Macromolecules **1980**, *13*, 711–716

Charged Macromolecules in External Fields. 2. Preliminary Remarks on the Cylinder[‡]

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Received November 28, 1979

ABSTRACT: The torque on the cylinder induced by a weak steady electrical field is calculated as a function of salt concentration. Numerical approximations, such as the assumption of a thin double layer, preclude a conclusive comparison with experiment. However, arguments are given to justify the qualitative applicability of the results at low salt concentrations. A preliminary comparison with experimental results on DNA gives encouraging agreement. The theoretical result in the limit of low salt concentrations is similar but not identical to the result for conducting rods in nonconducting media. A dependence on counterion charge persists in this limit. At finite salt concentrations a leakage of counterions through the double layer reduces the induced dipole moment. A brief analysis is given of the torque on an object with a permanent charge anisotropy, with respect to which the solution charge maintains equilibrium; i.e., the field induced anisotropy of the diffuse layer is artificially suppressed. The long ranged electrostatic potential is then screened, and consequently the torque is proportional to the moment of the ζ potential rather than to the moment of charge.

I. Introduction

Our objective in this work is to calculate the torque on a charged cylinder in a weak, steady, external electric field. The cylinder is smooth and is charged to a uniform surface density. The calculations are based on the boundary conditions derived in the preceding paper[1] and therefore are restricted in principle to thin double layers. However, arguments are given to justify a wider range of application for the results, and a comparison is made with experiments[2] that violate the restrictions. Reasonably good agreement is found.

The basis of the torque calculation is a determination of the long range (unscreened), electric dipole field of the cylinder, induced by the external field. The corresponding induced dipole moment of the macroion might seem to lead also to a result for the dielectric increment. Such an inference is often found in the literature,[3] and is no doubt permissible for nonelectrolyte solutions. However, as we have remarked in the preceding paper, the steady state dipole moment in conducting solutions leads only to the increment in steady state conductivity, and to (part of) the torque if the polarizability is anisotropic. The effects of a time dependent field have to be considered in order to calculate the dielectric increment, even the steady state value.[4] We have postponed the introduction of oscillating fields in the cylinder problem to avoid heavy numerical work in this preliminary study. However, if the double layer is thin the numerical problem comes down to the solution of a one-dimensional integral equation. Given the encouraging agreement with experiment for the steady state problem, this effort is certainly worthwhile. Most of the numerical problems are caused by the dependence of fields on translational position along the cylinder and attendant "end" effects. These effects will presumably disappear at high frequencies because of the exponential decay of diffusional Green's functions.

In section II the electrostatic problem is solved subject to the previously mentioned restrictions. The electrostatic potential obeys an integral equation which is similar to that for a conducting rod in an insulating fluid. Passage of counterions through the double layer modifies the equation and reduces the induced dipole moment. In section III the electrical and hydrodynamic contributions to the torque are considered. The total torque is invariant to the choice of surface on which the moment of force is computed, but the relative contributions are not. For a surface at infinity the hydrodynamic torque is concluded to be negligible if there is a long ranged (unscreened) electric dipole field. The latter vanishes if charge displacement in the diffuse layer due to the applied field is suppressed, even if the macroion has a permanent charge anisotropy. The present calculation does supply a long ranged field, and the associated torque is compared with experimental results for DNA. Since the calculation of counterion flux through the double layer is based on a boundary value approach and is strictly valid only if the Debye length is less than the macroion's radii of curvature, the comparison with experiment has mainly heuristic value. However, the counterion flux decreases with decreasing salt concentration, and it is reasonable to hope that moderate quantitative errors in the flux calculation will cause only small errors in the torque.

A nonquadratic dependence of the torque on the applied field may well be an important feature of some studies of DNA,[5] but our own calculations are restricted to weak fields. There are many potential sources of nonlinearity. Perhaps the favorite for theoretical study has been saturation of the displacement of bound or condensed counterions.[6] We have to add to that a consideration of the interaction between solvent flow and gradients of *neutral* salt concentration. It is a feature of the work in the preceding paper and this one that these gradients extend well out beyond the double layer. In the steady state the perturbations in salt concentration decay with distance at the same rate as the dipole potential itself, i.e., as r^{-2}.

II. Induced Dipole Moment

The previously established boundary conditions on the "far field" velocity potentials are[1]

$$\bar{C}_1\, \partial p_1/\partial b + \epsilon_1 \nabla_t^2 p_1 = 0 \qquad \text{(II.1)}$$

and

$$\partial p_2/\partial b = 0 \qquad \text{(II.2)}$$

Counterions are designated by subscript 1 and coions by subscript 2. The derivative with respect to b is a normal derivative; tangential derivatives are indicated by subscript t. These boundary conditions apply only to thin double layers, and the derivation was further restricted by the requirement that ϵ_1, the excess number of counterions over the extrapolated value per unit area of the double layer, is much larger than ϵ_2. At uncharged elements of surface both velocity potentials must have a vanishing normal

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[‡] Supported in part by NIH GM 13556 at Yale University and NIH GM 27945 at Colorado State University.

0024-9297/80/2213-0711$01.00/0

derivative. We have also supposed that the two species of mobile ions have the same friction constant β. $\bar{C}_i$ is the bulk concentration of i. The velocity potentials were related to a concentration potential h and the perturbation Φ in the electrostatic potential by

$$p_i = h + (q_i/k_BT)\Phi \qquad \text{(II.3)}$$

where q_i is the charge on i. The equations describing h and Φ are those that apply outside the double layer, an ordinary diffusion equation for h and Laplace's equation for Φ.

We now wish to apply the equations summarized above to the problem of a cylinder in a constant external electric field imposed parallel to the cylinder axis. A perpendicular component of the field is of course required to produce a torque on the molecule, but we assume that any distortion of the solution charge density is produced by the parallel component (a calculation along the lines of those in the preceding paper indicates that this is a good approximation for thin double layers). Our objective in this section is to calculate the induced dipole moment of the double layer charge distribution. In the next section the relationship of this dipole moment to the torque is considered. Since we are dealing with a time independent field, the diffusion equation for h reduces to Laplace's equation, which is obeyed by all the fields under consideration. Equations II.1 and II.2 at the charged elements of surface, $(\partial p_i/\partial b) = 0$ at the uncharged elements of surface, and $h \sim 0$ and $\Phi \sim -E_0z$ at infinity complete the boundary conditions required in principle to determine all fields.

Before setting about the practical business of actually constructing a solution, we wish to relate the perturbation ρ_a in solution charge density, i.e., charge/cm^2, to $(\partial\Phi/\partial b)$. This is a limiting value as the surface is approached from outside the double layer. Now Poisson's equation gives a discontinuity in $(\partial\Phi/\partial b)$ across the double layer equal to $-4\pi\rho_a/D$, where D is the dielectric constant, and a further discontinuity on passage into the interior of the molecule, where the dielectric constant is taken to be D_I:

$$D\,(\partial\Phi/\partial b)_+ = D_I\,(\partial\Phi/\partial b)_- \qquad \text{(II.4)}$$

$$(\partial\Phi/\partial b) - (\partial\Phi/\partial b)_+ = -4\pi\rho_a/D \qquad \text{(II.5)}$$

where + and − indicate limits at the cylinder boundary where the dielectric constant changes from D to D_I. Therefore

$$\partial\Phi/\partial b = -(4\pi\rho_a/D) + (D_I/D)\,(\partial\Phi/\partial b)_- \sim -(4\pi\rho_a/D) \qquad \text{(II.6)}$$

In the last step we have discarded the displacement vector in the interior region of the cylinder normal to the surface of interest. At most it constitutes an end correction, and it should be a negligible end correction at that, because $D_I/D \ll 1$ for systems of interest here. We may immediately conclude that the perturbed surface charge is confined to the cylinder sides, since all the far fields have vanishing normal derivatives at the butt ends. It may also be noted that ρ_a can be determined from the p_1 field, since eq II.2 and II.3 give

$$\frac{\partial p_1}{\partial b} = \left(\frac{q_1 - q_2}{k_BT}\right)\frac{\partial\Phi}{\partial b} \qquad \text{(II.7)}$$

Thus further attention may be confined to the velocity potential p_1 of the counterions, which obeys Laplace's equation with the previously stated boundary conditions on the surface and at infinity.

It has seemed convenient to express p_1 in terms of its asymptotic form and a field Φ_P that has the dimensions of the electrostatic potential, vanishes at infinity, and has a normal surface derivative simply related to the charge density. Thus

$$p_1 = -(q_1/k_BT)E_0z + [(q_1 - q_2)/k_BT]\Phi_P \qquad \text{(II.8)}$$

defines Φ_P. The boundary condition on the surface follows from eq II.1, II.6, and II.7. On the sides, where the external field has a vanishing normal component,

$$\partial\Phi_P/\partial a = -4\pi\rho_a/D \qquad \text{(II.9)}$$

$$\bar{C}_1\,(\partial\Phi_p/\partial a) + \epsilon_1\,(\partial^2\Phi_P/\partial z^2) = 0 \qquad -L \le z \le L \qquad \text{(II.10)}$$

We have introduced the cylinder radius a, which also serves to specify a value on the curved surface of the cylinder. L is half the length of the cylinder. Note that eq II.10 is the boundary condition. Equation II.9 merely expresses the quantity of ultimate interest, ρ_a, in terms of the Φ_P. The tangential derivative reduces to a z derivative because of axial symmetry. On the butt ends, which point in the z direction, the external field does contribute to the boundary condition, namely

$$\partial p_1/\partial z = -(q_1/k_BT)E_0 + [(q_1 - q_2)/k_BT]\,\partial\Phi_P/\partial z = 0 \qquad z = \pm L \qquad \text{(II.11)}$$

We have already remarked that ρ_a vanishes on the butt end; eq II.9 does not apply there.

Equation II.10 is incomplete as it stands, since the presence of a second derivative allows for two integration constants. The equation is readily completed with the observation that p_1 and Φ_P have continuous derivatives because they satisfy Laplace's equation. Therefore the limit of $(\partial p_1/\partial z)$ on the curved surface at $z = \pm L$ must agree with its vanishing value on the butt ends.[7] Therefore eq II.11 is not only obeyed for the normal derivative on the butt ends, but also for the limiting value of the tangential derivative on the curved surface, as z reaches either end.

The problem now comes down to the calculation of a potential Φ_P that satisfies Laplace's equation, eq II.9–II.11, and vanishes at infinity. A numerical study of the problem is underway, but for the present several approximations will be made. We begin with an approximate Green's function solution to Laplace's equation:

$$\Phi_P(z) = (2\pi D)^{-1}\int_{-L}^{L} dz' \int_0^{2\pi} d\varphi\, R^{-1}\nu(z') \qquad \text{(II.12)}$$

where

$$R^2 = (z - z')^2 + |\mathbf{a} - \mathbf{a}'|^2 = (z - z')^2 + 4a^2 \sin^2 \tfrac{1}{2}\varphi \qquad \text{(II.13)}$$

and

$$\nu = 2\pi a\rho_a \qquad \text{(II.14)}$$

Thus ν is the linear charge density. The approximation made here is first the use of R^{-1} in place of the proper Green's function that has a vanishing normal derivative on the cylinder surface. This Green's function is coincidentally the same as the potential of a point charge outside a cylinder of vanishing dielectric constant. Only the cylindrically symmetric part of the Green's function is required in eq II.12, and its Fourier transform is fairly easy to evaluate.[8] For large R (small wave numbers), the error is indicated to be small. We have also suppressed, in eq II.12, an integration of the normal derivative of Φ_P over the butt ends.

The integral in eq II.12 occurs in the theory of conducting cylinders in a parallel field[9] and may be approximated by

$$D\Phi_P(z) = \nu(z)\ln\left[\frac{4(L^2 - z^2)}{a^2}\right] + \int_{-L}^{L}\frac{\nu(z') - \nu(z)}{|z - z'|}\,dz' \qquad \text{(II.15)}$$

if $L \gg a$ and $L - |z| \gg a$. To obtain guidance in the general situation we first consider a special case in which our problem reduces completely to that of the conducting cylinder. This is the situation for very large ϵ_1. Then eq II.10 shows that $\partial^2\Phi_P/\partial z^2 = 0$, and Φ_P is linear in z. The boundary condition (eq II.11) then establishes the proportionality constant between Φ_P and z:

$$D\Phi_P(z) = [q_1E_0/(q_1 - q_2)]z \qquad \text{(II.16)}$$

With Φ_P proportional to z, eq II.15 is the same as obtains for a conducting needle in a parallel field, and the integral in eq II.15 is a small correction to the first term on the right-hand side. The integral may then be evaluated in zeroth approximation,[9] i.e., ν proportional to z, as $-2\nu(z)$. Thus

$$\nu(z) = D\Phi_P(z)\left(\ln\left(\frac{4(L^2 - z^2)}{a^2}\right) - 2\right]^{-1} \qquad \text{(II.17)}$$

Equations II.16 and II.17 give $\nu(z)$, and its moment is found to be

$$\mu = \int_{-L}^{L} z\nu(z)\,dz = [E_0Dq_1/(q_1 - q_2)]L^3/[3\ln(4L/a) - 7] \qquad \text{(II.18)}$$

For the general case where ϵ_1 is not assumed to be large enough to make Φ_P proportional to z, we will still assume an approximate proportionality between ν and Φ_P.

$$\nu(z) = KD\Phi_P(z) \qquad K \sim [2\ln(L/a)]^{-1} \qquad \text{(II.19)}$$

K is introduced as part of the proportionality constant. Its indicated asymptotic value derives from eq II.17, but the final value of K for finite L will be determined from the requirement that eq II.18 is recovered for $\epsilon_1 \to \infty$. An examination of these approximations will be given after eq II.23. It follows from eq II.9 and II.10 that

$$\partial^2\Phi_P/\partial z^2 = \gamma^2\Phi_P \qquad \text{(II.20)}$$

where

$$\gamma^2 \equiv 4\pi\bar{C}_1K/\epsilon \qquad \epsilon \equiv 2\pi a\epsilon_1 \qquad \text{(II.21)}$$

Here ϵ is the number of "bound" counterions/centimeter. The solution of eq II.20 is

$$\Phi_P(z) \propto \sinh(\gamma z) \qquad \text{(II.22)}$$

The proportionality constant in eq II.22 follows from the end point condition, eq II.11, and eq II.19 then gives

$$\nu(z) = KD[q_1/(q_1 - q_2)]E_0\sinh(\gamma z)/(\gamma\cosh(\gamma L)) \qquad \text{(II.23)}$$

The derivation of eq II.23 was based on the approximation that ν varies with z in proportion to $\Phi_P(z)$. The consistency of this approximation can be examined in retrospect through substitution of $\sinh(\gamma z)$ for $\nu(z)$ in eq II.15, numerical integration, and inspection of the ratio ν/Φ_P. The ratio was found to vary by no more than ±7% for $0 < |z/L| < 0.99$, for $\gamma L < 3.5$. This is the largest value of γ (corresponding to the largest value of $\bar{C}_1$), for which a comparison with experiment is made below. For still higher counterion concentrations the approximation worsens rapidly, and a numerical solution of the integral equation for $\nu(z)$ would have to be performed. (We are attempting such a solution and alternative numerical approaches which fully satisfy the boundary conditions on all elements of the cylinder surface.)

The dipole moment of the charge distribution (eq II.23) is found to be

$$\mu = \frac{2E_0q_1KDL}{(q_1 - q_2)\gamma^2}\left[1 - \frac{\tanh(\gamma L)}{\gamma L}\right] \qquad \text{(II.24)}$$

Comparison of this result with eq II.18 in the limit $\gamma \to 0$ gives

$$K = [2\ln(4L/a) - 14/3]^{-1} \qquad \text{(II.25)}$$

It turns out that the polarizability inferred from eq II.24, namely μ/E_0 (for a parallel field), may properly be compared with the polarizability used in the interpretation of electric dichroism or birefringence measurements. That is, the torque on the cylinder is $\mu \times \mathbf{E}_0$, where $\mathbf{E}_0$ now includes the perpendicular component of the external electric field. This result depends on the neglect of counterion polarization by the electric field perpendicular to the cylinder and also on neglect of the hydrodynamic torque. We have mentioned that the calculation of a perpendicular polarizability for thin double layers is quite similar to the calculation of the preceding paper[1] for spheres in the low-frequency limit. The result is indeed small (for a cylinder of small radius). The hydrodynamic torque is taken up in the next section.

III. Torque

The perpendicular component of the applied field may exert a torque on either the dipole moment induced by the parallel component or on a permanent dipole moment parallel to the cylinder axis, if such a moment is present. Since we are neglecting distortion of the solution charge density induced by the perpendicular field, the latter will simply be the applied part $\mathbf{E}_\perp$ plus a dipole correction proportional to[10] $(\nabla\nabla\ln r)\cdot\mathbf{E}_\perp$. The proportionality constant is chosen to make the normal part of the displacement vector, or rather its perturbation from equilibrium, continuous across the cylinder surface.

The torque is the moment of $\sigma\cdot d\mathbf{S}$ integrated over all elements $d\mathbf{S}$ of the polymer surface. σ is the total stress $\sigma^H + \sigma^E$. The polymer surface may be replaced by any surface that encloses it. Because our method of calculation has focused on the inference of asymptotic forms from boundary conditions on the double layer, it is advantageous to replace the polymer surface by a spherical surface of very large radius. Corresponding to the two stresses on this surface are the hydrodynamic and electric torques, $\mathbf{K}^H$ and $\mathbf{K}^E$, respectively.

Consider first the electrical torque. The electrical stress is bilinear in the electrical field, and any contribution to $\mathbf{K}^E$ arises from the cross terms involving the applied field $\mathbf{E}_0$ and the perturbation field induced by the cylinder. The latter must be a dipole field varying as[10] $\nabla\nabla R^{-1}$ to contribute to $\mathbf{K}^E$. Now we have found that the parallel component of $\mathbf{E}_0$ creates a dipole moment of the double layer, and with it a dipole field at infinity. The usual formula

$$\mathbf{K}^E \equiv \int \mathbf{R} \times (\sigma^E\cdot d\mathbf{S}) = \mu \times \mathbf{E}_0 \qquad \text{(III.1)}$$

with μ the moment computed in section II, is readily verified.

That $\mathbf{K}^E$ is nonvanishing depends entirely on (a) the absence of screening outside the double layer and (b) the existence of a nonvanishing total charge density $\rho_a(z) + \rho_S$. ρ_a is the complete solution charge/square centimeter in the (thin) double layer, and ρ_S is the macroion charge/square centimeter. For several common models (characterized by an equilibrium distribution of the diffuse layer of counterions with respect to the inner layer and polymer charge), this total charge density does vanish, and with it the electrical torque. We examine this problem below and then return to the results of section II, which allow for a net polarization of the double layer, for a comparison with experiment. It should be kept in mind in the following that a permanent moment is linear in E_0, and an induced moment is quadratic.

A. Screened Potentials. Consider an anisotropic polymer charge $\rho_S(z)$, with respect to which all solution ions (are artificially forced to) maintain an equilibrium distribution. Accordingly, ρ_S is neutralized within about a Debye length by mobile solution charges. The electrostatic potential due to the polymer charges is therefore screened and vanishes outside the double layer. Since the solution charge is assumed to be unperturbed by an applied field, in this model, the total field is simply the sum of the equilibrium and applied fields (again neglecting the small correction due to $D \neq D_I$). The screened potential obviously vanishes exponentially at infinity, and $\mathbf{K}^E = 0$. That is, there will be *no* electrical torque on a permanent dipole in salt solution in an applied field, if the equilibrium solution charge is not perturbed by it. (But the total torque does not vanish; see below.)

An identical conclusion can be drawn for those models of symmetrically charged cylinders (i.e., $\rho_S(z)$ is constant) which allow for distortion of the "condensed" or inner counterion layer by a parallel applied field but assume that the diffuse layer maintains equilibrium with the perturbed inner layer.[11,12] (This last assumption is implicit in the use of Debye–Hückel screened interactions between different parts of the inner charge layer, i.e., condensed ions plus ρ_S.) Again one concludes that $\mathbf{K}^E = 0$ because the screened potential drops off exponentially with distance.

That $\mathbf{K}^E$ vanishes for screened potentials is not quite so paradoxical as it may first appear. The total torque includes the hydrodynamic part $\mathbf{K}^H$, and this may not vanish. Moreover, $\mathbf{K}^E$ itself may not vanish if computed on the polymer surface rather than on the surface at infinity. Only the total torque $\mathbf{K}^H + \mathbf{K}^E$ is required to be invariant to the choice of surface, because only the total force density on the solution $\nabla\cdot(\sigma^H + \sigma^E)$ vanishes, and not the separate hydrodynamic and electrical contributions. Nevertheless, the vanishing of $\mathbf{K}^E$ on the distant surface is a warning against the simple transfer of formulas from nonelectrolytes to electrolytes. For electrolytes one has to consider solvent flow, as is well known in the theory of electrophoresis.

We will now give an elementary analysis of $\mathbf{K}^H$ for thin double layers, analogous to the calculation of electrophoretic velocities.[13] The electrical force density on the solution is $\rho\mathbf{E}$, where ρ is the solution charge density and vanishes outside the double layer. The electrical force perpendicular to the polymer surface is assumed to be compensated by a pressure gradient and the tangential part by a viscous shear resistance. The object of the calculation is to obtain the solvent velocity just outside the double layer. This velocity will be a boundary condition on the far field velocity, from which forces and torques can be computed by integration over a surface at infinity. Within the thin double layer the tangential component of velocity varies rapidly with the perpendicular distance b from the polymer surface and slowly with respect to the coordinates z and φ. So derivatives with respect to the latter coordinates may be omitted from the Navier–Stokes equation, and

$$\eta\, \partial^2\mathbf{v}_t/\partial b^2 = -\rho\mathbf{E}_t = (D/4\pi)\,(\partial^2\Psi^e/\partial b^2)\,\mathbf{E}_t \qquad \text{(III.2)}$$

To first order in the applied field, ρ is the equilibrium charge density and $\mathbf{E}_t$ is the perpendicular component of the applied field, plus a dipole correction due to $D \neq D_I$. Equation III.2 is applied to the interval $0 \le b \le B$, where B is the width of the double layer. Within this interval $B \ll a$, the field $\mathbf{E}_t$ is approximately constant. The surface of shear where $\mathbf{v}_t(b) = 0$ occurs at $b = 0$. (This point may be chosen to lie outside the polymer surface if one wishes to allow for a layer of immobilized solvent.) Multiplication of eq III.2 by b and integration over the interval gives, with the assumption that derivatives of $\mathbf{v}_t$ and Ψ^e vanish at $b = B$,

$$\mathbf{v}_t(B) = -(D/4\pi\eta)\zeta\mathbf{E}_t \qquad \text{(III.3)}$$

where ζ is the "zeta potential", i.e., Ψ^e evaluated at $b = 0$.

We assume that the ζ potential depends at most on z but not on φ. Then an angular average of eq III.3 over φ eliminates the dipole part of $\mathbf{E}_t$ and gives

$$\langle\mathbf{v}_t(B)\rangle = -(D/4\pi\eta)\zeta\mathbf{E}_\perp{}^0 \qquad \text{(III.4)}$$

If $\zeta(z)$ is constant with respect to z, the velocity field outside the double layer which satisfies eq III.4 on the cylindrical boundary $r = a + B$ (or just $r = a$ given that B is small) is the constant velocity $\mathbf{v}_\infty(\mathbf{r}) = \langle\mathbf{v}_t\rangle$, which is in turn equal to $-\mathbf{V}_c$. Under this circumstance the macroion moves with the constant electrophoretic velocity and the force acting on the macroion vanishes. If $\zeta(z)$ has a part $\zeta(z) = \zeta' z$, $-L \le z \le L$, with ζ' constant, then the boundary velocity also varies linearly with z. The boundary value problem for the velocity outside the double layer is then identical with that for a cylinder rotating with angular velocity Ω placed in a fluid at rest, with Ω given by

$$\Omega = -\langle\mathbf{v}_t(B)\rangle/z = (D/4\pi\eta)\zeta'|\mathbf{E}_\perp{}^0| \qquad \text{(III.5)}$$

The hydrodynamic torque on such a cylinder is the same on every surface that encloses it, since there is no applied electric field or electrical torque, and is equal to the hydrodynamic torque on the distant surface for our charged cylinder in the external field. Introduction of the torque proportional to Ω gives the following formula:

$$\mathbf{K} = \mu_P \times \mathbf{E}_0 \qquad \text{(III.6)}$$

where $\mathbf{K}$ is the *total* torque on the cylinder and μ_P is the apparent "dipole moment" parallel to the cylinder axis

$$\mu_P \sim 2D\zeta' L^3/3 \ln (L/a) \qquad \text{(III.7)}$$

The limitations of this formula should be recalled. It is derived for a long cylinder with a thin double layer and a permanent anisotropy of charge that gives a constant gradient in the ζ potential. Distortion of the solution charge distribution is omitted (of course if we are interested only in weak applied fields and a torque linear in the field, this assumption is quite justified).

Further consideration of the relationship between the ζ potential and the polymer surface charge density demonstrates that the apparent dipole moment given in eq III.7 is much less than the actual dipole moment of an anisotropic distribution. Our conclusions are, to be sure, somewhat limited by the restriction to thin double layers, i.e., high salt concentrations, for which the ζ potential is fairly close to its Debye–Hückel form. But one then finds that ζ' is proportional to the Debye length, and so decreases with increasing salt concentration, and has a ln (L/a) in the denominator in comparison with the actual moment of charge.

Although eq III.7 was derived for a permanent charge anisotropy, it should also be applicable to certain models of an induced dipole moment. In eq III.7 the solution charge distribution outside the surface of shear was as-

Table I
Parallel Component of Polarizability (10^{-15} cm^3) vs. Molar Salt Concentration for 1-1 and 2-1 Salts[a]

	1-1 salt		2-1 salt	
$\bar{C}_1$	theory	expt	theory	expt
0	2.87	2 ± 1	3.82	6 ± 2
10^{-4}	2.70		3.40	
10^{-3}	1.78		1.72	
2×10^{-3}	1.29		1.12	0.6 ± 0.2
8×10^{-3}	0.50	0.8 ± 0.3	0.37	
10^{-2}	0.42		0.30	
10^{-1}	0.05		0.03	

[a] Experimental results (for the difference in parallel and perpendicular components), from Hornick and Weill[2] for DNA of length 1800 Å.

sumed to be in equilibrium with any (anisotropic) distribution of charge inside the surface of shear. It makes no differences whether the latter is permanent or induced. So the result applies to any model which assumes, implicitly or explicitly, this sort of equilibrium in the diffuse layer. We stress, however, that the results of section II indicate that this assumption is quite erroneous.

B. Unscreened Potential. As we have remarked, the results of section II give a distortion of the total solution charge in the double layer and an unscreened dipole potential at large distances from the cylinder. So there is an electrical torque given by $\mu \times \mathbf{E}_0$, with μ given approximately by eq II.22. We have still to consider whether the perturbation in charge $\Delta\rho$ induced by the parallel field leads to a significant shearing force $\mathbf{E}_t\Delta\rho$ on the solution that in turn gives rise to a hydrodynamic torque. Now $\Delta\rho$, although a nonequilibrium charge density, is still related by Poisson's equation to the perturbation in potential Φ. So the analysis based on eq III.2 can be repeated, with Φ replacing Ψ^e. We have continuity of Φ and discontinuity of $\partial\Phi/\partial b$ across the double layer, so qualitative differences from eq III.3 arise. $\mathbf{v}_t$ is found to be proportional to the perturbation ν and $\mathbf{E}_t$, but also to the Debye length B, which has consistently been treated as a small quantity. We tentatively conclude that $\mathbf{K}^H$ is negligible under the conditions of our analysis, i.e., for the cylinder without a permanent moment, but with a highly charged, thin double layer.

C. Comparison with Experiment. The theoretical polarizability calculated in section II will now be compared with experimental results on DNA rods. We preface this comparison with a brief summary of the approximations underlying the theoretical result.

The most fundamental approximation occurred at the beginning, where the Smoluchowski mean field theory was postulated. We have elsewhere argued that the equilibrium limit of this theory (the Chapman–Gouy or Poisson–Boltzmann equation) is a good approximation for the low salt concentrations to be considered. The dynamical generalization is not especially suspect, in our view, for the low-frequency applications characteristic of polymer problems.

Next a very simple model of the system has been used. The macroion is an impenetrable dielectric object with a smooth surface distribution of charge. Solution properties such as dielectric constant, viscosity, and so on have been assumed homogeneous. Only electrostatic interactions between solution and polymer have been allowed. Our attitude here is heuristic; first learn to deal with simple things.

Finally, two numerical shortcuts have been taken. The double layer has been assumed thin, and the integral equation for the perturbed charge distribution in the double layer has been solved crudely. The first of these shortcuts is obviously suspect at low salt concentrations, and the second was seen to be erroneous at high salt concentrations. So it may seem that a comparison with experiment is questionable at any salt concentration. We will nevertheless make a comparison for two reasons. First, it will take a great deal of numerical effort to remove the first approximation, especially, and one would not wish to make this effort without some indication that the results will be experimentally relevant. Second, we do not expect that the numerical work will lead to qualitatively different results. We have already mentioned a check on the integral equation solution that indicates its acceptability at the highest experimental salt concentration. (Results for still higher salt concentrations are tabulated in Table I; these results *are* suspect.) The other approximation, that the double layer is thin compared to the cylinder radius, is invalid for any of the experimental concentrations in Table I. However, we believe that the theory actually makes little use of this approximation at low salt concentrations. The approximation enters the calculation of counterion flux into and out of the double layer and the attendant reduction in induced dipole moment. But the flux was found to vanish at low salt concentrations, and it is at least a reasonable hope that this qualitative conclusion will not be upset by better numerical work. Most of the charge *is* near the cylinder, even at $\bar{C}_1 = 0$.

Table I gives the theoretical polarizability μ/D_0 from eq II.22 for rods of length 1800 Å and radius 12 Å, in comparison to Hornick and Weill's[2] data on DNA of the same length. ϵ, the number of counterion charges per unit length, was taken to be the same as the number of phosphate charges per unit length (1/1.7 Å) for 1–1 salts and half that for 2–1 salts ($MgCl_2$). We consider the agreement sufficient to warrant a more extensive study of the calculations initiated here. More recent experiments[14] show some significant differences from the experimental results that we have used, if we accept literally the reported experimental error estimates.[2]

Acknowledgment. For discussions or comments on preliminary drafts we are indebted to E. Charney, D. Crothers, T. Odijk, S. Jagannathan, J. Skolnick, and D. Stigter. We also want to note, on the occasion of his 70th birthday, our debt to Professor Paul J. Flory. We treasure his character not less than his works, and thank him for both.

Addendum

(1) The discussion of torques in this paper is not self-contained. The preceding work[1] supplies more detail about several points here taken for granted, such as the freedom to calculate the torque on any surface enclosing the macromolecule.

(2) The boundary conditions, eq II.1 and II.2, were derived[1] from constancy, across the double layer, of tangential components of vectors such as the diffusional velocity field ∇p_i. But this constancy has seemingly paradoxical consequences when applied to spontaneous fluctuations of concentration. Specifically, constancy in the tangential derivative of the chemical part h_i of the electrochemical potential $p_i = h_i + (q_i/k_BT)\Phi$ implies that the (tangential variations of) relative concentration fluctuations are the same, inside and outside the double layer. The paradoxical aspect is that one thinks of the two fluctuations, inside and outside, as independent.

A response to this line of thinking must begin with the Smoluchowski equation itself, which associates a diffusional flux with a concentration gradient. This association of velocity and concentration fluctuations would be nonsensical for instantaneous fluctuations. As is well known, the association applies only to concentration fluctuations smoothed over a velocity relaxation time (less than a picosecond for the mobile ions). If we examine the relative concentration fluctuations on the two sides of a plane of discontinuity in the equilibrium (mean) concentration, we would require identity in the tangential derivatives to be established only after one or a few velocity relaxation times. So much is implicitly assumed at the very beginning, when we write down the Smoluchowski equation.

The constancy that we have used in the derivation of boundary conditions at the surface of thin double layers goes further than a requirement of continuity across a plane. We require that the tangential components of ∇p_i are constant along the normal to a finite, albeit thin, double layer. Proof of this constancy in $\nabla_t p_i$ must follow the mathematically identical inference for the electrical analogue (constancy of the tangential part of the electrical field). What is required in these derivations is smoothness, i.e., approximate constancy, in all three components of ∇p_i over tangential displacements large compared to the thickness of the double layer. It is not excluded, indeed it is expected, that the normal component $\mathbf{n}\cdot\nabla p_i$ will vary rapidly across the double layer; only tangential variation of $\mathbf{n}\cdot\nabla p_i$ must be smooth. It is a consequence of this condition of tangential smoothness, for p_i and h_i as well as for Φ, that the tangential derivatives of all three quantities are constant with respect to displacements normal to the double layer. Achievement of tangential smoothness in ∇p_i, or in its individual parts ∇h_i and $\nabla \Phi$, will require a time interval which will be much larger than the velocity relaxation time. It will be the time for a salt ion to diffuse over distances large compared to the Debye length, i.e., it will be the Maxwell relaxation time. As we noted at several earlier points in the discussion,[1] our calculations are restricted to processes slow on that time scale.

In conclusion, any paradox arising from intuition about coupling or lack of it, between instantaneous (equilibrium) concentration fluctuations inside and outside the double layer, has little bearing on the dynamical calculations which are the subject of this work.

References and Notes

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Molecular Dissection of an Enzyme that Recognizes Transfer RNA[1]

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Received November 29, 1979

ABSTRACT: An analysis of one member of a class of enzymes—aminoacyl-tRNA synthetases—is being carried out. For this purpose a dissection of the polypeptide chain and of the gene for the enzyme is done, making heavy use of recombinant DNA technology. The enzyme Ala-tRNA synthetase specifically attaches alanine to alanine specific transfer RNA chains in the first step of protein biosynthesis. It is a tetramer of a 95 000 dalton polypeptide chain. Sites for the amino acid activation reaction, whereby ATP and alanine condense to form alanyladenylate, have been localized to the amino terminal half of the protein. The gene (*alaS*) for the protein has been cloned with a pBR322 vector and a restriction enzyme map has been constructed of the recombinant plasmid. With the gene in hand it is possible to manipulate the polypeptide structure through a scheme which gives localized mutagenesis at defined sites in the gene. In this way, and with an appropriate selection scheme, enzyme molecules with altered tRNA recognition specificity can be constructed. Rapid DNA sequencing permits ready identification of polypeptide chain sequences (deduced from the DNA sequences) and a quick determination of the nature of any mutations that are introduced.

Aminoacyl-tRNA synthetases catalyze the first step in protein synthesis whereby amino acids are attached to their cognate transfer RNA chains according to the reactions[3]

0024-9297/80/2213-0716$01.00/0