

Hypernetted Chain Theory for the Distribution of Ions around a Cylindrical Electrode

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The hypernetted chain (HNC) approximation is applied to the distribution of ions around a cylindrical electrode. The equations obtained are analyzed under some extreme situations and agreement with well-known theories is achieved.

I. Introduction

In biochemistry, biophysics, and colloid chemistry a good number of systems can be modeled as a charged cylinder immersed in an ionic solution, e.g., benzopurpurine 4B,¹ axons,^{2,3} and some types of microelectrodes,^{2,3} fibrous proteins,⁴ and polyelectrolyte molecules like DNA.⁴⁻⁶ A simple model for this sort of system consists in assuming the ions as point charges, the solvent as a uniform dielectric medium everywhere in the solution, the solid phase as a hard, infinitely long, charged cylinder of a given radius R , and the material from which the cylinder is made as having the same dielectric constants as that of the solvent. This model has been studied by several authors, in particular by Brenner and McQuarrie⁷ through an analytical solution of the linearized Poisson-Boltzmann (PB) equation and by Stigter⁸ through a numerical solution of the nonlinear PB equation.

As is well-known, the nonlinear PB equation is inconsistent with its statistical mechanical basis,⁹ and the nonlinearity of the equation makes its analytical solution very difficult. However, apparently, it can be proved that under certain conditions the error made by using the nonlinear PB equation to study the electrical double layer of macromolecules is not large.^{10,11} This statement seems to be corroborated in planar double layer studies, where the Gouy-Chapman theory^{12,13} (a nonlinear PB equation) has had, in some cases, remarkable success.¹⁴ In addition, recent developments of numerical methods for solving nonlinear integral equations¹⁵⁻¹⁹ could allow a fast nu-

merical solution of an integral version of the nonlinear PB equation for the cylindrical double layer. This would permit a more detailed study of this model as well as the study of more complex systems, such as two or more interacting cylindrical double layers.

On the other hand, recent progress in the study of a model for the planar double layer, where the ions are taken to be hard spheres with charge in their centers, shows that several consistent statistical mechanical theories such as the hypernetted chain (HNC) approximation,^{18,19} the Born-Green-Yvon equation,¹⁵ and the modified Poisson-Boltzmann equation^{16,17} yield good agreement with Monte Carlo data for this model.^{20,21} Even though these theories are mathematically and computationally much more difficult to handle than the Gouy-Chapman theory, they allow a more general and systematic study of the planar double layer and they are the more promising theories at present. Therefore, it seems to be appropriate to try to apply these theories and the recent developments of numerical methods for solving nonlinear integral equations to the study of the cylindrical double layer.

By assuming that in an ionic solution one of the species consists of charged plates of infinite extension whose concentration tends to zero (direct method (DM)), in the past we have been able to derive planar double layer equations from electrolyte theories.²² These equations were shown²² to be equivalent to those obtained from the same electrolyte theory through other methods.²³⁻²⁵ In this paper we extend the DM to derive the HNC approximation for a cylindrical double layer. That is, we assume that in an electrolyte, described by the HNC theory, one of the species is made of hard, infinitely long, charged cylinders of radius R , whose concentration tends to zero.

To show the consistency of our equations with other theories, we analyze the particular case in which the ions in the solution are taken to be point charges and/or the radius of the cylinder is infinitely large.

In section II we apply the DM to the HNC theory for electrolytes to derive the HNC equations for a cylindrical double layer. In section III we make the radius of the cylinder infinitely large and show that our HNC cylindrical

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double layer equations reduce to the HNC planar double layer equations.²⁴ In section IV we take the limit of zero diameter for the ions in the solution and show that our equation reduces to the nonlinear PB equation.⁸ Finally, in section V some conclusions are presented.

II. HNC Approximation in the Cylindrical Double Layer

For a multicomponent system of P species the HNC equations are²⁶

$$g_{\alpha\gamma}(r_{12}) = \exp\left\{-\beta U_{\alpha\gamma}(r_{12}) + \sum_{m=1}^P \rho_m \int h_{\alpha m}(r_{13}) c_{m\gamma}(r_{23}) dv_3\right\} \quad (1)$$

$\alpha, \gamma = 1, 2, \dots, P$

where $h_{\alpha\gamma}(r_{12}) + 1 \equiv g_{\alpha\gamma}(r_{12})$ is the two-particle radial distribution function for ions 1 and 2 of species α and γ (respectively), $c_{m\gamma}(r_{23})$ is the direct correlation function, ρ_m is the concentration of species m , $U_{\alpha\gamma}(r_{12})$ is the direct interaction potential, and $\beta = 1/kT$, where k is Boltzmann's constant and T is the temperature.

Assuming that in eq 1 the species α corresponds to hard, infinitely long, charged cylinders of radius R such that $\rho_\alpha \approx 0$, and all the other species correspond to hard spheres with electric charge in their centers (ions), eq 1 becomes

$$g_{\alpha\gamma}(x) = \exp\left\{-\beta U_{\alpha\gamma}(x) + \sum_{m=1}^Q \rho_m \int h_{\alpha m}(t) c_{m\gamma}(s) dv_3\right\} \quad (2)$$

$\gamma = 1, 2, \dots, Q \quad \alpha \equiv P = 1 + Q$

where $s \equiv r_{23}$ is the radial distance between ions 2 and 3, x and t are the perpendicular distances of the centers of ions 2 and 3 (respectively) to the symmetry axis of the cylinder, and dv_3 is given in cylindrical coordinates.

For a two-species symmetrical electrolyte eq 2 can be written as

$$g_{\alpha+}(x) = \exp\left\{-\beta U_{\alpha+}^{\text{el}}(x) + 2\rho \int c_s(s) h_{\alpha s}(t) dv_3 + 2\rho \int c_d^{\text{sr}}(s) h_{\alpha d}(t) dv_3 - 2q\rho \int (1/s) h_{\alpha d}(t) dv_3\right\} \quad (3a)$$

$$g_{\alpha-}(x) = \exp\left\{-\beta U_{\alpha-}^{\text{el}}(x) + 2\rho \int c_s(s) h_{\alpha s}(t) dv_3 - 2\rho \int c_d^{\text{sr}}(s) h_{\alpha d}(t) dv_3 + 2q\rho \int (1/s) h_{\alpha d}(t) dv_3\right\} \quad (3b)$$

$x \geq R + a/2$

where $c_s(s) = (c_{++}(s) + c_{+-}(s))/2$, $c_d^{\text{sr}}(s) = (c_{++}(s) - c_{+-}(s))/2 + q/s$, $h_{\alpha s}(t) = (h_{\alpha+}(t) + h_{\alpha-}(t))/2$, $h_{\alpha d}(t) = (h_{\alpha+}(t) - h_{\alpha-}(t))/2$, $q = \beta e^2 z^2 / \epsilon$, e is the electronic charge, ϵ is the dielectric constant of the solvent, $z = z_+ = |z_-|$ is the valence of the ionic species, $\rho = \rho_+ = \rho_-$ is their concentration, $a \equiv a_+ = a_-$ is their diameter, and $U_{\alpha\gamma}^{\text{el}}(x)$ is the direct electrostatic potential between an ion of species γ ($= +, -$) and the cylinder. Notice that the last integral of eq 3 is the statistical mechanical average of the electrostatic interaction between two ions next to the cylinder.

Let us assume that the cylindrical coordinates of particle 2 are $(x, 0, 0)$ and those of particle 3 are (t, ϕ, ζ) , where ϕ is the position angle and ζ the position distance along the cylinder's symmetry axis. Thus

$$s^2 = \zeta^2 + x^2 + t^2 - 2xt \cos \phi \quad (4)$$

Substituting eq 4 into the last integral term of the right-hand side of eq 3, integrating over $d\phi$ and $d\zeta$, and

taking into account that by Gauss's law²⁷ the cylinder-ion electrostatic potential is given by $4\pi\beta e z_\gamma \sigma R \ln(x)/\epsilon$, we get from eq 3

$$g_{\alpha+}(x) = \exp\left\{(4\pi\beta e z_\sigma R / \epsilon) \ln(x) + 2\rho \int C_s(s) h_{\alpha s}(t) dv_3 + 2\rho \int c_d^{\text{sr}}(s) h_{\alpha d}(t) dv_3 + 4\pi\rho q \int_0^\infty f(x, t) h_{\alpha d}(t) t dt\right\} \quad (5a)$$

$$g_{\alpha-}(x) = \exp\left\{-(4\pi\beta e z_\sigma R / \epsilon) \ln(x) + 2\rho \int C_s(s) h_{\alpha s}(t) dv_3 - 2\rho \int c_d^{\text{sr}}(s) h_{\alpha d}(t) dv_3 - 4\pi\rho q \int_0^\infty f(x, t) h_{\alpha d}(t) t dt\right\} \quad (5b)$$

$x \geq R + a/2$

where $f(x, t) = \ln((x^2 + t^2 + |x^2 - t^2|)/2)$, σ is the charge density on the surface of the cylinder, and where we have set several arbitrary constant terms equal to zero.²⁸

Equations 5 are the HNC equations for a cylindrical double layer. The bulk direct correlation functions $c_s(s)$ and $c_d^{\text{sr}}(s)$ can be taken to be derived from the HNC or any another approximation, e.g., the mean spherical approximation (MSA).

In the limit of $x \rightarrow \infty$, the second and third terms in the exponential of eq 5a are equal to zero. Hence

$$g_{\alpha+}(x \rightarrow \infty) \rightarrow \exp\left\{(4\pi\beta e z_\sigma R / \epsilon) \ln(x) + 4\pi\rho q \int_0^\infty \ln(x^2) h_{\alpha d}(t) t dt\right\} \quad (6)$$

On the other hand, for the cylindrical double layer the electroneutrality condition is given by

$$-\sigma R = 2ez\rho \int_0^\infty h_{\alpha d}(t) t dt \quad (7)$$

Thus, substituting eq 7 into eq 6 shows that $g_{\alpha+}(x \rightarrow \infty) \rightarrow 1$. Similarly, $g_{\alpha-}(x \rightarrow \infty) \rightarrow 1$. This result shows the consistency of eq 5.

III. Limit of $R \rightarrow \infty$

In this section we let the radius, R , of the cylinder become infinitely large and show that in this case the HNC cylindrical double layer equations reduce to the HNC planar double layer equations.

If one defines the variables $x_0 \equiv x - R$, $t_0 \equiv t - R$, and $l = t\theta$, eq 5a becomes

$$g_{\alpha+}(x_0) = \exp\left\{(4\pi\beta e z_\sigma R / \epsilon) \ln(x_0 + R) + 2\rho \int_{-R}^\infty dt_0 \int_{-\pi(R+t_0)}^{\pi(R+t_0)} dl \int_{-\infty}^\infty d\zeta c_s(s) h_{\alpha s}(t_0) + 2\rho \int_{-R}^\infty dt_0 \int_{-\pi(R+t_0)}^{\pi(R+t_0)} dl \int_{-\infty}^\infty d\zeta c_d^{\text{sr}}(s) h_{\alpha d}(t_0) + 4\pi\rho q \int_{-R}^\infty f(x_0, t_0) h_{\alpha d}(t_0) (t_0 + R) dt_0\right\} \quad (8)$$

$x_0 \geq a/2$

where

$$s^2 = \zeta^2 + (R + x_0)^2 + (R + t_0)^2 - 2(R + x_0)(R + t_0) \cos \{l/(R + t_0)\} \quad (9)$$

$$f(x_0, t_0) = \ln \{1/2((x_0 + R)^2 + (t_0 + R)^2 + |(x_0 + R)^2 - (t_0 + R)^2|)\} \quad (10)$$

(26) See, for example, D. A. McQuarrie, "Statistical Mechanics", Harper and Row, New York, 1976.

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The first term in the exponential of eq 8 can be written as

$$(4\pi\beta e z \sigma R / \epsilon) \{ \ln(R) + \ln(1 + x_0/R) \} \quad (11)$$

The last term in the exponential of eq 8 can be written as

$$4\pi\rho q \ln(R^2) \int_{-R}^{\infty} (t_0 + R) h_{ad}(t_0) dt_0 + \\ 4\pi\rho q \int_{-R}^{\infty} \ln \left\{ 1 + \frac{x_0}{R} + \frac{t_0}{R} + \frac{1}{2} \left(\frac{x_0^2}{R^2} + \frac{t_0^2}{R^2} \right) + \right. \\ \left. \left| \left(\frac{x_0}{R} - \frac{t_0}{R} \right) + \frac{1}{2} \left(\frac{x_0^2}{R^2} - \frac{t_0^2}{R^2} \right) \right| \right\} (t_0 + R) h_{ad}(t_0) dt_0 \quad (12)$$

Therefore, expanding the logarithms of eq 11 and 12 and the term $\cos(l/(R + t_0))$ of eq 9 in a power series for small arguments, taking the limit of $R \rightarrow \infty$, and after some straightforward algebraic manipulation, we get from eq 8

$$g_{\alpha+}(x) = \\ \exp \left\{ (4\pi\beta e z \sigma / \epsilon) x + 2\rho \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dl \int_{-\infty}^{\infty} d\zeta c_s(s) h_{as}(t) + \right. \\ \left. 2\rho \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dl \int_{-\infty}^{\infty} d\zeta c_d^{sr}(s) h_{ad}(t) + \right. \\ \left. 4\pi\rho q \int_{-\infty}^{\infty} (x + t + |x - t|) h_{ad}(t) dt \right\} \quad (13)$$

where we have again set several arbitrary constant terms equal to zero²⁸ and dropped the subindex of the variables x and t ; the interionic distance is now given by

$$S^2 = \zeta^2 + (x - t)^2 + l^2 \quad (14)$$

Expression 14 gives the interionic distance in Cartesian coordinates. Thus, in bipolar coordinates, eq 13 becomes

$$g_{\alpha+}(x) = \exp \left\{ (4\pi\beta e z \sigma / \epsilon) x + \right. \\ \left. 2\pi\rho \int_{-\infty}^{\infty} h_{as}(t) dt \int_{|x-t|}^{\infty} s c_s(s) ds + 2\pi\rho \int_{-\infty}^{\infty} h_{ad}(t) dt \times \right. \\ \left. \int_{|x-t|}^{\infty} s c_d^{sr}(s) ds + 4\pi\rho q \int_{-\infty}^{\infty} (x + t + |x - t|) h_{ad}(t) dt \right\} \quad (15)$$

$$x \geq a/2$$

Similarly, it can be shown that

$$g_{\alpha-}(x) = \exp \left\{ -(4\pi\beta e z \sigma / \epsilon) x + \right. \\ \left. 2\pi\rho \int_{-\infty}^{\infty} h_{as}(t) dt \int_{|x-t|}^{\infty} s c_s(s) ds - 2\pi\rho \int_{-\infty}^{\infty} h_{ad}(t) dt \times \right. \\ \left. \int_{|x-t|}^{\infty} s c_d^{sr}(s) ds - 4\pi\rho q \int_{-\infty}^{\infty} (x + t + |x - t|) h_{ad}(t) dt \right\} \quad (16)$$

$$x \geq a/2$$

Equations 15 and 16 are the HNC equations for a planar double layer.²⁴

IV. Nonlinear Poisson-Boltzmann Equation

In the limit in which the diameter, a , of the ions becomes zero, eq 5 reduce to

$$g_{\alpha+}(x) = \\ \exp \left\{ (4\pi\beta e z \sigma R / \epsilon) \ln(x) + 4\pi\rho q \int_0^{\infty} f(x, t) h_{ad}(t) t dt \right\} \quad (17a)$$

(28) The constant terms are related with the point of zero potential and in no way affect our results.

$$g_{\alpha-}(x) = \{g_{\alpha+}(x)\}^{-1} \quad (17b)$$

$$x \geq R$$

Equation 17a can be written as

$$g_{\alpha+}(x) = \exp \left\{ (4\pi\beta e z \sigma R / \epsilon) \ln(x) + \right. \\ \left. 8\pi\rho q \int_0^x \ln(x) h_{ad}(t) t dt + 8\pi\rho q \int_x^{\infty} \ln(t) h_{ad}(t) t dt \right\} \quad (18)$$

Hence, when one uses the electroneutrality condition given by eq 7, eq 18 becomes

$$g_{\alpha+}(x) = \exp \left\{ -8\pi\rho q \int_x^{\infty} \ln(x/t) h_{ad}(t) t dt \right\} \quad (19)$$

On the other hand, for the cylindrical double layer, the mean electrostatic potential, $\psi(x)$, can be shown to be given by

$$\psi(x) = (4\pi e / \epsilon) \int_x^{\infty} \ln(x/t) \sum_{i=1}^Q z_i \rho_i g_{ai}(t) t dt \quad (20)$$

Therefore, eq 19 is given by

$$g_{\alpha+}(x) = \exp(-e z \beta \psi(x)) \quad (21)$$

and, from eq 17b

$$g_{\alpha-}(x) = \exp(e z \beta \psi(x)) \quad (22)$$

In cylindrical coordinates

$$\nabla^2 \psi(x) = \frac{1}{x} \frac{d\psi(x)}{dx} + \frac{d^2 \psi(x)}{dx^2} \quad (23)$$

Thus, if in eq 20 $g_{\alpha+}(t)$ and $g_{\alpha-}(t)$ are given by eq 21 and 22 (respectively), we get from eq 20

$$\frac{d\psi(x)}{dx} = \frac{4\pi e}{\epsilon x} \int_x^{\infty} \left(\sum_{i=1}^2 z_i \rho_i g_{ai}(t) \right) t dt \quad (24)$$

Differentiating eq 24, we get

$$\frac{d^2 \psi(x)}{dx^2} = -\frac{4\pi e}{\epsilon x^2} \int_x^{\infty} \left(\sum_{i=1}^2 z_i \rho_i g_{ai}(t) \right) t dt - \frac{4\pi e}{\epsilon} \sum_{i=1}^2 z_i \rho_i g_{ai}(x) \quad (25)$$

Therefore, from eq 23-25 we obtain

$$\nabla^2 \psi(x) = -\frac{4\pi e}{\epsilon} \sum_{i=1}^2 z_i \rho_i g_{ai}(x) \quad (26)$$

Equation 26 is the nonlinear PB equation for the distribution of point ions around a cylindrical electrode, in differential form.⁸ Thus, eq 17 are the integral form of the nonlinear PB equation. Expansion of the exponential of eq 17 and keeping terms to first order will give the linearized PB equation analytically solved by Brenner and McQuarrie.⁷

As we have shown in section III, by taking the limit $R \rightarrow \infty$ in the HNC equation for the cylindrical double layer (eq 8) one gets the HNC equation for the planar double layer (eq 15). However, if we assume the diameter of the ions equal to zero, the second and third terms of eq 8 and 15 are equal to zero. Thus, clearly, in the limit $R \rightarrow \infty$, the nonlinear PB equation for the cylindrical double layer (eq 17) becomes the Gouy-Chapman theory.^{12,13,29}

The analysis of second-order terms in the series expansion of the logarithms in the exponential of eq 17 (see eq 11 and 12) shows that the greatest differences between

(29) See the second reference of ref 22 for an integral representation of the Gouy-Chapman theory.

the nonlinear PB equation and the Gouy-Chapman theory^{12,13,29} are for low values of the radius of the cylinder. This behavior qualitatively agrees with the numerical results of Stigter.⁸

V. Conclusions

In this paper we derived the HNC equations for a cylindrical double layer. In these equations, we made the radius of the cylinder infinitely large to show the consistency of our equations with the HNC planar double layer equations.²⁴ Finally, we showed that in the limit of zero ionic diameters our equations reduce to the nonlinear PB equation for this system.

In the Introduction we pointed out the remarkable success that under certain conditions the Gouy-Chapman theory^{12,13} (a nonlinear Poisson-Boltzmann equation) had in the planar double layer studies. Hence, it is to be expected that also under certain conditions the nonlinear PB equation for a cylindrical double layer will give good results too. However, for certain systems, such as collagen, which can be modeled as rigid cylinders of very small diameters (13.6 Å⁴), the short-range interaction between the ions

could play a very important role. This interaction, by construction is taken into account by the HNC equation, whereas the PB equation does not.

Moreover, an unsymmetrically charged electrolyte next to a charged wall is well described by the HNC theory,¹⁹ whereas the Gouy-Chapman theory fails.¹⁴ This behavior is to be expected to persist in the cylindrical double layer. Therefore, a study of the cylindrical double layer through the HNC approximation is recommended.

Nevertheless, for symmetrical electrolytes at low concentrations and relatively large diameter of the cylinder the nonlinear Poisson-Boltzmann equation could correctly describe the relevant features of the cylindrical double layer. In a forthcoming paper we will present some calculations of the nonlinear PB equation (numerically solved as a nonlinear integral equation) and the HNC approximation for the cylindrical double layer.³⁰

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Formation of Hydrogen Atoms in Pyrolysis of 2,2-Dimethylpropane behind Shock Waves

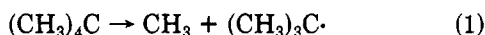
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Dilute mixtures (5–20 ppm) of 2,2-dimethylpropane (neopentane) were pyrolyzed behind reflected shock waves at temperatures of 1140–1300 K and total pressures of 2–3 atm. Progress of the reaction was followed by analysis for H atoms using resonance absorption spectroscopy. Appearance of H atoms was a first-order process with respect to time, an Arrhenius equation for the appearance of H atoms, based on 61 experiments, being $k_H = 2.65 \times 10^{17} \exp(-86300/RT) \text{ s}^{-1}$, where the activation energy is in calories. Taking into account two minor side reactions, the first-order rate constant for the first step in neopentane pyrolysis, $(\text{CH}_3)_4\text{C} \rightarrow (\text{CH}_3)_3\text{C} \cdot + \text{CH}_3$ (1) was found to be $k_1 = 1.7 \times 10^{17} \exp(-84000/RT) \text{ s}^{-1}$ with an estimated uncertainty of a factor of 2 in k_H and k_1 .

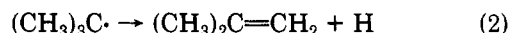
Introduction

Pyrolysis of 2,2-dimethylpropane (neopentane) has been investigated in two single-pulse shock tube studies.^{1,2} It has also been studied in static and flow reactors at somewhat lower temperatures; two recent papers using the flow technique^{3,4} contain references to the earlier work. They are in unanimous agreement that the initial step in the overall process is

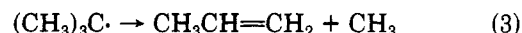


but in the studies done so far it has not been possible to measure the rate constant of reaction 1 directly, because of interference by subsequent reactions. Nearly all of the studies have led to expressions for k_1 that are in reasonably good agreement, but Pratt and Rogers⁴ quite recently deduced a rate constant at 983 K that lies a factor of 10 below the average curve of the other data. Using the atomic resonance absorption method to measure concen-

trations of H atoms we have been able to follow the progress of reaction 1, since essentially all of the *tert*-butyl radicals produced by reaction 1 dissociate within a few microseconds to produce H atoms:



From his product distributions from the dissociation of 2,2,3,3-tetramethylbutane, Tsang¹ considered that a small fraction of the *tert*-butyl radical dissociates by reaction 3. Bradley and West² considered this reaction to be fairly



important, while the most recent authors^{3,4} have taken it to be insignificant. In an earlier paper⁵ we considered that 90% of the radicals decomposed via reaction 2, and 10% via reaction 3, based on Tsang's data, and have continued to do so here.

Because our work has been done at very low concentrations of neopentane, 5–20 ppm, none of the subsequent reactions that complicated earlier results are important to us. The only other reaction that we included in our

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