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Notes

Potential of Interaction of a Counterion with the Fixed Charges on DNA

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Introduction

Even short DNA fragments, which resemble rigid cylindrical rods, exhibit dielectric and field on transient optical birefringence experiments with multiple relaxation rates. The general consensus is that the dynamics of the counterion atmosphere is the origin of the multiple dispersion—no consensus appears as to details of the microscopic mechanism.

One could easily suppose that a counterion in the vicinity of the surface of a rodlike DNA oligomer would see a potential that mimics the periodicity of the phosphate charges. Indeed Morita and Watanabe[1] proposed a "diffusion model" in which a counterion moves in a potential where the regularly spaced negative charges on the biopolymer create potential minima with a spacing equal to the separation of the negative charges projected onto the rod axis. A cosine form for the potential was adopted. Morita and Watanabe then solved the Smoluchowski equation for this potential with in addition an applied electric field. The bottom line of this theory is an expression for the polarization as a function of time. A salient feature is the discovery of relaxation modes on different time scales: a short-time process arising from motion within a potential minimum and a slower process resulting from the crossing of the potential maximum. Indeed this model gives microscopic support to a suggestion by Mandel[2] that DNA contains "subunits" in which facile motion is possible with the jump from one subunit to another being more difficult.

Lewis, Pecora, and Eden[3] considered that the Morita and Watanabe model might apply to their transient electric birefringence results (on a nonrigid sample, however) provided the potential wells are deep compared to the thermal energy. In this work we examine the potential experienced by a counterion to see if deep wells with the expected periodicity are present.

Theory

We have developed a microscopic theory of the dynamics of rod–counterion atmosphere assemblies with the aim of fitting experimental dielectric and transient electric birefringence data from our laboratory and from the literature.[4,5] This theory adopts the cylindrical shell model whereby the counterions (of a DNA oligomer) are contained in a cylindrical annulus with length equal to that of the rod and inner radius r_1 = 1.3 nm. The location of the outer radius is immaterial as long as it is large enough so that the number density of finding counterions near the outer boundary is small. We chose r_2 = 52 nm. An ingredient in the theory is the potential V'' of interaction of the counterions (coordinates $\{z_i, \phi_i, r_i\}$) with the n'' fixed (negative) charges of the rodlike biopolymer.

Two expressions for V''/k_BT are

$$\frac{V''}{k_BT} = \sum_{i=1}^{n''} \sum_{k=1}^{n''} \frac{-e^2}{4\pi\epsilon\epsilon_0 k_BT|\mathbf{r}_i - \mathbf{r}_k|} = \sum_{i=1}^{n''} \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} \sum_{k=0} C_{mnk} \cos\frac{m\pi z_i}{L} \exp(in\phi_i) L_{nk}(\omega_{nk} r_i) \quad (1)$$

The term on the right-hand side of eq 1 is the expansion of V''/k_BT in a Fourier–Bessel series. In eq 1 e is the electron charge, ϵ the relative permittivity of water, ϵ_0 the permittivity of free space, k_B Boltzmann's constant, and T the absolute temperature. The basis functions L_{nk} are linear combinations of cylindrical Bessel functions and ω_{nk} roots of the equation defining the L_{nk}.[4] What we are looking for is large values for some of the C_{mnk} for m in registry with the periodicity of the fixed charges. $\{\mathbf{r}_k\}$ are the coordinates of the fixed charges. For the purposes of the present work, we are not really interested in the k dependence, and the test counterion (i = 1 say) can be placed at r_1 = 1.3 nm (on the rod surface). This is the distance of closest approach and gives the best opportunity for strong interactions with the periodic array of phosphate charges. The basis set is reduced to $\{\cos(m\pi z/L), \cos(n\phi)\}$ since $C_{mnk} = C_{m-nk}$. Two expressions were used for the position of the (negative) fixed charges. In addition, a continuous line charge was considered.

The Discrete Line Charge. The negative charges are spaced uniformly along the cylinder axis. In this case the ϕ coordinate plays no role, and $C_{mn} = 0$ if $n \neq 0$. $C_{m0} = C_m$ can be found by projection using Romberg integration.

$$C_m = \sum_{k=1}^{n''} \frac{\epsilon_m}{L} \int_0^L dz \cos\frac{m\pi z}{L} \frac{-e^2}{4\pi\epsilon\epsilon_0 k_BT|\mathbf{r} - \mathbf{r}_k|} \quad (2)$$

where

$$|\mathbf{r} - \mathbf{r}_k| = \{r_1^{\,2} + (z - z_k)^2\}^{1/2} \quad (3)$$

The value of m appropriate to the negative charge spacing is 248, the same as n'' (L = 42.16 nm, t = 25 °C). Some values of C_m are shown in Table I. All C_m for odd m are of order 10^{-6}.

The Double-Helical Charge. The negative charges are spaced uniformly on two helices (180° out of phase) with radius 1.0 nm and a spacing corresponding to the number of base pairs (124 for the fragment considered here). The pitch of the helices is 3.4 nm per turn. Here the ϕ dependence must be considered. Values of C_{m0} and C_{m2} are shown in Table I. Additional values are reported elsewhere.[4] The C_{mn} are found by projection with numerical evaluation of the resulting two-dimensional integrals.

The Continuous Line Charge. Only $n = 0$ contributes. Values of $C_{m0} = C_{mL}$ are shown in Table I.

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Table I
Fourier Expansion Coefficients

m	C_m	C_{m0}	C_{m2}	C_{mL}
0	-2.7336×10^1	-2.7339×10^1	1.604×10^{-2}	-2.7375×10^1
2	3.296	3.162	1.599×10^{-2}	3.369
4	1.530	1.440	1.580×10^{-2}	1.575
6	9.213×10^{-1}	8.568×10^{-1}	1.556×10^{-2}	9.524×10^{-1}
8	6.222×10^{-1}	5.750×10^{-1}	1.528×10^{-2}	6.448×10^{-1}
10	4.490×10^{-1}	4.139×10^{-1}	1.499×10^{-2}	4.658×10^{-1}
20	1.411×10^{-1}			
40	3.607×10^{-2}			
80	8.636×10^{-3}			
124	3.555×10^{-3}	4.18×10^{-3}	-7.92×10^{-4}	3.576×10^{-3}
246	9.038×10^{-4}			
248	8.894×10^{-4}			8.968×10^{-4}
250	8.753×10^{-4}			

Results

The magnitudes of the C_m (or C_{mn}) decrease monotonically with m. There is not much difference between the discrete axial line charge and the double-helical distribution as C_{m2} is a small fraction of C_{m0} and C_{m0} is close to C_m.

The main observation of significance here is that C_{124} (for the double helix) and C_{248} (for the discrete line charge) are not suddenly large, which would indicate a strong role of the phosphate charge periodicity in determining the potential of interaction of a counterion with the fixed charges.

Discussion and Conclusions

We see from the above that V'' does not reflect the periodicity of the fixed charges. A reason for this is that the phosphate–counterion Coulombic interactions are long-ranged and not limited to contributions from a few fixed charges in the vicinity of the counterions.

In fact, the discrete distributions are not significantly different from the continuous line charge that has no inherent periodicity.

The observations are not unique to $r_1 = 1.3$ nm. We repeated the calculations for $r_1 = 5.0$ nm, and the C_m (C_{mn}) showed the same dependence on m and n.

We used for ϵ the relative permittivity of bulk water at 25 °C. One could argue that the value of ϵ is too large as the water molecules close to the DNA molecule are structured and consequently less polarizable. However, a smaller value for ϵ would merely scale the expansion coefficients are not affect their relative values.

A conclusion is that the Morita–Watanabe model calculation is not relevant for describing the counterion dynamics for rodlike DNA.

References and Notes

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(2) Mandel, M. *Mol. Phys.* **1961**, *4*, 489.
(3) Lewis, R. J.; Pecora, R.; Eden, D. *Macromolecules* **1987**, *20*, 2579.
(4) Sonnen, W. E. Thesis, University of Wisconsin—Madison, 1991.
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