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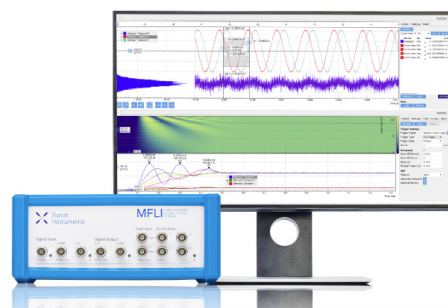
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The Poisson-Boltzmann equation and its application to polyelectrolytes^{a)}

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The validity of the Poisson-Boltzmann (PB) equation is reconsidered on the basis of functional expansion techniques supplemented by the mean spherical approximation. In the application of greatest interest a strong Coulomb potential originating in an external source, such as a polyelectrolyte molecule, acts on a salt solution of small mobile ions. Where the local charge density of mobile ions is high, substantial errors may occur in the PB approximation that relates charge density to mean potential. However, the solution to the PB equation is nevertheless a good approximation in the indicated application because a quite small percentage change in the electrostatic potential can compensate large errors in the Boltzmann distribution. An application to DNA illustrates this compensation, and also its impending failure at bulk salt concentrations in excess of 0.1M. A two phase (or condensation) model is derived as an approximation to the PB equation and retains fair accuracy even at substantial salt concentrations, where the limiting laws lose theoretical validity.

I. INTRODUCTION

At least five main themes may be discerned in the theoretical study of polyelectrolytes that are charged to potentials beyond the domain of validity of the Debye-Huckel equation: (1) the Poisson-Boltzmann (PB), or Gouy-Chapman equation, its validity,¹ and its application to special models² or dilute solutions³; (2) the limiting laws of Manning, their origin, and application⁴; (3) the two phase model of Oosawa,⁵ and the notion of counterion condensation^{4,5}; (4) cluster expansions,⁶ intended as a theoretical framework more fundamental than the PB equation or its feasible improvements; and (5) modifications of theory, in any of the preceding contexts, to accommodate ion-specific interactions.⁷ The classification is truncated and overlapping, but will serve to identify the objectives of this work. Our first objective is to reconsider, on the basis of functional expansion techniques⁸ (a now classical alternative to infinite cluster summations), the validity of a generalized PB equation. The generalization consists in allowing for non-Coulombic parts of the potential in the formal stage of analysis. The errors are concluded to be small or, more precisely, inconsequential in applications of greatest interest. Secondly, we show that a certain version of the two phase model may be derived from the PB equation. Moreover, approximations introduced to facilitate numerical solution of the two phase model retain reasonable agreement with the PB equation, as judged by a direct comparison of potentials, or by the more sensitive calculation of salt exclusion coefficients.

If the PB equation is once accepted, in either its simplest form or as elaborated to account for specific interactions, any alternative formulation such as a two phase model must be regarded as an approximation made for special purposes. These purposes will generally stem from the relative calculational simplicity of the model equation or its solution. For problems with simple geometry, one dimensional problems or problems with spherical or cylindrical symmetry, the PB equation is sufficiently easy to solve numerically that approxima-

tions to it offer only minor benefits. However, the symmetry is destroyed for curved cylinders such as the worm model, and significantly modified even for finite straight cylinders, especially when the latter are in strong external fields. For many of these complicated problems, the calculational simplification achieved by a two phase model is probably still necessary. We would nevertheless stress that the PB approximation, if adequate, is both simpler to formulate and more general in its consequences than any particular conclusion, such as counterion condensation, that may be drawn from it.

In Sec. II, the formal theory of the response of a system to an external field is applied to the polyelectrolyte problem. The response of the singlet densities of mobile species, or of the free energy, to the field is derived from a Boltzmann distribution in the mean field, and corrections. The mean field is not simply the external field, but also contains additions to it that result from the redistribution of mobile species. With the neglect of corrections, the mean field and the potential of average force coincide; this is the PB approximation. The corrections depend on the difference between the direct correlation function and the intermolecular potential. All this, we repeat, is rather formal. The mobile species may be small ions or polymers, and the external field may arise from arbitrary sources with specified coordinates, such as polymers, small ions, or electrodes.

In Sec. III, the corrections are estimated on the basis of the mean spherical approximation to the direct correlation function.⁹ The mobile species are taken to be small ions with a rigid core (the "restricted primitive model"). For large local counterion concentrations, a value of 1M is used, the apparent correction to the PB estimate of charge density is found to be potentially large (20% for ions of 4 Å diameter). However, it is noted that this error is estimated for a fixed mean potential; the errors in the solution to the PB equation are much less for the example of main interest, a cylindrical polyelectrolyte, because of the buffering action of the "condensed phase."

In Sec. IV, a reformulation of the PB equation into an

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integral equation is physically motivated on the basis of two phase models. The equation is converted to an approximate algebraic equation for the surface potential on the polymer, and reasonable agreement with the solutions to the original PB equation is found. The algebraic equation is easily modified to show the effects of errors in the PB equation itself, of non-Coulombic forces, and of curvature in the cylinder, and some preliminary work along these lines is reported. An additional test of the approximate equation for the potential is discussed in Sec. V, where the effect of the polyelectrolyte on the chemical potential of small ions is calculated. Numerical results for the salt exclusion coefficient are in fair agreement with exact results. Except for the purely formal work of Sec. II, the calculations deal with noninteracting polymer molecules, and are therefore restricted to dilute solution. Some problems in the theory of interacting chains are briefly mentioned in Sec. VI.

II. POISSON-BOLTZMANN DISTRIBUTION

The system to be considered consists of one or more species of mobile molecules in the presence of an external potential field. The quantities to be calculated are the configurational free energy $A(q)$ and the mean singlet densities of mobile species $n_i(\mathbf{r}, q)$; q is a coupling parameter that controls the magnitude of the external field. The initial analysis is rather general, and the nature of the field is arbitrary. Later a Coulomb field is specified, and in the natural application the mobile molecules are small ions, and the external field arises from a single polyelectrolyte molecule. All these restrictions apply in Sec. III, where errors in the PB equation are estimated, and in the subsequent specific calculations of Secs. IV and V. However, here the mobile molecules may be any molecules with unconstrained coordinates, and the source may be any "molecules" with constrained coordinates. Part or all of the external field may vary with q .

Examples of external sources include macromolecules immersed in the solution with specified configuration, an external electrode, and a single mobile ion temporarily fixed in position. The variable part of the field has an interaction energy $u_i(\mathbf{r}, q)$ with a mobile molecule of species i at position \mathbf{r} , and $u_i(\mathbf{r}, q)$ vanishes at $q=0$. By an obvious generalization of notation, applied either to the spatial coordinate \mathbf{r} or the species index i , molecules with internal coordinates may be included in the formalism.

A. General equations

In this part, results will be obtained for arbitrary external fields. Specialization to electrostatic interactions will be made subsequently. The configurational free energy $B(q)$, a part of $A(q)$, is defined by

$$\exp[-\beta B(q)] = \int \exp[-\beta(U^* + E^*)] dx = Q(q), \quad (2.1)$$

where $\beta = 1/kT$, x stands for a point in the configurational phase space of mobile species, E^* is the interaction energy of mobile molecules with each other and with the fixed part of the external field, and U^* is the vari-

able part of the interaction energy. U^* is given by

$$U^* = \sum_i \int u_i(\mathbf{r}, q) n_i^*(\mathbf{r}) d\mathbf{r}, \quad (2.2)$$

where $n_i^*(\mathbf{r})$ is the instantaneous number density of mobile species i . The mean singlet densities for coupling parameter q are given by

$$\begin{aligned} n_i(\mathbf{r}, q) &\equiv \langle n_i^*(\mathbf{r}) \rangle_q \\ &\equiv Q^{-1} \int n_i^*(\mathbf{r}) \exp[-\beta(U^* + E^*)] dx. \end{aligned} \quad (2.3)$$

It must be stressed that the definition of $B(q)$ excludes any work required to turn on the field U^* against other fixed sources, or against the interactions between different parts of the variable source. These contributions have to be added to $B(q)$ to obtain the total free energy $A(q)$, but as they do not depend on the coordinates of mobile species, the addition may be postponed. Also, $A(q)$ itself may not be the final answer to the question of interest. For example, the work required to charge a mobile ion to q is $-kT \ln \langle \exp[-\beta \Delta A(q)] \rangle$, where $\langle \rangle$ stands for an average with weight $\exp[-\beta A(0)]$ over the position of the mobile ion, which is temporarily fixed in position during the charging process; and

$$\Delta A(q) \equiv A(q) - A(0).$$

The symbol Δ will indicate generally this change in a quantity as q increases from zero.

Differentiation of Eq. (2.1) provides one familiar route to the calculation of $B(q)$ in terms of the potential acting on the source

$$\begin{aligned} dB(q)/dq &= \langle \partial U^* / \partial q \rangle_q \\ &= \sum_i \int n_i(\mathbf{r}, q) [\partial u_i(\mathbf{r}, q) / \partial q] d\mathbf{r}. \end{aligned} \quad (2.4)$$

Since this formula may not seem to reduce to the conventional electrostatic calculation, a brief elaboration may be useful. Suppose that

$$u_i(\mathbf{r}, q) = qq_i \int G(\mathbf{r}, \mathbf{s}) n(\mathbf{s}) d\mathbf{s}, \quad (2.5)$$

where $G(\mathbf{r}, \mathbf{s})$ is the symmetric Green's function for a source charge at \mathbf{s} and a test charge at \mathbf{r} , and $n(\mathbf{s}) d\mathbf{s}$ is the fraction of all source charge q that lies in $d\mathbf{s}$. In the simplest case of uniform dielectric constant D , $G(\mathbf{r}, \mathbf{s}) = 1/D|\mathbf{r} - \mathbf{s}|$. However, regardless of the special form of $G(\mathbf{r}, \mathbf{s})$, Eqs. (2.4) and (2.5) give, after interchange of the order of integration,

$$dB(q)/dq = \int n(\mathbf{s}) \Psi_m(\mathbf{s}, q) d\mathbf{s}, \quad (2.6)$$

where

$$\Psi_m(\mathbf{s}, q) \equiv \sum_i \int G(\mathbf{r}, \mathbf{s}) q_i n_i(\mathbf{r}, q) d\mathbf{r} \quad (2.7)$$

and Ψ_m is the contribution to the potential at the source due to mobile molecules. Evidently, the same conventional expression (2.6) for $dB(q)/dq$ in terms of an integration over the source distribution can be derived for arbitrary nonelectrostatic interactions. One need only delete q_i and add a subscript i to $G(\mathbf{r}, \mathbf{s})$.

We turn next to the calculation of the derivative of u_i with respect to q . The purpose of this calculation is not, however, the further development of $B(q)$ from Eq. (2.4). The calculation of $B(q)$ from Eq. (2.6) seems easier in practice than the elaboration of Eq. (2.4). Rather, we are aiming now at a generalized PB equation for $n_i(\mathbf{r}, q)$. Differentiation of Eq. (2.3) gives

$$\partial n_i(\mathbf{r}_1, q)/\partial q = \sum_j \int d\mathbf{r}_2 F_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) [-\beta \partial u_j(\mathbf{r}_2, q)/\partial q], \quad (2.8)$$

where $F_{ij}(\mathbf{r}_1, \mathbf{r}_2, q)$ is the pair correlation function

$$F_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) \equiv \langle n_i^x(\mathbf{r}_1) n_j^x(\mathbf{r}_2) \rangle_q - n_i(\mathbf{r}_1, q) n_j(\mathbf{r}_2, q). \quad (2.9)$$

Equation (2.8) could be made the basis of a perturbation calculation in which the response of the singlet density to a weak perturbation in potential is obtained. The pair correlation function supplies the linear term in a Taylor series expansion in powers of q . However, the modern theory of liquids has vindicated the hope of Ornstein and Zernike that inverse relationships, in terms of the direct correlation function, converge more rapidly. Inversion of Eq. (2.8) gives

$$-\beta \partial u_i(\mathbf{r}_1, q)/\partial q = \sum_j \int d\mathbf{r}_2 K_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) \partial n_j(\mathbf{r}_2, q)/\partial q, \quad (2.10)$$

where K is defined as an inverse to F by the relation

$$\sum_k \int d\mathbf{r}_3 F_{ik}(\mathbf{r}_1, \mathbf{r}_3, q) K_{kj}(\mathbf{r}_3, \mathbf{r}_2, q) = \delta_{ij} \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (2.11)$$

and K in turn defines the direct correlation function C_{ij} through

$$K_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) = [\delta_{ij} \delta(\mathbf{r}_1 - \mathbf{r}_2)/n_i(\mathbf{r}_1, q)] - C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q). \quad (2.12)$$

Specific assumptions about C_{ij} will have to be made later. For the present formal integration of Eq. (2.10) with this expression for K_{ij} gives

$$-\beta u_i(\mathbf{r}_1, q) = \ln[n_i(\mathbf{r}_1, q)/n_i(\mathbf{r}_1, 0)] - \sum_j \int d\mathbf{r}_2 \int_0^q dq C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) \partial n_j(\mathbf{r}_2, q)/\partial q. \quad (2.13)$$

A similar integration of $dB(q)/dq$ is readily obtained, but the resultant forms seem not so useful as Eq. (2.6).

Equation (2.13) has still to be rearranged before it can be discussed as a corrected Poisson-Boltzmann distribution. In electrolyte theory, the charge distribution is related not to the external potential alone, i.e., to $u_i(\mathbf{r}, q)$, but rather to the complete mean potential W_i defined by

$$W_i(\mathbf{r}_1, q) = u_i(\mathbf{r}_1, q) + \sum_j \int d\mathbf{r}_2 v_{ij}(\mathbf{r}_1, \mathbf{r}_2) n_j(\mathbf{r}_2, q) \quad (2.14)$$

or

$$\Delta W_i(\mathbf{r}_1, q) = u_i(\mathbf{r}_1, q) + \sum_j \int d\mathbf{r}_2 v_{ij}(\mathbf{r}_1, \mathbf{r}_2) \Delta n_j(\mathbf{r}_2, q), \quad (2.15)$$

where $v_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ is the Coulomb interaction between mo-

bile species i and j . For the present, we want to be more general and take v_{ij} to be an arbitrary part of the pair potential, whatever the latter may be. It follows from Eqs. (2.13) and (2.15), with v_{ij} defined to be independent of q , that

$$\ln[n_i(\mathbf{r}_1, q)/n_i(\mathbf{r}_1, 0)] = -\beta \Delta W_i(\mathbf{r}_1, q) + \sum_j \int d\mathbf{r}_2 \int_0^q dq [C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) + \beta v_{ij}(\mathbf{r}_1, \mathbf{r}_2)] \partial n_j(\mathbf{r}_2, q)/\partial q. \quad (2.16)$$

The terms that supplement ΔW_i on the right hand side now constitute a correction to the generalized PB approximation to $n_i(\mathbf{r}, q)$. If long ranged interactions are present, experience indicates that $C_{ij} + \beta v_{ij}$ is much shorter ranged than v_{ij} itself. For the mean spherical model, to be employed below, the combination $C_{ij} + \beta v_{ij}$ vanishes by definition if r_{12} exceeds the molecular diameter.

B. Electrostatic interactions

We now specialize the potential u_i to the Coulomb interaction in the fairly general form given in Eq. (2.5). The first problem is to find whether the resultant mean potential W_i of Eqs. (2.14) or (2.15) satisfies Poisson's equation. If it does, the description of Eq. (2.16) as a corrected PB equation is justified, and we can turn to an estimate of the magnitude of the corrections. The external potential can easily be generalized so that an arbitrary potential is turned on simultaneously with the Coulomb part. However, these other parts are presumed to be set aside for the present, and added later to the Coulomb part of ΔW_i prior to evaluation of $n_i(\mathbf{r}, q)$ from Eq. (2.16). [Of course, the external potential, whatever it may be, must in principle exert some influence on $C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q)$ in Eq. (2.16). However, in practice, our estimate of the correction term will be based on $C_{ij}(\mathbf{r}_1, \mathbf{r}_2, 0)$, which is independent of u_i .] We do require of the source that variation of its strength parameter q must not alter the interaction v_{ij} between mobile species. A dielectric discontinuity that affects v_{ij} must have its effect incorporated into a q independent v_{ij} . Thus, the singlet potential $u_i(\mathbf{r}, q)$ is rather flexible, and image potentials or other parts of u_i that are independent of the source charge can be incorporated into ΔW_i at various stages.

The defined part of the pair potential that was labeled v_{ij} is here chosen to be the electrostatic contribution

$$v_{ij}(\mathbf{r}_1, \mathbf{r}_2) = q_i q_j G(\mathbf{r}_1, \mathbf{r}_2). \quad (2.17)$$

For the sake of definiteness, we suppose that $G(\mathbf{r}_1, \mathbf{r}_2)$ is the Green's function of a self-adjoint differential operator

$$\nabla_r \cdot \mathbf{D}(\mathbf{r}) \cdot \nabla_r G(\mathbf{r}, \mathbf{s}) = -4\pi \delta(\mathbf{r} - \mathbf{s}) \quad (2.18)$$

and vanishes at infinity. Therefore, $G(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric in \mathbf{r}_1 and \mathbf{r}_2 , and incorporates the effects of arbitrary dielectric tensor fields $\mathbf{D}(\mathbf{r})$.

According to Eqs. (2.5) and (2.15), the energy ΔW_i is given by

$$\begin{aligned}\Delta W_i(\mathbf{r}, q) &= q_i \Delta \Psi(\mathbf{r}, q) \\ &\equiv q_i [\Delta \Psi_s(\mathbf{r}, q) + \Delta \Psi_m(\mathbf{r}, q)],\end{aligned}\quad (2.19)$$

where $\Delta \Psi_m$ is given by Eq. (2.7) with n_i replaced by Δn_i , and

$$\Delta \Psi_s(\mathbf{r}, q) = q \int G(\mathbf{r}, \mathbf{s}) n(\mathbf{s}) d\mathbf{s} . \quad (2.20)$$

This part of $\Delta \Psi$ is the direct contribution from the source to the potential. Equations (2.18)–(2.20) yield Poisson's equation for the potential $\Delta \Psi$:

$$\begin{aligned}\nabla_r \cdot \mathbf{D}(\mathbf{r}) \cdot \nabla_r \Delta \Psi(\mathbf{r}, q) \\ = -4\pi \left[qn(\mathbf{r}) + \sum_j q_j \Delta n_j(\mathbf{r}, q) \right],\end{aligned}\quad (2.21)$$

and the solution to this equation gives the work necessary to increase q :

$$\begin{aligned}dA(q)/dq &= \int n(\mathbf{s}) \Psi(\mathbf{s}, q) d\mathbf{s} , \\ \Psi(\mathbf{s}, q) &= \Psi(\mathbf{s}, 0) + \Delta \Psi(\mathbf{s}, q) , \\ \Delta \Psi(\mathbf{s}, q) &= \Delta \Psi_s(\mathbf{s}, q) + \Delta \Psi_m(\mathbf{s}, q) ,\end{aligned}\quad (2.22)$$

or

$$\begin{aligned}\Delta A(q) &= q \int n(\mathbf{s}) \Psi(\mathbf{s}, 0) d\mathbf{s} \\ &+ \int_0^q dq \int n(\mathbf{s}) \Delta \Psi(\mathbf{s}, q) d\mathbf{s} .\end{aligned}\quad (2.23)$$

The free energies $A(q)$ and $B(q)$ differ in that the latter, given in Eq. (2.6), derives only from the potential Ψ_m due to mobile molecules. $A(q)$ contains also the direct contribution Ψ_s from the sources of fixed configuration and either fixed or variable charge.

For Eq. (2.23) to be a useful route to the free energy change, the potential at the source before it is charged must be known, and the change in potential during charging. The latter $\Delta \Psi(\mathbf{s}, q)$ is a solution to Poisson's equation (2.21) with $\Delta n_j(\mathbf{r}, q)$ obtained from Eqs. (2.16) and (2.19). For certain singular distributions (line or point sources), $\Delta \Psi(\mathbf{s}, q)$ will diverge due to self-energy terms, and the divergent part must be deleted. For a point source, this deletion amounts to subtraction of the unscreened Coulomb potential due to the source from $\Delta \Psi(\mathbf{r}, q)$ before the limit $\mathbf{r} \rightarrow \mathbf{s}$ is taken.

If the combination $C_{ij} + \beta v_{ij}$ is neglected in Eq. (2.16), we have a Poisson-Boltzmann set of equations, modified to include (1), any forces that make the densities $n_i(\mathbf{r}, q)$ position dependent for vanishing q , and (2) non-Coulombic parts of ΔW_i . The magnitude of these neglected terms will be estimated in the next section.

III. MEAN SPHERICAL APPROXIMATION TO CORRECTIONS

Equation (2.16) becomes a modified Poisson-Boltzmann equation if the correction terms $C_{ij} + \beta v_{ij}$ are neglected. The main purpose of this section is to estimate the neglected terms. Other errors that derive from an approximate application of the PB equation, such as neglect of the spatial dependence of the dielec-

tric tensor $\mathbf{D}(\mathbf{r})$ or non-Coulombic forces that may affect $n_i(\mathbf{r}, 0)$ [and also $\Psi(\mathbf{s}, 0)$ and $A(q)$] are not considered.

The correction terms in Eq. (2.16) may be displayed separately:

$$\ln[n_i(\mathbf{r}, q)/n_i(\mathbf{r}, 0)] = -\beta q_i \Delta \Psi(\mathbf{r}, q) + C_i(\mathbf{r}, q) , \quad (3.1)$$

where

$$\begin{aligned}C_i(\mathbf{r}, q) &\equiv \sum_j \int d\mathbf{r}_2 \int_0^q dq [C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) \\ &+ \beta v_{ij}(\mathbf{r}_1, \mathbf{r}_2)] \partial n_j(\mathbf{r}_2, q) / \partial q .\end{aligned}\quad (3.2)$$

The corrections will be estimated on the basis of the restricted primitive model of the solution of mobile ions, treated in the mean spherical approximation.⁹ Thus, the mobile ions have a common hard sphere diameter σ , and other than this core repulsion have only a simple Coulomb interaction $v_{ij}(r_{12})$. The mean spherical approximation may be defined by the requirements that $C_{ij} + \beta v_{ij}$ vanishes if $r_{12} > \sigma$, and that the radial distribution functions vanish if $r_{12} < \sigma$. If the solute charges vanish, the Percus-Yevick approximation is recovered. Alternative descriptions in the languages of graph theory or lattice statistics are available.⁹ It now follows that the integrand in Eq. (3.2) vanishes unless $r_{12} < \sigma$, and the subsequent discussion is confined to that range of r_{12} . The mean spherical approximation has the advantage, compared to other approximations to the restricted primitive model, of analytic expressions for the direct correlation functions, and at the same time retains an accuracy comparable to superior approximations.^{9(b)}

The dependence of C_{ij} on q will be neglected; the dominant part of the correction comes from v_{ij} , and this by definition is independent of q . The merit of this approximation $C_{ij}(\mathbf{r}_1, \mathbf{r}_2, q) \approx C_{ij}(r_{12}, 0)$ is difficult to judge. It is equivalent to the truncations of functional expansions often used to derive approximate integral equations for distribution functions, but is used here only to estimate correction terms. If q is sufficiently small that the correction terms are small, it is reasonable to expect the approximation to C_{ij} to be adequate. Improvement of the approximation would require that the mean spherical approximation to C_{ij} , or any approximation used in its place, be solved for a system with non-vanishing net charge density. For $q=0$, i. e., for the neutral electrolyte solution of mobile ions, $C_{ij}(r, 0)$ divides in the mean spherical approximation into two parts. The first is the Percus-Yevick hard sphere function, and the second is a correction, present only for charged solutes, that vanishes with ionic strength. The hard sphere part is known analytically for any uniform solute density, and does not vary much with density in the range that has to be considered. Neglect of the variation with q of the electrolyte part of C_{ij} is a more obscure approximation, but this is the smallest part of the total correction.

On the basis of the preceding discussion, and with explicit neglect in Eq. (3.2) of the spatial variation of $n_j(\mathbf{r}_2, q)$ in the region $r_{12} < \sigma$, Eq. (3.2) may be written

$$C_i(\mathbf{r}, q) \approx \sum_j (H_{ij} + E_{ij} + V_{ij}) \Delta n_j(\mathbf{r}, q) , \quad (3.3)$$

where the hard sphere part H_{ij} is given by

$$H_{ij} = \int_0^\sigma C_{\text{HS}}(r) 4\pi r^2 dr \\ = (\pi\sigma^3/6)(\eta - 4)(\eta^2 + 2)/(1 - \eta)^4 \quad (3.4)$$

and, with n distinguished from the source distribution $n(\mathbf{s})$,

$$\eta \equiv n\pi\sigma^3/6, \quad n \equiv \sum n_i(\mathbf{r}, 0).$$

An alternative formula for H_{ij} in terms of the compressibility of a hard sphere fluid is

$$H_{ij} = n^{-1}[1 - \beta(\partial p_{\text{HS}}/\partial n)].$$

The electrolyte part E_{ij} is given by

$$E_{ij} = -\pi\sigma^3(\beta q_i q_j / D\sigma)(\frac{2}{3}B - B^2), \quad (3.5)$$

and with κ^{-1} the Debye screening length,

$$B \equiv x^{-1}[1 + x - (1 + 2x)^{1/2}], \quad x \equiv \kappa\sigma.$$

The "cavity potential"¹ V_{ij} is given by

$$V_{ij} = \beta \int_0^\sigma v_{ij}(r) 4\pi r^2 dr = 2\pi\sigma^3(\beta q_i q_j / D\sigma). \quad (3.6)$$

The numerical values of H_{ij} , E_{ij} , and V_{ij} have been calculated for a 1-1 salt solution with ionic strength 0.1M ($n=0.2M$) and $\sigma=4 \text{ \AA}$. This gives $\eta=0.004$, $H_{ij} = -272 \text{ \AA}^3$, $E_{ij} = -134 \text{ \AA}^3$, and $V_{ij} = 704 \text{ \AA}^3$, for i and j of the same charge.¹⁰ For an increment in counterion density $\Delta n_c \approx 1M$ at the surface of a polymer, the correction C_i is about 0.2 for counterions, and -0.5 for coions. If σ is increased, the counterion correction 0.2 will at first decrease, and then go negative. Exponentiation of these numbers gives the correction factors to the ion concentrations at the polymer surface.

Errors of this magnitude may seem large, but in practice their effect is likely to prove small for several reasons. First, the co-ion concentration at and near the surface is ordinarily quite small, and errors in its exact magnitude will have little effect on the surface potential or the coion activity. The smaller errors in counterion concentration are significantly compensated by a buffering action of the polyelectrolyte, i.e., a large value of C_i for counterions in Eq. (3.1) is compensated by a small percentage decrease of the potential term, and neither the counterion concentration or the potential change by a significant fraction. Numerical illustration of this compensation will be given in the next section.

With the tentative assumption that correction terms of the indicated magnitude are negligible, we will proceed to the relation between the PB equation and an improved version of the two state model.

IV. RELATIONSHIP TO CONDENSATION

In this section, a relationship will be established between the Poisson-Boltzmann equation and a certain form of the two state or condensed phase model of counterion distribution. Many such models have been proposed on the basis of various criteria. Our own criteria

are two: that the two state model be formally equivalent to the PB equation, and that any approximations necessary to the simplification of the two state model should not seriously affect quantitative agreement with the PB equation. These criteria are tenable only for dilute polymer solutions. Concentrated solutions pose problems concerning the validity of the PB equation, as well as with its practical manipulation, that will be discussed below.

One of the reasons for interest in the two state model is its utility in the study of complex polymer shapes and end effects. Specialization to the infinite cylinder model will therefore be briefly postponed. The polymer molecule is taken to be an arbitrarily shaped domain, within or on the surface of which an arbitrary source charge density $qn(\mathbf{r})$ exists, and an arbitrary dielectric tensor $\mathbf{D}(\mathbf{r})$ is specified. Then,

$$\nabla \cdot \mathbf{D}(\mathbf{r}) \cdot \nabla \Psi(\mathbf{r}) = -4\pi[\rho(\mathbf{r}) + qn(\mathbf{r})], \quad (4.1)$$

where $\Psi(\mathbf{r})$ is the increase in potential and $\rho(\mathbf{r})$ is the increase in mobile charge density, each induced by the source charge.

A connection with the two state model is initiated through the definition of an excess charge density $E(\mathbf{r})$:

$$E(\mathbf{r}) \equiv \rho(\mathbf{r}) + [d^2(\mathbf{r})/4\pi]\Psi(\mathbf{r}), \quad (4.2)$$

where $d(\mathbf{r})$ is chosen to make $E(\mathbf{r})$ vanish in the region of low potential. This subtraction procedure is intended to isolate for special treatment that region of space where condensation might be imagined to take place. In general,

$$\rho(\mathbf{r}) \equiv \sum q_i [n_i(\mathbf{r}, q) - n_i(\mathbf{r}, 0)] \\ \approx \sum q_i n_i(\mathbf{r}, 0) \{ \exp[-\beta q_i \Psi(\mathbf{r})] - 1 \},$$

and far from the source, where Ψ is small,

$$\rho(\mathbf{r}) \sim - \left[\beta \sum q_i^2 n_i(\mathbf{r}, 0) \right] \Psi(\mathbf{r}) \quad (4.3)$$

so

$$d^2(\mathbf{r}) \equiv 4\pi\beta \sum q_i^2 n_i(\mathbf{r}, 0), \quad (4.4)$$

and Eq. (4.1) may be written

$$\nabla \cdot \mathbf{D}(\mathbf{r}) \cdot \nabla \Psi(\mathbf{r}) - d^2(\mathbf{r})\Psi(\mathbf{r}) = -4\pi[E(\mathbf{r}) + qn(\mathbf{r})]. \quad (4.5)$$

For definiteness, the source distribution $n(\mathbf{r})$ will be confined to the polymer surface and $n(\mathbf{r})$ is deleted from Eq. (4.5). The equation then applies only outside the polymer domain, and boundary conditions must be imposed. These conditions are that $\Psi(\mathbf{r})$ vanishes at infinity and, from Eq. (4.1), that the normal component of $\mathbf{D}(\mathbf{r}) \cdot \nabla \Psi(\mathbf{r})$ has a discontinuity across the surface given by -4π times the surface charge density at the specified point. The interior value of $\mathbf{D}(\mathbf{r}) \cdot \nabla \Psi(\mathbf{r})$ would ordinarily be negligible for smoothed surface charge distributions.

The solution to Eq. (4.5) will be expressed in terms of the Green's function that satisfies

$$\nabla_r \cdot \mathbf{D}(\mathbf{r}) \cdot \nabla_r G(\mathbf{r}, \mathbf{p}) - d^2(\mathbf{r})G(\mathbf{r}, \mathbf{p}) = -4\pi\delta(\mathbf{r} - \mathbf{p}), \quad (4.6)$$

vanishes at infinity, and satisfies arbitrary boundary conditions on the polymer surface. The solution $G = \exp(-\kappa|\mathbf{r} - \mathbf{p}|)/D|\mathbf{r} - \mathbf{p}|$, where $\kappa^2 = d^2/D$ is a correct choice, but not a unique one, for uniform D and d . A different choice that satisfies the same boundary conditions as $\Psi(\mathbf{r})$ is possible. For a given G , the solution to Eq. (4.5) is

$$\Psi(\mathbf{r}) = -(4\pi)^{-1} \int [G(\mathbf{r}, \mathbf{s})\mathbf{D}(\mathbf{s}) \cdot \nabla_s \Psi(\mathbf{s}) - \Psi(\mathbf{s})\mathbf{D}(\mathbf{s}) \cdot \nabla_s G(\mathbf{r}, \mathbf{s})] \cdot d\mathbf{S} + \int G(\mathbf{r}, \mathbf{p})E(\mathbf{p})d\mathbf{p}, \quad (4.7)$$

where $d\mathbf{S}$ is an element of surface area pointing from the polymer into the solution, \mathbf{s} is a point on the surface, and \mathbf{p} lies outside the polymer.

For the essential features of a two state model to be correct, the volume integral over the excess charge density $E(\mathbf{p})$ in Eq. (4.7) must converge sufficiently rapidly that it can be replaced by a surface integral. The excess charge density on the surface is known in terms of $\Psi(\mathbf{s})$, and if the width of the distribution can be estimated, Eq. (4.7) evaluated for $\mathbf{r} \rightarrow \mathbf{s}$ becomes an integral equation for $\Psi(\mathbf{s})$ that will be much easier to solve than the original differential equation for curved rods, end effects, and like problems. It will also be easier for infinite cylinders, but the benefits are mainly conceptual because the original differential equation is numerically quite tractable.

Approximations to the volume integral over $E(\mathbf{p})$ will be inferred from the study of a uniformly charged, straight cylinder of radius a and infinite length. These approximations, which amount to a two state model, can be justified *a priori* and are found to work well where the potential is large, on the surface of the polymer. They cannot be justified and do not work well where the potential is small, far from the polymer.

For the cylindrical test polymer, Ψ will depend only on the radial distance r , and G may be integrated over the cylindrical coordinates ϕ and z as a first step. With

$$g(r, p) \equiv (2\pi)^{-1} \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dz G(\mathbf{r}, \mathbf{p}) \quad (4.8)$$

and d and D independent of position, Eq. (4.7) simplifies to

$$\Psi(r) = -\frac{1}{2}aD [g(r, a)\partial\Psi(a)/\partial a - \Psi(a)\partial g(r, a)/\partial a] + 2\pi \int_a^{\infty} g(r, p)E(p)p dp. \quad (4.9)$$

With G the screened Coulomb potential, g can be obtained from Eq. (4.8), or more simply from a preliminary integration of Eq. (4.6) over ϕ and z :

$$g(r, p) = (2/D) \cdot \begin{cases} K_0(\kappa r)I_0(\kappa p), & r > p, \\ I_0(\kappa r)K_0(\kappa p), & r < p. \end{cases} \quad (4.10)$$

A dimensionless measure of potential now proves convenient. Let

$$\psi(r) = \beta e \Psi(r). \quad (4.11)$$

The boundary condition on the polymer surface $r = a$ is

$$a\psi'(a) = -2\xi, \quad \xi = \beta eq/LD,$$

where (q/L) is the charge per unit length and e is the absolute value of the electronic charge. The following analysis requires the general behavior of the solution to the PB equation: First, in the absence of excess charge density, Eq. (4.9) has the Debye-Hückel solution

$$\psi_{\text{DH}}(r) = 2\xi K_0(\kappa r)/\kappa a K_1(\kappa a). \quad (4.12)$$

The general solution will be written in the same form

$$\psi(r) = 2X(r)K_0(\kappa r)/\kappa a K_1(\kappa a), \quad (4.13)$$

$X(r)$ playing the role of an effective charge parameter at radial distance r . Other arguments of $X(r)$, namely, ξ and the charges and initial concentrations of all mobile species, will not be displayed. Manning's postulates⁴ state that $X(r)$ is either ξ or unity, whichever is less, for a 1-1 salt as $\kappa \rightarrow 0$. For the qualitative considerations of the next paragraph, this is good enough, although in fact we will be considering finite κ , and moreover, $X(r) < X(a)$ even for $\kappa \rightarrow 0$, if $\kappa r > 0$ (see Fig. 1).

We can now examine Eq. (4.9) for the two limits of $r = a$ and $r \gg \kappa^{-1}$. For the first limit,

$$\psi(a) = K_0(\kappa a) [2\xi I_0(\kappa a) + \psi(a)\kappa a I_1(\kappa a)] - I_0(\kappa a)\kappa^2 \int_a^{\infty} K_0(\kappa p)F(p)p dp, \quad (4.14)$$

where

$$F(p) \equiv -4\pi\beta e E(p)/D\kappa^2 = -(4\pi e\beta/D\kappa^2)\rho(p) - \psi(p). \quad (4.15)$$

For a 1-1 salt, $F(p)$ is $\sinh\psi - \psi$. For large r ,

$$\psi(r) \sim K_0(\kappa r) \left\{ 2\xi I_0(\kappa a) + \psi(a)\kappa a I_1(\kappa a) - \kappa^2 \int_a^{\infty} I_0(\kappa p)F(p)p dp \right\}. \quad (4.16)$$

In Eq. (4.14), significant contributions must diverge as $K_0(\kappa a)$, i.e., as $-\ln(\kappa a)$, for small κ . The integral over excess charge density can contribute such a term only from the region of small p , close to the cylinder, because the contribution from large p , where the integrand behaves as $K_0\psi^3$, or $(K_0)^4$, is finite, i.e., the integral of $[K_0(x)]^4 x$ from a finite value of x to infinity is finite. So a truncation of the integral in the formula for $\psi(a)$ [Eq. (4.14)] is plausible, at least for small κ . The situation for large r , described by Eq. (4.16), is different. All contributions have the common factor $K_0(\kappa r)$, and the finite part of the integral arising from large p makes a definite contribution that is not negligible compared to other terms. This distinction shows up in the numerical solutions to the differential PB equation, which show that $X(\infty) < X(a)$, even at infinite dilution.

If κ is large, the integral in Eq. (4.14) may be truncated at small p because all factors in the integrand converge rapidly to zero, and therefore a two state approximation has practical utility regardless of the presence

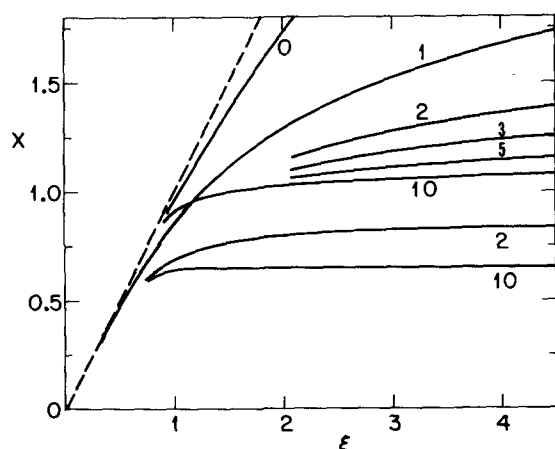


FIG. 1. The effective charge parameter $X(r)$ versus the reduced charge density ξ for various concentrations of 1-1 salt. The screening parameter is $\kappa a = 10^{-k}$, where the integer k is given on the graph. The lowest two curves refer to $X(\infty)$, the remainder to $X(a)$. The dashed line gives the Debye-Hückel approximation $X(r) \equiv \xi$ to the reduced potential $\psi(r) = 2X(r)K_0(\kappa r)/\kappa a K_1(\kappa a)$. The limiting law $X(a) = \min(1, \xi)$ is reached rather slowly as κ decreases, and $X(\infty)$ approaches a limit significantly different from $X(a)$.

of condensation phenomena. To get Eq. (4.14) into tractable form, we will make and test the following extremely crude approximations¹¹:

$$K_0(\kappa p) \approx K_0(\kappa a) \exp[-(p-a)f_1/a], \quad (4.17)$$

$$pF(p) \approx aF(a) \exp[-(p-a)f_2/a], \quad (4.18)$$

where f_1 and f_2 are inferred from the initial slopes of these functions

$$f_1 = -a[\partial K_0(\kappa a)/\partial a]/K_0(\kappa a) = \kappa a K_1(\kappa a)/K_0(\kappa a), \quad (4.19)$$

$$f_2 = -C[1 + aF'(a)/F(a)], \quad (4.20)$$

TABLE I. The effective charge parameter $X(a)$ versus screening parameter κa and reduced charge density ξ for a 1-1 salt solution. The X_e are exact and the X_a derive from the two state approximation discussed in the text. f_1 and f_2 are the two contributions to the decay rate of the excess charge. The width of the excess charge distribution is $a/(f_1 + f_2)$.

	ξ	f_1	f_2	X_a	X_e	X_a^B	X_a^C
$\kappa a = 1$	0.5	1.43	1.718	0.491	0.494	0.483	1.042
	1		1.916	0.939	0.956	0.897	1.579
	2		2.544	1.658	1.723	1.520	2.249
	4		4.187	2.610	2.734	2.333	3.054
$\kappa a = 0.1$	0.5	0.406	0.253	0.478	0.479	0.462	0.724
	1		0.609	0.855	0.855	0.796	1.066
	2		1.539	1.287	1.290	1.180	1.407
	4		3.516	1.667	1.675	1.538	1.727
$\kappa a = 0.01$	0.5	0.212	0.039	0.491	0.481	0.483	0.744
	1		0.504	0.870	0.834	0.828	1.012
	2		1.501	1.160	1.141	1.095	1.214
	4		3.500	1.363	1.357	1.293	1.387
$\kappa a = 0.0001$	0.5	0.107	0.001	0.500	0.489	0.499	0.815
	1		0.500	0.908	0.856	0.883	0.998
	2		1.500	1.083	1.066	1.048	1.107
	4		3.500	1.186	1.180	1.150	1.196

and C is an adjustable constant that would have to be unity if Eq. (4.18) were required to give the correct initial slope. However, a good estimate of the integral in Eq. (4.14) requires a smaller value of C because the excess charge density at small p has a slower than exponential variation with p . A value $C=0.5$ gives good agreement with numerical solutions of the PB equation under a variety of conditions. The success of these crude approximations is of course not due to their merit, but to the insensitivity of $\psi(a)$ to the width of the excess charge distribution at the two extremes of small and large excess charge (or condensed counterions). The total amount of excess charge associated with unit area of polymer surface is proportional to $\exp\psi(a)$ times the width, and the solution for $\psi(a)$ varies logarithmically with the width, if the excess charge is large.¹²

Substitution from Eqs. (4.17) and (4.18) into Eq. (4.14) gives

$$\psi(a) = K_0(\kappa a)[2\xi I_0(\kappa a) + \psi(a)\kappa a I_1(\kappa a) - I_0(\kappa a)\kappa^2 a^2 F(a)/(f_1 + f_2)], \quad (4.21)$$

a transcendental equation for $\psi(a)$. The unknown value $\psi(a)$ and the known value of $a\psi'(a) = -2\xi$ occur explicitly in Eq. (4.21), and also implicitly in the ratio $F'(a)/F(a)$ that determines f_2 from Eq. (4.20).

From numerical results shown in Fig. 1 and Table I, the condensation approximation (4.21) is seen to work reasonably well. Under conditions such that $(f_1 + f_2)$ is comparable to unity, or larger, it should be acceptable to replace volume integrals over excess charge by surface integrals in the study of more complicated polymer shapes or end effects. It will be noticed that the limiting law is not obeyed very well under accessible conditions. (An example is DNA, for which $\kappa a = 0.1$ corresponds to an 0.001M concentration of 1-1 salt, while $\xi \cong 4$. Then, X is 4 with Debye-Hückel linearization, X is 1.7 from the PB equation, and $X = 1$ according to the

limiting law. The latter is approached extremely slowly with increasing dilution.)

Table I also gives values for X_a^B and X_a^G , which are solutions of the approximate equation for $X(a)$ modified to account roughly for two special effects. These are (1) a change in the Green's function from its value for the infinite cylinder, shown in X_a^G , and (2) other changes that may originate in either (a) a value $C \neq 0.5$, (b) binding, or (c) corrections to the PB equation. The latter effects are shown in X_a^B . The results for X_a^G are obtained by doubling the Green's function $K_0(\kappa a)$ in Eq. (4.21), and (are intended to) show the effects of bending an infinite cylinder, thereby increasing charge interactions and the surface potential. The effect is pronounced for small surface charges, i. e., for small ξ . For large ξ , the change in X_a is much less, especially for low salt concentrations, because the excess charge increases and almost entirely eliminates the effect. The results for X_a^B are obtained by doubling the value of $F(a)$ in Eq. (4.21), i. e., replacing $F(a)$ by $2F(a)$, and the change in X_a is found to be relatively small under all circumstances.

Calculations for a 2-1 salt were made, and lead to conclusions identical to those drawn from Table I for a 1-1 salt, i. e., Eq. (4.21) works rather well, and the inferred value of X_a is rather insensitive to modifications of the excess charge approximation. The reason for this lack of sensitivity is simple. For small ξ , there is very little excess charge, and a (percentage) error in its value has no effect. For large ξ , the potential is ordinarily large (unless κ is also very large), and occurs in an exponential expression for the counterion concentration. So small percentage changes in X_a compensate for big changes elsewhere.

The factor of two used to correct the excess charge density in the computation of X_a^B is of course somewhat arbitrary. The choice was motivated by the results of Sec. III, where a 20% error was found for a 1M increase in surface counterion density over the bulk value, and by the consideration of DNA. For DNA, the PB approximation gives a surface counterion concentration of about 2M in the limit of infinite dilution, and the value increases quite slowly to about 3M for a bulk salt concentration of 0.1M. These estimates are based on $\xi = 4$ and $a = 12 \text{ \AA}$. It should be noted that $\kappa a = 1$, the largest value considered, corresponds to a bulk salt concentration of only 0.064M for DNA. However, the magnitude of the correction factor changes very slowly with bulk salt concentration, and should be about $\exp(3 \times 0.2) \cong 2$.

We have asserted that the solution charge density as well as the potential is insensitive to errors in the Boltzmann distribution used to derive the PB equation. This remark will now be illustrated for a cylinder with a high surface charge $\xi = 4$. We assume that the potential at and near the surface is sufficiently large that the surface counterion concentration is much larger than the bulk value, as will certainly be true for our largest value of $\kappa a = 1$, and well beyond. Then the total surface charge density, the counterion charge density, and the "excess charge" density all coincide. (We recall that

the excess charge density is defined as the Boltzmann charge density less the linearized density evaluated for the same ψ .) So the precise question is taken to be the degree to which the surface counterion density $n_c(a)$ is affected by an *ad hoc* change in the formula that relates that density to ψ . The results given in Table I for X_a and X_a^B , the latter obtained by doubling the excess charge for given ψ , permit a ready calculation of the ratio of these two estimates

$$n_c(a)/n_c^B(a) = \frac{1}{2} \exp[2(X_a - X_a^B)K_0(\kappa a)/\kappa a K_1(\kappa a)]. \quad (4.22)$$

The ratio is found to be 0.74, 0.94, 0.97, and 0.98, for $\kappa a = 1, 0.1, 0.01$, and 0.0001, respectively.

The calculated error in the surface counterion charge density is, like the error in ψ , much less than the error in the Boltzmann approximation. Under the worst conditions considered, the errors are 25% in the former and 200% in the latter, for a bulk salt concentration of 0.1M. As the bulk salt concentration increases beyond 0.1M, errors may well prove significant in magnitude, and the magnitude must depend sensitively on the details of counterion interactions with each other. The increased error at high bulk salt concentrations is not due to an increase in surface counterion density, which stays relatively constant. Rather, the increased screening lowers the surface potential, and therefore also lowers the buffering capacity of the polyelectrolyte.

A more complete numerical study of the corrected PB equation will be required for a quantitative study of errors at salt concentrations in excess of (roughly) 0.1M. Our expectation is that the PB equation will retain semiquantitative utility, because the correction terms decrease away from the polyelectrolyte surface exponentially in ψ .

V. CHEMICAL POTENTIALS OF SMALL IONS

The effect of polyelectrolyte on the chemical potentials μ_i of small ions has been determined according to several theoretical methods, models, and experiments; in this section, the revised condensation approximation of Sec. IV will be applied to one aspect of the problem. We restrict the study to low polymer concentrations, i. e., to a linear dependence of μ_i on polyelectrolyte concentration. A few comments on finite polyelectrolyte concentration will be made in the Discussion.

Two different approaches to the statistical thermodynamic problem have been made.^{3,13} One method requires the potential of average force on a small ion everywhere in solution, outside the polyelectrolyte domain. The second method requires the mean electrostatic potential at the surface of the polymer as a function of the polymer charge. Of course, the potential of average force and the mean potential are the same in the PB approximation.

The first method is based on an osmotic equilibrium between the polyelectrolyte solution and a pure salt solution. A grand canonical distribution applied to a system open to all components, including the polymer, gives

$$\begin{aligned} (\partial n_i / \partial \mu_P)_{T, V, \mu} &= n_P (\partial n_i / \partial \Pi) \\ &= (n_i n_P / kT) \int [g_i(r) - 1] dr, \end{aligned} \quad (5.1)$$

where n_P and μ_P are the number density and chemical potential of polymer, and $g_i(r)$ is the radial distribution function for small ions relative to a polymer center. (Strictly, it is an average of such a function over polymer orientation and/or conformations, if the polymer has internal degrees of freedom.) Equation (5.1) gives the salt exclusion coefficient A_1 in the series

$$n_s / n_s^* = 1 + A_1 n_P^e + \dots \quad (5.2)$$

that relates the salt concentration inside n_s and outside n_s^* , the polyelectrolyte solution; n_P^e is the polyelectrolyte concentration measured in equivalents/volume. The electrostatic part of A_1 for a 1-1 salt, that shares counterions with the polymer, is

$$A_1^{e1} = n_s^* (Le/q) \int_a^\infty (e^{-\psi} - 1) 2\pi r dr, \quad (5.3)$$

where e , q , and the dimensionless potential ψ are all presumed positive. An excluded volume contribution may be added to this expression, or any of the other exact and approximate expressions we consider, to obtain the total A_1 .

The alternative formula is based on the charging expression

$$\begin{aligned} (\partial \mu_i / \partial q_T)_{T, V, n} &= [\partial (dA/dq_T) / \partial n_i]_{T, V, n} \\ &= \partial (\Psi_P - \Psi_C) / \partial n_i, \end{aligned} \quad (5.4)$$

where q_T is the total charge on all polyelectrolyte molecules, Ψ_P is the mean polyelectrolyte surface potential, and Ψ_C is the mean potential on the surface of a counterion. For infinite polymer dilution, and again for a 1-1 salt that shares counterions, Eq. (5.4) gives

$$\begin{aligned} A_1^{e1} &= -\frac{1}{2} \left[1 + (n_s^* / q) \int_0^q (\partial \psi / \partial n_s^*) dq \right] \\ &= -\frac{1}{2} \left[1 + (n_s^* / \xi) \int_0^\xi (\partial \psi / \partial n_s^*) d\xi \right], \end{aligned} \quad (5.5)$$

where ψ is the dimensionless potential $e\Psi_P/kT$.

Equations (5.3) and (5.5) should agree if the exact PB potential is used (this can be verified numerically to a certain precision, $\sim 0.1\%$ in our work and Stigter's¹³). In Fig. 2, exact (PB) values of A_1^{e1} are compared with Manning's limiting law expression and with the revised condensation approximation. Stigter has already observed that the limiting law is in serious disagreement with exact results and with experiments on DNA.^{3(b), (c)} Our own conclusion is simply that the revised condensation approximation agrees rather well with the exact results for A_1^{e1} . However, the agreement is not so good as it is for ψ itself. The reason for this worsened agreement is partly the necessity for construction of a derivative of ψ , which inevitably exaggerates errors, and also the roughness of the condensation approximation in the region of $\xi=1$, which was not given much importance when approximations were determined in Sec. IV. The percentage errors in A_1^{e1} are largest at the dilute salt

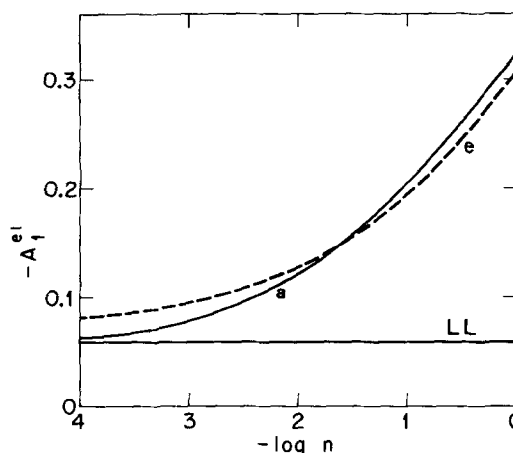


FIG. 2. The electrical part of $-A_1$ versus $-\log_{10} n$, where $n = n_s^*$ is the molar concentration of 1-1 salt. The curve labeled (e) gives exact values, curve (a) gives values from the two state approximation to the PB equation, and (LL) gives the limiting law result. Parameters are $a = 12 \text{ \AA}$ and $\xi = 4.24$, roughly appropriate for DNA.

end of Fig. 2, where Eq. (5.5) takes a small difference between two large numbers. For still greater dilution, the estimates of A_1^{e1} converge.

VI. DISCUSSION

In these concluding remarks, we wish to stress certain similarities and differences between this work and other work on similar topics, and also to mention some difficulties that will have to be faced in further work along the same lines.

For an isolated polymer molecule in a salt solution, we have found some evidence that the PB equation is adequate for the primitive model. The greatest error (the "cavity potential") is the one least subject to uncertainty of evaluation. Elaboration of the PB equation to include dielectric inhomogeneities or non-Coulombic interactions of mobile ions with the polymer or each other should not significantly modify the error estimates. However, our acceptance of the PB equation under conditions where it is ordinarily thought to fail, at local ionic concentrations of 2 to 3M, is based on the buffering capacity of a high surface potential. If the bulk salt concentration is very high, perhaps only greater than 0.1M for DNA, the surface potential will be lowered sufficiently again to jeopardize the PB equation. We nevertheless remain optimistic concerning its utility, pending additional calculations.

We have also noticed from the numerical work (see Fig. 1), in agreement with Stigter,^{3(b)} that the validity of the Debye-Hückel potential at infinite dilution is only partially restored through use of an effective charge parameter $X(r) = \min(1, \xi)$ for a 1-1 salt. This works in the limit $\kappa \rightarrow 0$ for any fixed r , but not for $X(r)$ with κr fixed. We actually know of no claim that the simpler behavior, namely, $X(\infty) = X(a)$ in the limit $\kappa \rightarrow 0$, has been proved, but some of the discussion in Manning^{4(a)} and MacGillivray¹⁴ might allow an unwary reader to draw a contrary conclusion. MacGillivray's limiting lower bound¹⁴ to $X(r)$ is stated for $r = a$, $\kappa \rightarrow 0$ and fails if, in-

stead, κr is fixed. The behavior of X at large r is required in the theory of intermolecular¹⁵ or intramolecular¹⁶ interactions.

Although we have not made a detailed comparison, we suspect that the modified two phase model developed here for finite salt concentrations will bear a family resemblance to the models of Oosawa,^{5(a)} Manning,^{5(b)} Iwasa,¹⁷ and perhaps others. We have not pursued a comparison because our point of view is somewhat different. Instead of basing a theory on a two phase model of the system, we arrive at the two phase model as an approximation to the PB equation. Our position is that the basic assumption underlying the PB equation is so simple and general, and fairly close to being right, that the PB assumption is a natural focus for effort intended to correct the approximation or to derive its consequences.

It should be noted that the two phase model derived here applies only to the surface potential. The nonlinear dependence of charge density on potential far out in the solution, at distances $0(\kappa^{-1})$, though it has a minor effect on $X(a)$, leads to a significant difference between $X(a)$ and $X(\infty)$ unless ξ is quite small. At present, we see no alternative to the PB equation for $X(\infty)$.

The problem of concentrated polyelectrolyte solutions has been studied by Katchalsky *et al.*² on the basis of a lattice model, and to some degree has been included in Manning's limiting laws.⁴ These laws seem close enough to the topics discussed here that we shall attempt to clarify the way in which polymer concentration enters as a variable in Manning's work, and is omitted from our two state approximation. We have dealt specifically with an isolated polymer molecule in salt solution, and no matter how dilute the latter may be, it provides a contribution, the only contribution unless one allows for water dissociation, to the bulk ionic strength. However, Manning allows for a nonvanishing contribution to the ionic strength from counterions that dissociate from added polyelectrolyte. This contribution may be the only one, i. e., there may be a finite screening length even in the absence of added salt. However, no interaction between polymers is allowed. No attempt was made to rationalize this apparently contradictory procedure, yet the results have met with a certain amount of experimental confirmation.

What is wanted to resolve this difficulty, or to bring it within the bounds of study, is a model of the concentrated polymer solution which on the one hand asserts the charging free energy of a single polymer molecule to be calculable without explicit account of the potential field due to other polymers, but yet takes all the other polymers and especially their counterions to be present. We first remark that explicit consideration of electrostatic interactions between polymers may always be avoided because these interactions are generated implicitly from Poisson's equation and the polymer part of the total charge density. Therefore, we focus on the total charge density. Consider first a single central polymer with variable charge q , and immersed in the solution of fully charged polymers. For $q = 0$, it seems reasonable

to take the mean charge density to vanish, to a first approximation, everywhere outside the central polymer. Therefore, the mean field acting on the central polymer will also vanish. The uniform charge density of small ions is exactly compensated by a uniform polymer charge density outside the central uncharged polymer.

If the central polymer is now gradually charged, what happens to the charge density in solution? One might suppose, from the omission of interactions in Manning's hypotheses, that the fully charged polymers immediately depart for infinity in response to the charging process. However, this interpretation, even if acceptable on other grounds, would not justify the implicit treatment of charge density in the limiting laws. The charge density is treated in the Debye-Hückel approximation and includes only small ions in the ionic strength. The Debye-Hückel form for the surface potential implies a linearization, with which we are not here concerned, and also the boundary condition that the charge density vanishes far from the central polymer at a rate governed by the finite ionic strength. If all other polymers have left the vicinity of the central polymer, but their counterions remain behind, the net charge density will not vanish properly. This objection does not apply to the lattice model of Katchalsky *et al.*,² because boundary conditions on the potential apply at the cell boundary instead of at infinity.

The other extreme assumption is that all other polymers maintain a random distribution while the central ion is being charged, and only the small ions rearrange according to a Boltzmann distribution. This assumption seems to justify Manning's treatment [disregarding quantitative errors in the treatment of $X(a)$ at finite ionic strength], and the question then becomes the justification of this randomness. We wish to point out here merely that the assumption has some precedent in polymer solution theory. It is used in the Flory-Huggins theory of nonelectrolyte polymers and is believed to be roughly valid at polymer concentrations sufficiently high to force a great deal of overlapping of polymer domains. So the assumption may be plausible enough for further study. It may also happen that the predicted results are fairly immune to errors in the polymer distribution, since the lattice model of Katchalsky *et al.*² often gives similar results. A possible key to the similarity for salt free polymer solutions is that the lattice model is a two dimensional array of infinite cylinders. The separation between cylinders is the scaling length for the decay of the potential, and is inversely proportional to the square root of polymer concentration; so also is the Debye length in Manning's hypotheses.

We wish finally to call attention to a very recent paper by Henderson and Blum on an electrolyte solution near a charged wall.¹⁸ They also conclude that the PB equation is adequate at high salt concentrations if the surface charge is very large.

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- ¹G. M. Bell and S. Levine, in *Chemical Physics of Ionic Solutions*, edited by B. E. Conway and R. G. Barradas (Wiley, New York, 1966), p. 409.
- ²(a) A. Katchalsky, *Pure Appl. Chem.* **26**, 327 (1971); (b) R. M. Fuoss, A. Katchalsky, and S. Lifson, *Proc. Natl. Acad. Sci. (U.S.)* **37**, 579 (1951); (c) T. Alfrey, P. W. Berg, and H. Morawetz, *J. Polym. Sci.* **7**, 543 (1951).
- ³(a) J. A. Schellman and D. Stigter, *Biopolymer* **16**, 1415 (1977); (b) D. Stigter, *J. Phys. Chem.* **82**, 1603 (1978); (c) G. S. Manning, *J. Phys. Chem.* **82**, 2349 (1978).
- ⁴(a) G. S. Manning, *J. Chem. Phys.* **51**, 924 (1969); (b) G. S. Manning, *Q. Rev. Biophys.* **11**, 179 (1978).
- ⁵(a) F. Oosawa, *Polyelectrolytes* (Dekker, New York, 1971); (b) G. S. Manning, *Biophys. J.* **7**, 95 (1977).
- ⁶(a) F. P. Buff and F. H. Stillinger, *J. Chem. Phys.* **39**, 1911 (1963); (b) G. S. Manning and B. H. Zimm, *J. Chem. Phys.* **43**, 4250 (1965); (c) K. Iwasa and J. C. T. Kwak, *J. Phys. Chem.* **81**, 408 (1978).
- ⁷M. T. Record, Jr., C. F. Anderson, and T. M. Lohman, *Q. Rev. Biophys.* **11**, 103 (1978).
- ⁸(a) J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964); (b) For recent references, see Y. Singh and F. F. Abraham, *J. Chem. Phys.* **67**, 537 (1977).
- ⁹(a) E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**, 3086, 3093 (1972); (b) D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), Chap. 15.
- ¹⁰Bell and Levine¹ and Buff and Stillinger^{6a} also find that the cavity potential correction is the largest.
- ¹¹We have not worked to improve Eqs. (4.17) and (4.18) for the infinite cylinder because the values of $\psi(a)$ are rather insensitive to the modifications, and we had no need for especially precise values (which are easily obtained from the PB equation). For more complicated geometries, a convincing and significant improvement on these extrapolations from surface values seems still less profitable.
- ¹²The excess charge is measured by $E(\rho)$ or $F(\rho)$, and should be distinguished from an effective surface charge that might be inferred from the value of $X(a)$ that replaces ξ in Eq. (4.13).
- ¹³D. Stigter, *J. Colloid Interface Sci.* **53**, 296 (1975); *J. Phys. Chem.* **64**, 838 (1960).
- ¹⁴A. D. MacGillivray, *J. Chem. Phys.* **57**, 4071, 4075 (1972).
- ¹⁵D. Stigter, *Biopolymers* **16**, 1435 (1977).
- ¹⁶M. Fixman and J. Skolnick, *Macromolecules* **11**, 863 (1978).
- ¹⁷K. Iwasa, *J. Phys. Chem.* **81**, 1829 (1977).
- ¹⁸D. Henderson and L. Blum, *J. Chem. Phys.* **69**, 5441 (1978).