Investigation of the electric potential near the DNA-solvent interface: Conclusions about the stability of B-DNA

D. Ouroushev
Department of Condensed Matter Physics, Faculty of Physics, Sofia University, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria
(Received 13 April 2000; revised manuscript received 27 September 2001; published 6 March 2002)

In the present paper DNA is treated as a crystal with symmetry corresponding to a double-helix surface charge density, due to the phosphate groups, immersed in a weak electrolyte. The surrounding solvent is treated via the nonlinear Poisson-Boltzmann equation and the boundary conditions of electrostatics are exactly fulfilled on the DNA-solvent interface. Analytical solutions for the electric potentials and fields inside and outside DNA are obtained. The results give the possibility for a map of the surface potential of DNA to be created. They also show that the electric field inside DNA may decay in two different ways if we change the chemical content of the surrounding solvent. According to this we can draw conclusions about the stability of DNA with respect to the internal and changeable parameters of the system such as chemical content of the aqueous solvent. The position of the condensed counterions around DNA in the Manning cloud can be determined.

DOI: 10.1103/PhysRevE.65.031913 PACS number(s): 87.15.−v, 41.20.Cv, 02.60.Lj

I. INTRODUCTION

The purpose of this paper is the problem of finding the electric field emanating from dissolved DNA from both inside and outside this macromolecule. The correct consideration of the field of the surrounding ion atmosphere reveals new properties of this field and helps to predict changes in the structure of DNA due to changes of the internal parameters of the DNA-solvent system. The creation of a relatively realistic model of the electric field outside and inside DNA is important for the determination of the influence of this field on DNA protein [1] and DNA-DNA interactions [2,3], for investigation of the thermodynamic properties of the system of DNA and the surrounding solvent, and for attempts to image DNA with scanning force microscopy [4].

Born, Onsager, and Kirkwood [5–7] have shown that a molecule in a solvent must be considered as a ''low ε'' cavity and the surrounding solvent as a media with different ε. If we investigate the electrostatic properties of this system, the boundary conditions for electrostatics on the surface of the biopolymer must be fulfilled.

The next step in developing the main ideas from [5–7] is to consider DNA as a crystal immersed in an electrolyte and to take into account the surface charge distribution, which has a special concrete form.

In the beginning, DNA was considered to be a homogeneously charged cylinder and the Debye-Huckel theory for the treatment of the solvent was used [8]. After that, the nonlinear Poisson-Boltzmann equation (NPBE) was considered for the description of the solvent [9].

In recent years, the double-helix charge distribution due to the charge of the phosphate groups on the surface of DNA was taken into account [10,11], but the solvent was considered to be a continuous dielectric medium with two different ε, corresponding to the Manning cloud and to the solvent outside it. The same authors developed their model, using the Debye-Huckel theory [12]. Another approach to the consideration of the surface double-helix charge in nonorthogonal coordinates is presented in [13] and discussed in [14]. In [13] the solvent was neglected. As is pointed out in [15], in the case of DNA and some proteins, such as lypolisine (because they are highly charged biopolymers), the NPBE must be used for the correct description of the solvent.

Here we will consider DNA as a special crystal with corresponding symmetry, taking into account the double-helix surface charge distribution and treating the surrounding solvent via NPBE. We will also use proper nonorthogonal coordinates consistent with the internal symmetry of this system.

Our investigations in this direction started with the paper [16] in which the Laplace equation inside the dielectric cylinder and the NPBE in the solvent outside were solved and the boundary conditions of the electrostatics on the cylindrical surface were fulfilled. In [16] the surface charge is an arbitrary function of the polar angle θ.

Our next paper [17] applies the mathematical method presented in [16] to the case of B-DNA. In both cases the method is purely analytical and circumvents the bottleneck problems [18] of the numerical simulations due to the large length of the DNA as well as the large amount of solvent that has to be taken into account.

Here we will develop a model where the helical structure of the surface charge of DNA will be considered. The general mathematical approach for satisfying the boundary conditions that were developed in [16] will be applied. This will help to evaluate main ideas from [5–7] and obtain the required results.

II. SOLUTIONS OF THE NPBE

We will use the nonorthogonal helical coordinates presented in [13], which are a variant similar to the helical coordinates from [19]. The coordinates from [13] have the advantage of being orthogonal on the cylindrical surface with radius b, which helps the boundary conditions of electrostatics to be correctly fulfilled on this surface.

The relations between these coordinates and the cylindrical ones are given by

$$\overline{\rho}=\overline{\rho},$$

$$\overline{t}=b\,\theta\sin\beta-z\cos\beta,$$

$$\overline{s}=b\,\theta\cos\beta+z\sin\beta. \tag{1}$$

Here b is the radius of the cylinder on which the helical coordinates are orthogonal and β is the angle of the helix with pitch ρ,

$$\tan\beta=\frac{p}{2\pi b}. \tag{2}$$

As is shown in [13], the Laplacian in the coordinates $\overline{\rho},\overline{s},\overline{t}$ has the form

$$\Delta\Psi=\left\{\left[\frac{1}{\overline{\rho}}\frac{\partial}{\partial\overline{\rho}}\left(\overline{\rho}\frac{\partial}{\partial\overline{\rho}}\right)\right]+\frac{\partial^2}{\partial\overline{t}^2}+\frac{\partial^2}{\partial\overline{s}^2}+\left(\frac{a^2}{\overline{\rho}^2}-1\right)\right.$$
$$\left.\times\left(\sin\beta\frac{\partial}{\partial\overline{t}}+\cos\beta\frac{\partial}{\partial\overline{s}}\right)^2\right\}\Psi. \tag{3}$$

In order to solve analytically the NPBE in the solvent around DNA and to satisfy the boundary conditions of the electrostatics on its surface, we shall make an assumption. This assumption simplifies the Laplacian (3) and makes it less complicated for the corresponding solutions of the NPBE around DNA to be found. A reason for this assumption is that the origin of the electric field inside and outside DNA are charges distributed on a cylindrical surface on lines with t −const and displaced at 7.0 Å along these lines. This gives us ground to assume that the electric field is oriented mainly in the t direction near the surface of the DNA. Figure 3 from the paper [12] presents the results from the Debye-Huckel treatment, and the good coincidence of the structure of the potential from [12] and that following from our investigations is instructive of the fact that the compromises made in our model are reasonable. The coincidence with our results is good enough although an all-atom model of DNA is used in paper [12]. According to this, the Laplacian (3) can be rewritten in the form in which $\overline{s}$ dependence is disregarded,

$$\Delta\Psi=\left\{\frac{1}{\overline{\rho}}\frac{\partial}{\partial\overline{\rho}}\left(\overline{\rho}\frac{\partial}{\partial\overline{\rho}}\right)+\left[\cos^2\beta+\frac{b^2\sin^2\beta}{\overline{\rho}^2}\right]\frac{\partial^2}{\partial\overline{t}^2}\right\}\Psi. \tag{4}$$

Of course, including the s dependence in our investigations and decomposing the charged lines on the surface of DNA into discrete point charges will be one of the next steps in our work.

The experimental and numerical estimations and calculations in [10–12] show that the effective decay length for the helical information in the local electric field is about 20 Å beyond the surface of the DNA. Our further calculations will show that the approach presented here is valid in the interval $0\leqslant\overline{\rho}\leqslant22.3$ Å. In this region the first term in the brackets in front of the derivative $\partial^2\Phi/\partial\overline{t}^2$ in Eq. (4) or $\cos^2\beta$ can be neglected with respect to the second one. Having in mind that the two terms in these brackets are positive and that no pole exists, this means that we have to slightly change the solution in $\overline{\rho}$ direction. The approximation is completely correct where $\overline{\rho}\to0$ or when we are near the axis of the DNA. In the whole interval of investigation we neglect a small constant term in the brackets mentioned above, but we keep the functional dependence of $\overline{\rho}$ in it.

Accordingly, in our model the NPBE has the form

$$\frac{\partial^2\Psi}{\partial\overline{\rho}^2}+\frac{1}{\overline{\rho}}\frac{\partial\Psi}{\partial\overline{\rho}}+\frac{b^2}{\overline{\rho}^2}\sin^2\beta\frac{\partial^2\Psi}{\partial\overline{t}^2}=-\frac{4\pi nN}{\varepsilon}\exp(-q\Psi/kT). \tag{5}$$

The dimensionless form is obtained via the transformations

$$\rho=\overline{\rho}f,\quad \overline{\Phi}=-\frac{\psi q}{kT},\quad t=\frac{\overline{t}}{b\sin\beta} \tag{6}$$

or

$$\frac{\partial^2\overline{\Phi}}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial\overline{\Phi}}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2\overline{\Phi}}{\partial t^2}=\exp(\overline{\Phi}). \tag{7}$$

Here $f=[(4\pi nN/\varepsilon)L]^{1/2}$, where $L=q^2/kT$ is the Bjerrum length. Also n is a normalization factor defined by

$$n^{-1}=\int_{V_s}\exp\left(-\frac{q\Psi}{kT}\right), \tag{8}$$

where the V_s is the volume of the solvent under consideration and N is the number of counterions with charge q per unit axial length. The NPBE can be rewritten in the form

$$\frac{\partial^2\Phi}{\partial x^2}+\frac{\partial^2\Phi}{\partial t^2}=\exp(\Phi), \tag{9}$$

where

$$x=\ln(\rho),\quad \Phi=\overline{\Phi}+2x,$$

$$t=\theta-\frac{z}{b}\cot g\beta. \tag{10}$$

As is shown in our previous paper [16], using Backlund transformations and the original idea of Liouville [20], the following general solution of Eq. (9) can be found:

$$\Phi=\ln\left\{\frac{2\left(\frac{\partial W(x,t)}{\partial x}\right)^2+2\left(\frac{\partial W(x,t)}{\partial t}\right)^2}{W^2(x,t)}\right\}. \tag{11}$$

Here $W(x,t)$ is an arbitrary harmonic function of x and t. Consequently for the self-consistent potential, which is a solution of NPBE, we have

$$\Psi=-\frac{kT}{q}\left\{\frac{2\left[\rho\left(\frac{\partial W(\rho,t)}{\partial\rho}\right)^2+2\left(\frac{\partial W(\rho,t)}{\partial t}\right)^2\right]}{\rho^2W^2(\rho,t)}\right\}. \tag{12}$$

III. FORMULATION OF THE PROBLEM AND BOUNDARY CONDITIONS

We will look for a solution of the NPBE in the interval $b \leqslant \bar{\rho} \leqslant \bar{\rho}_0$. The value of ρ_0 is determined by the requirement of Ψ_2 to be normalized in this interval and the electroneutrality condition to be fulfilled in it. Inside DNA we shall solve the Laplace equation. The solutions of the Laplace equation inside DNA and the NPBE outside the DNA must satisfy the boundary conditions of the electrostatics at $\bar{\rho} = b$,

$$(\vec{D}_2 - \vec{D}_1)\cdot\bar{\rho} = 4\pi\sigma(t), \quad \bar{\rho} = b,$$

$$(\vec{E}_2 - \vec{E}_1)\times\bar{\rho} = 0, \quad \bar{\rho} = b, \tag{13}$$

where $\varepsilon(\rho)$ is

$$\varepsilon(\bar{\rho}) = \varepsilon_1, \quad 0 \leqslant \bar{\rho} < b,$$

$$\varepsilon(\bar{\rho}) = \varepsilon_2, \quad b \leqslant \bar{\rho} \leqslant \bar{\rho}_0. \tag{14}$$

Here $\bar{\rho}$ is the outward unit radial vector and the indexes 1 and 2 refer to the regions inside and outside the cylinder modeling DNA

$$4\pi\sigma(t) = \frac{\gamma}{b}[\delta(t) + \delta(t - t_0)], \tag{15}$$

where both δ functions model the double-helix space charge distribution of DNA. The value of t_0 is given in [13] and it is

$$t_0 = \pi - 2\times\frac{1.57}{10}\times\cot(\beta). \tag{16}$$

In the case of B-DNA the value of t_0 can be accepted as $\frac{4}{5}\pi$ with an accuracy of 0.15%. In this case, for $\sigma(t)$ we obtain

$$\sigma(t) = \frac{\gamma}{b\pi}\left[\sum_{m=1}^{\infty}\cos(5mt) + \frac{1}{2}\right]. \tag{17}$$

Here γ is the linear charge density on the two helical lines.

IV. CALCULATION OF THE ELECTRIC POTENTIAL AND FIELD AND THE SPACE CHARGE DISTRIBUTION OF THE IONS IN THE SOLVENT

Having in mind that we have to match on the boundary surface, the solution of the Laplace equation and the solution of the NPBE containing an arbitrary harmonic function of x and t we make the following substitution, which solves the Laplace equation inside the cylinder:

$$\Psi_1 = \sum_{m=1}^{\infty}\bar{A}^1_{5m}\left(\frac{\bar{\rho}}{b}\right)^{5m}\cos(5mt). \tag{18}$$

For the function $W(x,t)$ in Eq. (12) we set

$$W(x,t) = C\ln(\rho_1\rho) + \left(\frac{\bar{A}}{\rho^5} + \bar{B}\rho^5\right)\cos(5t), \quad x = \ln\rho. \tag{19}$$

The form of $\sigma(t)$, Eq. (17), determines the exponents 5 in the exponential functions in Ψ_1 and $W(x,t)$. Only if we choose the exponents equal to 5, the analytical solution of the problem can be found. This is an important feature of the presented model and consequences of it will be shown below.

In Eqs. (18) and (19) $\bar{A}'_{5m}$, C, $\bar{A}$, $\bar{B}$, and ρ_1 are arbitrary coefficients. For these expansion coefficients in Ψ_1 and Ψ_2, we have a nonlinear system of algebraic equations. The system and its solutions are given in the Appendix. Using expressions (18) and (19) and the boundary conditions (13), we obtain the following expressions for the potentials Ψ_1 and Ψ_2 inside and outside the DNA:

$$\Psi_1 = \sum_{m=1}^{\infty}\bar{A}^1_{5m}r^{5m}\cos\left[5m\left(\theta - \frac{2z}{b}\right)\right], \tag{20}$$

$$A^1_5 = -\frac{4\varepsilon_2(C/B + \alpha + 1)}{5\varepsilon_1(\alpha + 1)},$$

$$A^1_{10} = 1 - \frac{4\varepsilon_2(C/B + \alpha + 1)}{5\varepsilon_1(\alpha + 1)},$$

where

$$5(m+1)A'_{5(m+1)} = \tfrac{1}{2}[5mA^1_{5m} + 5(m+2)A'_{5(m+2)}],$$

$$m = 1,2,3,..., \tag{21}$$

$$\Psi_2 = -\frac{kT}{q}\ln\left\{50\frac{\left\{\frac{C}{5} + \left(r^5 - \frac{\alpha}{r^5}\right)\cos\left[5\left(\theta - \frac{2z}{b}\right)\right]\right\}^2 + \left\{\left(\frac{\alpha}{r^5} + r^5\right)\sin\left[5\left(\theta - \frac{2z}{b}\right)\right]\right\}^2}{\left\{-(1+\alpha) + C\ln r + \left(\frac{\alpha}{r^5} + r^5\right)\cos\left[5\left(\theta - \frac{2z}{b}\right)\right]\right\}\frac{b^2r^2}{r_D^2}}\right\}. \tag{22}$$

In Eqs. (22) and (20) $r=\overline{\rho}/b$ and r_D is the Debye radius. Also

$$\alpha=\frac{8\varepsilon_2-5\varepsilon_1}{12\varepsilon_2+5\varepsilon_1}. \tag{23}$$

From Eq. (22) for the space charge density of the counterions ρ_c we have

$$\rho_c=50\left\{\frac{\left\{\frac{C}{5}+\left(r^5-\frac{\alpha}{r^5}\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]\right\}^2+\left\{\left(\frac{\alpha}{r^5}+r^5\right)\sin\left[5\left(\theta-\frac{2z}{b}\right)\right]\right\}^2}{\left\{-(1+\alpha)+C\ln r+\left(\frac{\alpha}{r^5}+r^5\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]\right\}^2\frac{4\pi qb^2r^2}{\varepsilon_2 kT}}\right\}. \tag{24}$$

We will obtain the components of the electric field E_r, E_θ, and E_z in cylindrical coordinates using the relation $\vec{E}=-\mathrm{grad}\,\Psi$ and following [13]. From Eqs. (20) and (22) using expression (17) for the components of the field E_r^2, E_θ^2, and E_z^2 outside DNA we have

$$E_{\overline{\rho}}^2=\frac{kT}{bq}\left\{\frac{10\left\{\frac{C}{5r}+\left(r^4-\frac{\alpha}{r^6}\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]\right\}}{\left\{C\ln r-(1+\alpha)+\left(\frac{\alpha}{r^5}+r^5\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]\right\}}-\frac{2}{r}\right\}, \tag{25}$$

$$E_\theta^2=-10\frac{kT}{bq}\frac{1}{r^2}\left\{\frac{\left(\frac{\alpha}{r^5}+r^5\right)\sin\left[5\left(\theta-\frac{2z}{b}\right)\right]}{C\ln r-(1+\alpha)+\left(\frac{\alpha}{r^5}+r^5\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]}\right\}, \tag{26}$$

$$E_z^2=10\frac{kT}{bq}\frac{\cos\beta}{\sin\beta}\frac{1}{r^4}\left\{\frac{\left(\frac{\alpha}{r^5}+r^5\right)\sin\left[5\left(\theta-\frac{2z}{b}\right)\right]}{C\ln r-(\alpha+1)+\left(\frac{\alpha}{r^5}+r^5\right)\cos\left[5\left(\theta-\frac{2z}{b}\right)\right]}\right\}. \tag{27}$$

The normalization of the NPBE solution and the electroneutrality condition demand

$$\gamma L=\int_{V_s}qnN\exp\left(-\frac{\psi_2 q}{kT}\right)d\nu. \tag{28}$$

Here L is the length of the helical line per pitch and V_s is the regarded volume of the solvent

$$V_s=\pi(\overline{\rho_0}-b)^2z_0, \tag{29}$$

where $z_0=31.56$ Å.

Finally we obtained a family of solutions of the electric potentials depending on the arbitrary constant C. The value of C may be determined by a investigation of the free energy of the system. As can be seen from the expression for the space charge density of the solvent (24), by changing C we compress the counterions closer to the DNA macromolecule. This exact analysis and the determination of the concrete solutions corresponding to the reality will be subject of our future work.

The result from the Appendix gives the components of the electric field inside DNA,

$$E_{\overline{\rho}}^1=-\frac{kT}{qb}\sum_{m=1}^{\infty}5mA_{5m}^1r^{5m-1}\cos\left[5m\left(\theta-\frac{2z}{b}\right)\right], \tag{30}$$

$$E_\theta^1=\frac{kT}{qb}\frac{1}{r^2}\sum_{m=1}^{\infty}5mA_{5m}^1r^{5m}\sin\left[5m\left(\theta-\frac{2z}{b}\right)\right], \tag{31}$$

$$E_z^1=-\frac{kT}{qb}\frac{1}{r^4}\frac{\cos\beta}{\sin\beta}\sum_{m=1}^{\infty}5mA_{5m}^1r^{5m}\sin\left[5m\left(\theta-\frac{2z}{b}\right)\right]. \tag{32}$$

These results show that to obtain a realistic picture of the electric field inside B-DNA ($0\leqslant r\leqslant 1$) it is enough to consider just the first terms in the rows in Eqs. (30)–(32). Keep-

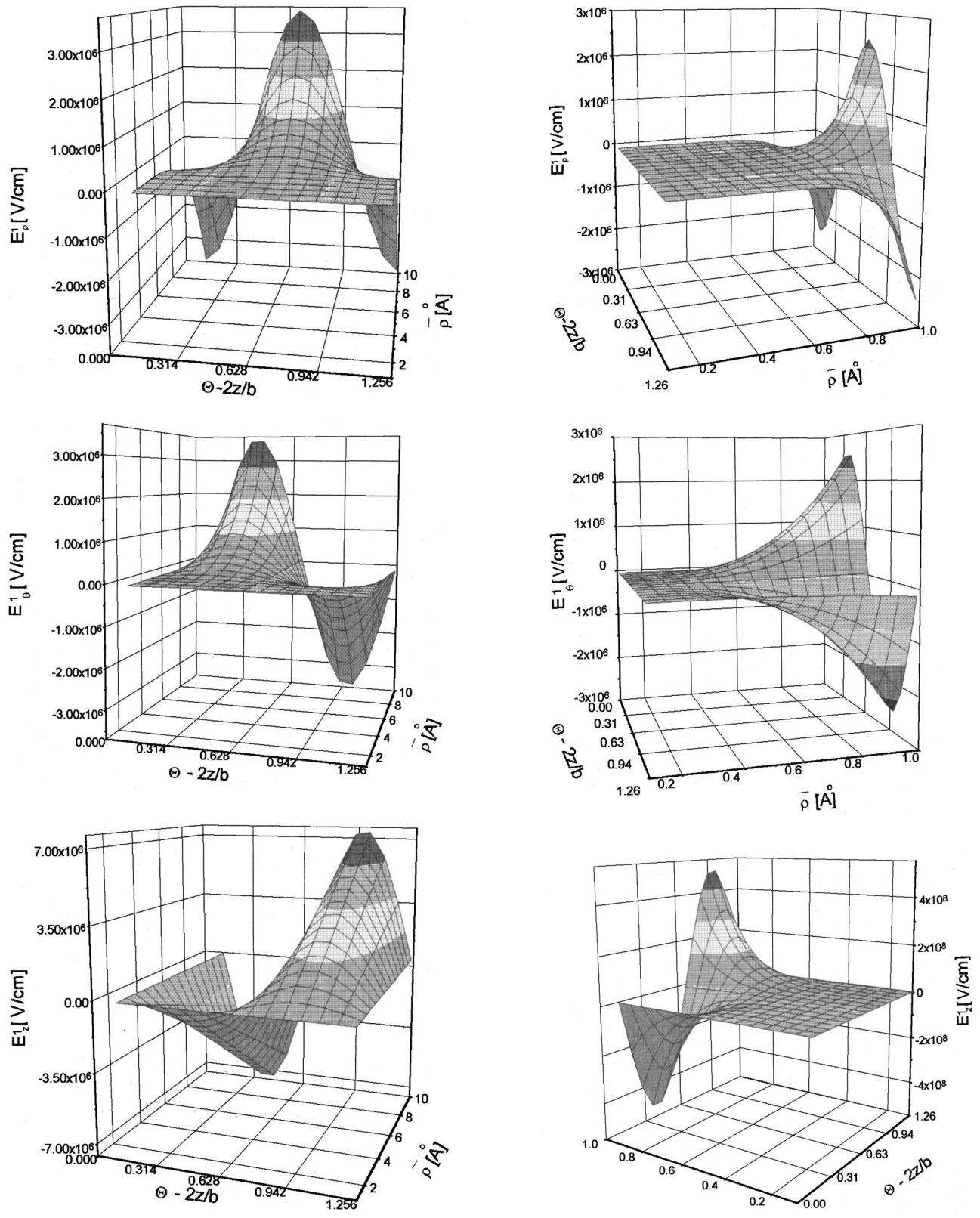

FIG. 1. The components of the electric field inside B-DNA. (a) $E^1_{\rho},E^1_{\theta},E^1_z$ in the case of B-DNA as a function of θ and r, $\varepsilon_1=2.4$, $\varepsilon_2=59.4$, $T=310$ K, $C=10$, $b=10$ Å, $z=0$. In this case the counterions are distributed at larger distances from DNA and larger variations of the electric field occur inside it. In this case the value of C is larger than in case (b). (b) $E^1_{\rho},E^1_{\theta},E^1_z$ in the case of B-DNA as a function of θ and r, $\varepsilon_1=2.4$, $\varepsilon_2=59.4$, $T=310$ K, $C=-1-\alpha$, $b=10$ Å, $z=0$. This is a case of an almost complete shielding of B-DNA. The physical reason for this effect is the space distribution of the counterions near the surface of B-DNA at smaller value of C $(-1-\alpha\sim-5/4)$. The electric field inside the macromolecule is partially compensated by the field due to the counterions.

ing just the first term in the rows, in Fig. 1 are presented E^1_ρ, E^1_θ, and E^1_z for two values of C. The value of E^1_z is the largest, which is in agreement with the experimental data [10,14].

This is an interesting result giving simple expressions of the electric field inside B-DNA and revealing possibilities of changes in its proteins being easily predicted. The formula for A^1_m shows that $\overline{E^1}$ depends on ε_2 or the value of the electric field inside DNA and its decay can be influenced by the value of ε_2 or the type of conterions and their concentrations in the solvent.

V. THE VOLUME OF THE MANNING CLOUD

The component E^2_ρ of the electric field derived by us (the cylindrical coordinates) has the form (26). b is the radius of the cylinder, C is an arbitrary constant, and for α we have the expression

$$\alpha=\frac{8\varepsilon_2-5\varepsilon_1}{12\varepsilon_2+5\varepsilon_1}. \tag{33}$$

In Eq. (33) ε_1 and ε_2 are the dielectric constants inside DNA and in the aqueous solvent. In the intervals $1<r<2.23$ and $-50<C<50$ the following inequality is fulfilled:

$$-(1+\alpha)+C\ln r<\alpha/r^5+r^5. \tag{34}$$

In these intervals for r and C there exists a cylinder with radius r_0 inside which the electroneutrality condition is fulfilled. Using Eq. (1) and the Gauss theorem we obtain an equation for the radius of the Manning cloud. The improper integral, which must be evaluated in order to apply the Gauss theorem, considering Eq. (34), possesses a finite main value [21], and the following equation for the radius r_0 is obtained:

$$\frac{\alpha/r_0^6-r_0^4}{\alpha/r_0^5-r_0^5}=\frac{2}{r_0}. \tag{35}$$

From Eq. (35) for the radius of the above-mentioned cylinder, we obtain $r_0=2.23$, or the radius of the Manning cloud is 22.3 A. This result in the frames of our ''shell model'' coincide well with the experimental data for the radius of the Manning cloud [8,9].

VI. POSITION OF THE COUNTERIONS IN THE MANNING CLOUD

The above-mentioned radial position will be determined from the expression for the space charge density given by Eq. (24). In Eq. (24) the denominator is zero where

$$-(1+\alpha)+C\ln r+\left(\frac{\alpha}{r^5}+r^5\right)\cos\left[5\left(\vartheta-2\frac{z}{b}\right)\right]=0. \tag{36}$$

It must be underlined that the improper integral from ρ_c over the volume of the cylinder with radius r_0 is finite [21]. As is shown in our article [22], on the singular surfaces determined by the condition (36) we have particle condensation.

The expressions for the electric field inside B-DNA have the forms (30)–(32). For the coefficient A^1_5 we have

$$A^1_5=-\frac{kT4\varepsilon_2(C+\alpha+1)}{q^5\varepsilon_1(\alpha+1)}. \tag{37}$$

It is clear that if $C=-(1+\alpha)$, A^1_5 is zero. Consequently the largest component of the electric field E^1_z in this case decays inside DNA proportional to r $(0<r<1)$. The fact that E^1_z is the largest component of the electric field follows from the structure of the surface charge of DNA as was pointed out in [14]. For all values of C different from $-(1+\alpha)$, E^1_z decays as r^6. This means that we have two different states of the system of DNA and the surrounding aqueous solvent. We may have an electric field inside DNA that may change its structure or one that cannot influence it. Keeping in mind the expression (24) for the space charge density of the counterions and the fact that in the denominator of this expression we have the term $C\ln r$, conclusions about the space distribution of these ions can be made. At larger values of the free constant C, the denominator in Eq. (24) is larger than when r tends to 1, and the counterions are located further from the surface of B-DNA ($r=1$ corresponds to the surface of DNA). For small values of C we compress the counterions to the surface of B-DNA. The charges closely distributed to the surface compensate to a certain extent for the electric field inside the macromolecule, and it is electrically shielded. In the other case of larger values of C, we have larger variations of the electric field inside B-DNA due to the location of the counterions at larger distances from it. ε_2 depends on the chemical content of the solvent. Decreasing ε_2 we increase the electric field produced by the surface charge of DNA inside the solvent. This means compression of the counterions to the surface DNA, materialization of a solution with smaller C, and decreasing of the electric field inside the macromolecule. All this coincides with the speculations presented above.

A detailed explanation of the ''two ways of decay'' of the electric field inside DNA can be performed by investigation of the free energy of the DNA-solvent system. This energy is a function of C and ε_2 and such a study is one of the purposes of our future work.

VIII. CONCLUDING REMARKS

It must be underlined that the singularities in ρ_c might be interpreted as Manning's condensation of counterions. The point here is that the radial position of the condensed charge is determined. The exact value of this charge and its influence on the electric field of the DNA-solvent system will be the subject of our future work.

The approach in this paper is completely analytical and the obtained formulas for the electric field inside and outside DNA reveal clear possibilities of influencing its structure and properties. This can be done by changing the chemical content of the surrounding aqueous solvent. It is shown that DNA and the surrounding solvent is a two level system and that in one of its states the DNA macromolecule is almost electrostatically shielded. Of course this might be important

for the protection of DNA from external electromagnetic influences. This fact is mainly due to the position of the phosphate groups on the surface of the DNA and may be achieved by changing in a proper way the content of the surrounding aqueous solvent as is shown in this paper. On the base of the obtained results, also a map of the electric field inside DNA might be created.

APPENDIX

We introduce the relations

$$\overline{A}^1_m = \frac{kT}{q} A^1_m, \tag{A1}$$

$$\frac{\overline{A}}{(bf)^5} = A, \quad \overline{B}(bf)^5 = B. \tag{A2}$$

From the boundary conditions (13) and the expressions for Ψ_1 and Ψ_2 we will obtain the following system of nonlinear algebraic equations for the expansion coefficients in Ψ_1 and Ψ_2. In the following formulas the expression (17) for $\sigma(t)$ is used. So we have

$$A^1_1 A^2_0 + 3A^1_6 A^2_5 - 2A^1_4 A^2_5 = 0, \tag{A3}$$

$$2A^1_2 A^2_0 + \tfrac{7}{2} A^1_7 A^2_5 - \tfrac{3}{2} A^1_3 A^2_5 = 0, \tag{A4}$$

$$3A^1_3 A^2_0 + 4A^1_8 A^2_5 - A^1_2 A^2_5 = 0, \tag{A5}$$

$$4A^1_4 A^2_0 + \tfrac{9}{2} A^1_9 A^2_5 - \tfrac{1}{2} A^1_1 A^2_5 = 0, \tag{A6}$$

$$A^1_5 A^2_0 + A^1_{10} A^2_5 = A^2_5, \tag{A7}$$

$$\varepsilon_1 [A^1_1 A^1_0 + 3A^1_6 A^2_5 + 2A^1_4 A^2_5] = \frac{\gamma}{\pi b} [A^2_0 + A^2_5], \tag{A8}$$

$$\varepsilon_1 [2A^1_2 A^2_0 + \tfrac{7}{2} A^1_7 A^2_5 + \tfrac{3}{2} A^1_3 A^2_5] = \frac{\gamma}{\pi b} [A^2_0 + A^2_5], \tag{A9}$$

$$\varepsilon_1 [3A^1_3 A^2_0 + 4A^1_8 A^2_5 + A^1_2 A^2_5] = \frac{\gamma}{\pi b} [A^2_0 + A^8_5], \tag{A10}$$

$$\varepsilon_1 [4A^1_4 A^2_0 + \tfrac{9}{2} A^1_9 A^2_5 + \tfrac{1}{2} A^1_1 A^2_5] = \frac{\gamma}{\pi b} [A^2_0 + A^2_5], \tag{A11}$$

$$5(m+1) A'_{5(m+1)} = \tfrac{1}{2} [5m A^1_{5m} + 5(m+2) A'_{5(m+2)}], \quad m = 1,2,..., \tag{A12}$$

$$5\varepsilon_1 [A^1_5 A^2_0 + A^1_{10} A^2_5] - \varepsilon_2 [-12A + 8B] = \frac{\gamma\pi}{b} [A^2_0 + A^2_5], \tag{A13}$$

$$\varepsilon_1 \tfrac{5}{2} A^1_5 A^2_5 + 2\varepsilon_2 [C - C \ln \rho_1 b] = \frac{\gamma\pi}{b} [A^2_0 + A^2_5], \tag{A14}$$

$$5(m+1) A'_{5(m+7)} - \tfrac{1}{2} [5m A^1_{5m} + 5(m+2) A'_{5(m+2)}] = \frac{\gamma}{2\pi b} [A^2_0 + A^2_5], \quad m = 1,2,... . \tag{A15}$$

The system of equations (A3)–(A15) has the nontrivial solution

$$A^1_{5m+1} = A^1_{5m-2} = A^1_{5m+3} = A^1_{5m+4} = 0 \quad m = 0,1,2,3..., \tag{A16}$$

$$A^1_5 = -\frac{4\varepsilon_2 (C/B + \alpha + 1)}{5\varepsilon_1 (\alpha + 1)}, \tag{A17}$$

$$A^1_{10} = 1 - \frac{4\varepsilon_2 (C/B + \alpha + 1)}{5\varepsilon_1 (\alpha + 1)}, \tag{A18}$$

$$\frac{A}{B} = \alpha = \frac{8\varepsilon_2 - 5\varepsilon_1}{12\varepsilon_2 + 5\varepsilon_1}, \tag{A19}$$

$$5(m+1) A'_{5(m+1)} = \tfrac{1}{2} [5m A^1_{5m} + 5(m+2) A'_{5(m-2)}] \quad m = 1,2,3,.... \tag{A20}$$

Here B is an arbitrary constant of which the solutions are independent.

[1] B. Pullmon and A. Pullmon, Prog. Nucleic Acids Res. Mol. Biol. **9**, 327 (1981).
[2] W. R. Gzuen, S. Marcelja, and B. A. Pailthrope, Chem. Phys. Lett. **82**, 315 (1981).
[3] D. C. Rau, B. Lee, and V. A. Parsegian, Proc. Natl. Acad. Sci. U.S.A. **81**, 262 (1984); S. Leiken, D. Leiken, D. C. Rau, and V. A. Parsegain, Phys. Rev. A **44**, 5272 (1991).
[4] See, e.g., G. Binning, Bull. Am. Phys. Soc. **31**, 217 (1986).
[5] Von M. Born, Z. Phys. **45** (1920).
[6] L. Onsager, J. Am. Phys. Soc. **58**, 86 (1936).
[7] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).
[8] T. L. Hill, Arch. Biochem. Biophys. **57**, 229 (1955).
[9] J. Schellman, Biopolymers **16**, 1415 (1977).
[10] D. Hochberg, T. W. Kephart, and G. Edwards, Phys. Rev. E **49**, 851 (1994).
[11] G. Edwards, D. Hochberg, and T. W. Kephart, Phys. Rev. E **50**, R698 (1994).
[12] K. Wagner, E. Keyes, T. W. Kephart, and G. Edwards, Biophys. J. **73**, 21 (1997).
[13] P. J. Lin-Chund and A. K. Rajagopal, Phys. Rev. E **52**, 901

(1995).
[14] D. Hochberg, G. Edwards, and T. W. Kephart, Phys. Rev. E **55**, 3765 (1997).
[15] B. Honig and A. Nicholis, Science **268**, 1144 (1995).
[16] D. Ouroushev, J. Phys. A **31**, 3897 (1998).
[17] D. Ouroushev (unpublished).
[18] D. Ouroushev, Philos. Mag. B **80**, 1473 (2000).
[19] R. A. Waldron, Q. Appl. Math. **XI**, 438 (1958).
[20] J. Louville, J. Math. Pures Appl. **18**, 71 (1853).
[21] I. Gradstein and I. Rijik, Tables of Integrals, Sums, Rows and Products (unpublished).
[22] D. Ouroushev, J. Phys. A **21**, 2587 (1988).