric potential $\psi = 2$ (corresponding to $\sigma^* \simeq 2.3$ when $\kappa h \to \infty$). This system provides a reasonable model for the interaction between a DNA rod and a lipid bilayer composed of cationic and neutral lipids, where the charged lipids are freely diffusing ($\psi$ = constant), so as to minimize the internal free energy. Upon approaching the plane, the cylinder induces a charge modulation in the planar surface.[9] Figure 5b shows the charge density profile on the surface, as a function of the distance ($\kappa y$) from the projection on the plane of the rod axis, for a fixed cylinder-plane separation ($\kappa h = 0.4$), for several different values of the rod charge density $\sigma_c^*$. Not surprisingly, for high values of $\sigma_c^*$ opposite charges on the "membrane" accumulate in the vicinity of the rod. On the other hand, for low charge densities on the cylinder there is a reduction of charge density on the plane near the cylinder. A qualitative explanation of this effect can be given as follows. If the cylinder is very weakly charged (say neutral), it acts as a confining wall with respect to the counterions in the gap between the rod and the plane. This leads to an excess of counterion (osmotic) pressure, which can be partly relieved by the escape of some counterions from the gap and, concomitantly, of surface charges from this region. Indeed, the onset of this reduction is observed close to the point where the charge densities on the plane and cylinder are equal.

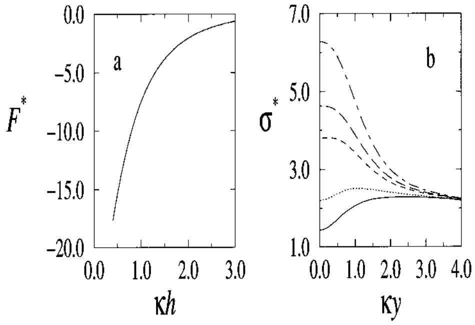

**Figure 5.** (a) Interaction free energy $F^*$ as a function of separation distance for a cylinder of radius $\kappa a = 1$ and constant charge density $\sigma_c^* = -6$ and a plane of constant potential $\psi^* = 2$. (b) Surface charge density on a plane of constant potential ($\psi^* = 2$) as a function of the distance from the projection of the cylinder axis on the plane ($\kappa y$). The constant cylinder−wall distance is $\kappa h = 0.4$. The cylinder radius is $\kappa a_c = 1$. The curves correspond to surface charge densities (top to bottom) of $\sigma_c^* = -6, -4, -3, -1$, and 0 on the cylinder.

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