

# Thermodynamic Theory of Counterion Association in Rigid Polyelectrolytes

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**Abstract.** — We present a new theory of rodlike polyelectrolyte solutions. It is found that at *low* densities, and *below* temperature  $T_{cl}$ , the counterions associate with the polyions forming clusters consisting of one polyion and  $n$  counterions. The distribution of clusters sizes is Gaussian, leading to strong logarithmic corrections to the limiting laws obtained by Manning. In the mathematical limit of infinite dilution the distribution of the cluster sizes approaches a delta function centered on the value postulated by Manning. Above  $T_{cl}$  the solution consists of free (unassociated) counterions and polyions, and the limiting laws remain unaffected. Finally, unlike some recent suggestions, we demonstrate that the counterion condensation is distinct from the Kosterlitz-Thouless transition. In fact, the association phenomena inside a polyelectrolyte solution can be compared to a formation of micelles in amphiphilic systems. There is, however, an important difference. While the amphiphilic micelles can be diluted away (broken apart) by increasing the amount of solvent, the strong electrostatic interactions keep the polyion-counterions clusters from dissociating, even as the concentration of polyelectrolyte is decreased all the way down to zero.

## 1. Introduction

Many complex organic molecules such as DNA and other polyphosphates, upon dilution in aqueous solutions, become ionized. The importance of a polyelectrolyte nature of these polymers has been realized for a long time, and is expected to strongly affect how these molecules interact with their environment. Because of the paramount role that polyphosphates play in nature the desire to understand the ionized state of these molecules has attracted tremendous amount of effort over the years. In this respect polyelectrolyte chemists have been at a great disadvantage compared to their colleagues involved in research on simple electrolytes. For over seventy years electrolyte chemists have possessed an important tool at their disposal, Debye-Hückel limiting, low density, laws for pressure and other thermodynamic functions [1]. The knowledge of the limiting laws is of a great importance since it allows the extrapolation of the measurements done at a finite concentration into a very dilute region providing a “reference point”. The “deviation from the limiting law” can then be measured and an appropriate theory

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can be attempted attributing the deviation to the effects not taken into account in the derivation of the law, such as molecular nature of the solvent, the presence of short range forces, *etc.* [2]. In addition, the Debye-Hückel (DH) theory provides a simple and an intuitive picture of an electrolyte solution at low densities. Thus, the unusual properties of the electrolytes, as compared to the systems in which short range forces play the dominant role, can be traced to the statistical distribution of the electrostatic potential inside the solution. This, in turn, forces the ions to arrange themselves in such a way as to screen the interactions between the particles, thus reducing the *effective* range of the potential. Furthermore, the DH theory can be extended from the low density limit to an intermediate regime if the allowance is made for the fact that oppositely charged ions have a tendency to stick together, forming dipolar pairs [3]. In fact, it has recently been shown that this extended Debye-Hückel-Bjerrum (DHBj) theory [4] can account for the observed liquid-liquid and liquid-gas phase separation in ionic systems [5]. In the case of the Restricted Primitive Model of Electrolyte (RPM), which consists of a gas of hard spheres half of which carry a positive charge while the other half carry a negative charge, the DHBj theory predicts a coexistence curve in an excellent agreement with the Monte Carlo simulations (MC) [6]. Furthermore, the theory can be easily extended to general dimensions and, in particular, reproduces Kosterlitz-Thouless result [7] of an infinite order line of metal-insulator transitions in two dimensions, but in addition predicts that this line will terminate in a tricritical point, after which an insulating vapor phase will coexist with a conducting fluid [8], the conclusion which is once again in agreement with the MC [9].

The situation regarding the polyelectrolyte solutions is far less clear. The difficulty lies in the fact that a polyion contains on an order of a thousand charged groups. Thus, in addition to the already difficult problem of long range inter-particle Coulomb interactions, one must also account for the conformational state of the polyions [10]. Fortunately, this latter difficulty can be overcome for one important class of polyelectrolytes, which are the subject of this study.

Many biological macromolecules, such as polyphosphates and polysaccharides, are intrinsically rigid. This rigidity is responsible for the "rodlike" shape characteristic of these biomolecules on short length scales. The local linearity of these polymers dramatically simplifies their study. Even though, for a long time there remained some doubt if the whole concept of limiting laws is applicable to the polyelectrolyte solutions [2]. It was argued that a strong electrostatic potential produced by a polyion will lead to a high concentration of the counterions in its vicinity. The problem would then be that of a concentrated solution, even for a polyelectrolyte at very low densities, and no limiting laws should be anticipated. Fortunately these fears have since proven to be unjustified [2].

A number of approaches have been tried in order to find a solution to this complex problem. Because of a strong electrostatic potential produced by a polyion, and because of its almost linear conformation, most of the early attempts have relied on solving the full non-linear Poisson-Boltzmann equation (NLPBE) in a cylindrical geometry. Although promising, these approaches fell short of elucidating the full physics of the problem. Nevertheless, as long ago as 1951 Fuoss, Katchalsky and Lifson noted that their exact solution of the cylindrically symmetric NLPBE exhibited qualitatively different behavior for small and large temperatures [11]. The peculiarity of the low temperature solution of the NLPBE, was interpreted by Imai, Omishi and Oosawa as corresponding to the fact that a certain number of counterions have "condensed" onto a polyion [12].

One of the major problems of all approaches based on solving the NLPBE is the internal inconsistency of its solutions. This inconsistency, already noticed by Onsager in the context of a simple electrolyte [13], makes all the conclusions derived on the basis of the NLPBE suspect. The process of linearization of the NLPBE, besides simplifying the calculations, restores the internal self consistency of the theory. This, of course, comes at a price since linearization

effectively reduces the Boltzmann weight of the configurations in which oppositely charged ions come into a close contact to form clusters, such as dipoles, tripoles, quadrupoles *etc.* The success of the DHBj theory is exactly due to the fact that through the assumption of chemical equilibrium it reintroduces these important nonlinear configurations back into the DH theory while preserving its internal consistency [4,14].

The most promising approach to the problem of strong polyelectrolyte was developed by Manning in a pioneering paper published a quarter of a century ago [2]. In order to explain Manning's approach, as well as to proceed farther, we shall first define a Primitive Model of a Polyelectrolyte (PMP).

1.1. PMP AND MANNING'S APPROACH. — The PMP consists of  $N$  polyions inside a volume  $V$ . The molecules are idealized as long cylinders of cross-sectional diameter  $a_p$  and length  $L$ , each carrying  $P$  ionized groups of charge  $-q$  spaced uniformly, with separation  $b$ , along the axis of the cylinder. A total of  $PN$  counterions are present to preserve the overall charge neutrality of the system. The counterions are assumed to be spherical in shape with a diameter  $a_c$ , each carrying a charge  $q$ . It will prove convenient to define the distance of closest approach between the centers of a polyion and a counterion,  $a = (a_p + a_c)/2$ . The solvent is modeled as a uniform medium of a dielectric constant  $D$ . The PMP should give a good representation of a stiff polymers such as DNA and polysaccharides, while for flexible chains such as polyacrylic and polystyrenesulfonic acids it should be at most qualitative. In this respect the recent simulations of flexible polyelectrolytes by Stevens and Kremer are not directly applicable to PMP [15].

In the low density limit, we shall neglect the discrete nature of the charge distribution and assume a uniform charge density  $\sigma_0 = -Pq/L = -q/b$  along the polyion. It is then easy to see that, sufficiently close to the polyion  $r < R$ , the interaction potential between it and a counterion is given by an unscreened form

$$\phi(r) = -2q(\sigma_0/D)\ln(r/r_0), \quad r < R \quad (1)$$

where  $r_0$  is an arbitrary zero point of the potential and the arbitrary distance  $R$  is less than the characteristic Debye length inside the polyelectrolyte solution (see the discussion following Eq. (11)). Following Onsager, Manning observed that below certain temperature  $T_c$ , in the limit of a vanishing hardcore size ( $a \rightarrow 0$ ) this potential will result in an infinite contribution to the partition function [2]. Namely,

$$L \int_a^R e^{-\frac{\phi(r)}{k_B T}} d^2r = \pi L r_0^2 \frac{((R/r_0)^{2-2\xi} - (a/r_0)^{2-2\xi})}{(1-\xi)} \quad (2)$$

where  $\xi = |q\sigma_0|/Dk_B T = q^2/Dk_B T b$ , will diverge logarithmically as  $\xi \rightarrow 1^-$  and  $a \rightarrow 0$ . Manning then interpreted the divergence above  $\xi = 1$  as signifying that  $n$  counterions have condensed onto a polyion, thus reducing its charge density from  $\sigma_0$  to  $\sigma_n = \sigma_0(P - n)/P$ . He then assumed that the number of condensed counterions will be such as to prevent the effective value of  $\xi$ ,  $\xi_{ef} = |q\sigma_n|/Dk_B T$ , from ever becoming greater than one, and in this way preclude the phase integral from becoming divergent. Thus, for all  $\xi > 1$ , Manning assumed that  $\xi_{ef} = 1$ . For this to be true the number of condensed counterions must be  $n_c = P(1 - 1/\xi)$ . Using this simple observation and treating the uncondensed counterions within usual linearized DH theory, Manning was able to derive a set of limiting laws for the polyelectrolytes, which have since proven to work quite well [2].

Notwithstanding its success, there are remain quite a few problems with the theory described above. In particular, since the condensation phenomena is not a result of a free energy

minimization, but is instead based on a somewhat *ad hoc* assumption, it appears to violate the law of mass action. This point, already noticed by Manning [16], has been left unanswered for a quarter of a century, in view of otherwise successful predictions of the theory. It would, to say the least, seem strange that a success of a *classical* theory would rely on a breakdown of one of the most fundamental laws of Statistical Mechanics.

A different problem with the approach outlined above is the divergence of the integral, but only, in the limit of a vanishing hardcore size. If the polyion is treated as a cylinder of finite diameter, no divergence occurs, and it then becomes more difficult to come up with the proper basis for the theory of counterion condensation [17]. In fact, one is quite naturally led to observe a similarity between the Manning's theory of counterion condensation and the Kosterlitz-Thouless (KT) theory of metal-insulator transition in a two dimensional hard disk Coulomb gas [7]. The interaction potential between two oppositely charged coulombic particles in two dimensions is given by equation (1) with a substitution  $\sigma_0 \rightarrow -q$  (or  $b \rightarrow 1$ ). In this case it is found that below certain temperature all ions will associate into dipolar pairs. Just as in equation (2), one finds that, in the limit of vanishing ionic size, the phase integral diverges logarithmically at the temperature  $k_B T_c D/q^2 = 1$ . However, once the hardcore is restored, no singularity is observed at this temperature and the true phase transition, between a plasma and a dipolar phase, occurs at  $k_B T_{KT} D/q^2 = 1/2$  [7]. Furthermore, even in this case one can show that the law of mass action is not violated [8].

One might then wonder if the counterion condensation belongs to the same class of phase transitions as a two-dimensional gas of Coulomb *point* particles studied by Hauge and Hemmer [18]. These authors found that although partition function for point ions is divergent, the equation of state is well defined in the limit  $a \rightarrow 0$ . In this case the transition to an insulating (dipolar) state does indeed happen at  $T_c = 2T_{KT}$ . This phase transition, however, is associated with a singular specific heat diverging as  $|T - T_c|^{-2}$ , leading to a non integrable free energy. It is, therefore, apparent that the phase transition found by Hauge and Hemmer is an unlikely candidate for describing any natural phenomena. Furthermore, the system of point particles is not realistic, since in practice no two ions can approach each other closer than their respective Bohr radii. Hence, one must either apply quantum statistical mechanics or introduce a hardcore for each ion. In all classical applications the latter, of course, is sufficient [19].

The crucial dependence of all the properties of a two-dimensional Coulomb gas on the size of ions is an intrinsic characteristic of a system whose entities interact through a logarithmic potential. Since a polyelectrolyte solution is also a realization of such a system, a particular care must be taken in treating both counterions and polyions as realistic molecules of finite volume.

The purpose of this papers is to explore the properties of a polyelectrolyte solution at low densities. A new theory will be presented which addresses and resolves all the issues raised above [20]. The paper is organized in four sections. In Section 2 we shall develop a fully self consistent thermodynamic theory of a neutral polyelectrolyte solution in the absence of a monovalent salt. In Section 3 this theory will be extended to allow for the presence of simple 1:1 salt, and its effects on the properties of a polyelectrolyte solution will be analyzed. In Section 4 some concluding remarks will be presented.

## 2. Debye-Hückel-Bjerrum Theory of a Polyelectrolyte Solution

We shall work in the context of the PMP defined above. The overall density of polyions is  $\rho = N/V$ , while the total density of counterions is  $P\rho$ . The reduced density is defined as

$\rho^* = \rho a^3$ . The bare interaction potential between a polyion and a counterion at separation  $r$  is:

$$\phi(r) = \begin{cases} +\infty, & r < a, \\ -2q(\sigma_0/D) \ln(r/a), & r \geq a, \end{cases} \quad (3)$$

where to simplify notation we have set  $r_0 = a$ . It is important to remember that we are modeling a polyion as a *long* cylinder of a uniform charge density, and for this reason neglect all the end effects.

Because of a strong electrostatic interaction between the polyions and the counterions, we expect that a polyelectrolyte solution will be composed of clusters, consisting of one polyion and of  $1 \leq n \leq P$  associated counterions, with density  $\rho_n$ , as well as free unassociated polyions of density  $\rho_0$ , and free unassociated counterions of density  $\rho_+$ . We are then led to two conservation equations,

$$\rho = \sum_{n=0}^P \rho_n, \quad (4)$$

$$P\rho = \rho_+ + \sum_{n=0}^P n\rho_n, \quad (5)$$

Equivalently we have

$$P \sum_{n=0}^P \rho_n = \rho_+ + \sum_{n=0}^P n\rho_n. \quad (6)$$

The pressure can be expressed as a Legendre transform of the Helmholtz free energy density,  $f = -F/V$ ,

$$p(T, \rho_+, \{\rho_n\}) = f(T, \rho_+, \{\rho_n\}) + \sum_s \mu_s \rho_s, \quad (7)$$

where the chemical potential of a specie  $s$  is,  $\mu_s = -\frac{\partial f}{\partial \rho_s}$ , and the sum is over all the species, polyions, counterions and clusters. The free energy, is constructed as a sum of the most relevant contributions, starting with an ideal gas (entropic) term

$$\beta f^{\text{Ideal}} = \sum_s \rho_s [1 - \ln(\rho_s \Lambda_s^{3k_s} / \zeta_s)], \quad (8)$$

where  $\beta = 1/k_B T$ , and  $k_s$  is the number of entities comprising species  $s$ , *i.e.*,  $k_+ = k_0 = 1$ ,  $k_n = n + 1$ . The thermal wavelengths are

$$\Lambda_s(T) = \frac{h}{\sqrt{2\pi \bar{m}_s k_B T}}, \quad (9)$$

where  $\bar{m}_s$  is the geometric mean mass for a specie  $s$ . For a  $n$ -cluster  $\bar{m}_n = (m_p m_c^n)^{1/k_n}$

The internal counterion, polyion, and a  $n$ -cluster partition functions are respectively,  $\zeta_+ = \zeta_0 = 1$ ,  $\zeta_{n \geq 1}(T)$ . The expression for  $\zeta_1$  is given by the equation (2). To obtain the higher cluster internal partition functions, we shall assume that the counterions are "territorially bound" to the polyion, that is, they are free to move along the length of the cylinder. This assumption seems to be consistent with experiments on polyphosphates, and has been extensively discussed by Manning [19]. Alternatively, since we are considering equilibrium association, counterions are in a constant flux of binding and unbinding with the polyion. This process can be visualized as a random motion of the counterions along the length of the polyion. This, then, leads to

an effective renormalization of the charge density of the polyion. We shall assume that the charge density of an  $n$ -cluster is  $\sigma_n = \sigma_0(P - n)/P$ . Since the already bound counterions contribute only to the renormalization of the surface charge, the internal partition function for the formation of a  $n$ -cluster, from a  $(n - 1)$ -cluster and a counterion, is given by an integral in equation (2) multiplied by  $a^{3(n-1)}$  and a substitution  $\sigma \rightarrow \sigma_{n-1}$  [22].

We are still left with an arbitrary distance  $R$  which defines the separation between a polyion and a counterion at which they can be interpreted as forming a cluster. The presence of an arbitrary cutoff is a usual artifact of a Bjerrum type of approach [14]. The final answers should be insensitive to the exact value of the cutoff, which for concreteness we can set equal to  $2a$ . For an extensive discussion of the equilibrium constant in the case of a simple electrolyte see reference [14].

Next we consider the expression for  $f^{\text{DH}}$ , the excess free energy arising from the electrostatic interactions. There are in principle three distinct contributions to the electrostatic free energy coming from: (1) polyion-polyion interactions; (2) counterion-counterion interactions; and (3) polyion-counterion interactions. It seems impossible to find a general theory that would incorporate all three of the above mentioned mechanisms in a self consistent fashion. However, since we are only interested in a limiting behavior,  $\rho \rightarrow 0$ , a number of major simplifications are applicable. First consider the polyion-polyion interaction. At present no simple mean field theory of the DH type is available to find a leading order virial contribution due to a polyion-polyion interaction. Nevertheless we can make some general statements to its effect. Certainly the interaction between two polyions will be screened by the cloud of counterions. Thus, although the bare interaction between two polyions is long ranged, the screening by counterions is expected to make the effective interaction short ranged, acting only over a distance of an order of the screening length. If this is indeed the case, then the polyion-polyion contribution to the free energy density is expected to behave in a usual van der Waals fashion characterized by a second virial term,  $\beta f_{\text{pp}} \approx L^2 \rho^2 \approx (P\rho)^2$ . Even if this assumption is oversimplifying, nevertheless, at most we can expect that  $\beta f_{\text{pp}} \approx (P\rho)^x$ , where  $x > 1$  [23].

In the limit of small density the counterion-counterion contribution to the free energy density can be easily estimated from the standard DH theory. Thus we find that  $\beta f_{\text{cc}} \approx (P\rho)^{3/2}$ . Finally, it will be demonstrated later on that the polyion-counterion interaction results in a contribution which scales as  $\beta f_{\text{pc}} \approx P\rho \ln(P\rho)$ . Since we are concerned only with the low density limit ( $P\rho^* \ll 1$ ), both the polyion-polyion and the counterion-counterion contributions to the free energy will be negligible compared to the polyion-counterion contribution. Similarly the short ranged forces will be irrelevant in the limit of low densities. We shall now proceed to calculate the polyion-counterion contribution to the free energy.

Let us concentrate our attention on one polyion  $\mathcal{P}_i$ , see Figure 1. Because of the hardcore repulsion, counterions are excluded from a cylinder  $r < a$  centered on  $\mathcal{P}_i$ . Thus, the electrostatic potential  $\varphi(r)$  in this region satisfies the Laplace equation  $\nabla^2 \varphi = 0$ , with a cylindrical symmetry.

Outside the exclusion sphere the mean charge distribution will be specified by a polyion-counterion pair correlation functions,  $g_{-+}(r)$ . Within the DH theory this is approximated by a Boltzmann factor leading to the charge density

$$\rho_q = - \sum_{n=0}^P (P - n) q \rho_n + q \rho_+ e^{-\beta q \varphi(r)} \quad (10)$$

Notice that only free, unassociated, counterions are assumed to get polarized while the polyions and clusters are too massive to be affected by the electrostatic fluctuations, and contribute only to the neutralizing background. Substituting  $\rho_q$  into the Poisson equation,  $\nabla^2 \varphi = -4\pi \rho_q / D$ ,

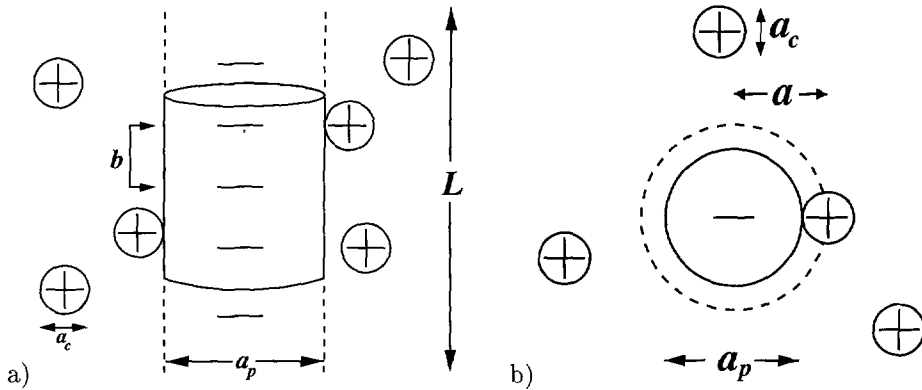


Fig. 1. — a) The side view of a salt free polyelectrolyte solution in a vicinity of the polyion. The polyion is approximated as a very long cylinder of a cross-sectional diameter  $a_p$  carrying  $P$  ionized groups uniformly distributed along the major axis. The counterions are represented by the hard spheres of diameter  $a_c$ . b) A top view of a polyion molecule. The dashed circle represents the excluded volume region of radius  $a$  into which no counterion can penetrate. Inside this region the electrostatic potential satisfies the Laplace equation. Outside the counterions are distributed according to the Boltzmann distribution, equation (10), and the electrostatic potential satisfies the Helmholtz equation (11).

leads to a nonlinear Poisson-Boltzmann equation (NLPBE). As a second approximation of the DH theory, the exponential factor in the equation (10) is linearized leading, with a help of equation (6), to a Helmholtz equation,

$$\nabla^2 \varphi = \kappa^2 \varphi, \quad (11)$$

where the inverse Debye length  $\kappa = 1/\xi_D$  is given by  $\kappa^2 a^2 = 4\pi\rho_+^*/T^*$ , and the reduced temperature  $T^* = k_B T D a / q^2$  is related to Manning's condensation parameter through  $\xi = a/T^* b$ . As was discussed in the introduction, besides the technical simplifications linearization insures that the theory satisfies important electrostatic selfconsistency condition which the full NLPBE is lacking [13]. Naively one might expect that the linearization is only valid in the high temperature limit, namely when  $\beta\varphi \ll 1$ . This, however, turns out to be incorrect and, in particular, when the formation of clusters is taken into account the extended theory appears to have validity far into the nonlinear regime [14].

Both the Laplace and the Helmholtz equation can now be solved. As the boundary conditions one must require that both  $\varphi(r)$  and the electric field  $-\nabla\varphi$ , are continuous across the exclusion cylinder  $r = a$ , and that  $\varphi(r)$  vanishes as  $r \rightarrow \infty$ . In the exterior region,  $r > a$ , we find [8.23]

$$\varphi(r) = \frac{2\sigma_0}{D} \frac{K_0(\kappa r)}{(\kappa a)K_1(\kappa a)}, \quad (12)$$

where  $K_\nu(x)$  is a modified Bessel function of order  $\nu$ . Since for large  $x$ ,  $K_0(x)$  decays exponentially, we find the anticipated Debye screening. For  $r \leq a$  the electrostatic potential is

$$\varphi(r) = -\frac{2\sigma_0}{D} \ln(r/a) + \frac{2\sigma_0}{D} \frac{K_0(\kappa a)}{(\kappa a)K_1(\kappa a)}. \quad (13)$$

It is evident that the first term of the equation (13) is just the potential produced by the polyion itself. The second term is more interesting and corresponds to the potential of a polyion with

respect to the ionic atmosphere. The electrostatic free energy due to the polyion-counterion interaction is then given exactly by a Debye charging process. Denoting the potential of a polyion with respect to the counterions by

$$\psi(q) = \frac{2\sigma_0}{D} \frac{K_0(\kappa a)}{(\kappa a)K_1(\kappa a)}. \quad (14)$$

the free energy density of all unassociated polyions is given by Debye charging process

$$f_0^{\text{DH}} = -\sigma_0 L \rho_0 \int_0^1 d\lambda \psi(\lambda q). \quad (15)$$

The integral can be easily performed using a Bessel function identity

$$\frac{d(xK_1(x))}{dx} = -xK_0(x). \quad (16)$$

Since the counterion association leads to an effective renormalization of the charge density, the free energy of the clusters is found by replacing  $(\sigma_0 \rightarrow \sigma_n, \rho_0 \rightarrow \rho_n)$  in the above formulas. The electrostatic free energy density of an  $n$ -cluster is then given by.

$$\beta f_n^{\text{DH}}(\rho_+, \rho_n) = \frac{\rho_n^*(P-n)^2}{2\pi L a^2 \rho_+^*} \ln(\kappa a K_1(\kappa a)). \quad (17)$$

The total free energy density of a polyelectrolyte solution is

$$f(\rho_+, \{\rho_n\}) = f^{\text{Ideal}}(\rho_+) + \sum_{n=0}^P f^{\text{Ideal}}(\rho_n) + \sum_{n=0}^P f_n^{\text{DH}}(\rho_+, \rho_n). \quad (18)$$

Given the free energy all the thermodynamic functions can in principle be found.

The respective density of all the species is controlled by the law of mass action,  $\mu_n = \mu_0 + n\mu_+$ , which upon substitution of the definition of chemical potentials in terms of free energy reduces to

$$\rho_n^* = K_n(T) \rho_0^* (\rho_+^*)^n e^{\beta \mu_0^{\text{Ex}} + n\beta \mu_+^{\text{Ex}} - \beta \mu_n^{\text{Ex}}}, \quad (19)$$

where the equilibrium constant is

$$K_n(T) = \frac{\zeta_n(T)}{a^{3n}} = \frac{2\pi L}{Z_n a} (1 - (R/a)^{-Z_n}); \quad Z_n = 2\xi \left( \frac{P-n+1}{P} \right) - 2, \quad (20)$$

and the excess chemical potentials are  $\mu_s^{\text{Ex}} = -\frac{\partial f^{\text{Ex}}}{\partial \rho_s}$ , with  $f^{\text{Ex}} = \sum_{n=0}^P f_n^{\text{DH}}$ . In general trying

to solve the set of coupled equation (19) under the constraint of equations (4, 5) is quite a formidable task, in particular since we are interested in a long polyions with a large number of charged groups. In the limit of low densities the problem, however, simplifies dramatically. We first observe that

$$\beta \mu_n^{\text{Ex}} = -\frac{(P-n)^2}{P} \xi \left[ \frac{2\gamma_E - 1}{2} + \ln \left( \frac{\kappa a}{2} \right) \right] + O(\rho_+), \quad (21)$$

$$\beta \mu_+^{\text{Ex}} = -\sum_{n=0}^P \frac{(P-n)^2 \rho_n^*}{2P \rho_+^*} \xi + O(\rho_+). \quad (22)$$



where  $\gamma_E$  is the Euler constant,  $\gamma_E = 0.577215664\dots$ . Inserting these expressions into the equation (19) and using the explicit form of  $\kappa a$ , it becomes evident that, in the limit of small densities, equation (6) is organized in the powers of  $\rho_+^{g(n)}$  where  $g(n) = n - n\xi + n^2\xi/2P$ . In the mathematical limit  $\rho_+ \rightarrow 0$  only the term with  $n_c = P(1 - 1/\xi)$  such that  $g(n_c)$  is at its minimum, will survive. But this is exactly the Manning's assumption that  $P(1 - 1/\xi)$  counterions will condense onto a polyion! Although, we have started with a very different set of assumption about the structure of a polyelectrolyte solution at low density, we have reached the same conclusion as Manning. It is, however, important to remember that while Manning's result was based on a somewhat *ad hoc* assumption about the divergence of a two-body polyion-counterion partition function in the limit of vanishing hardcore size, our result is firmly imbedded in the framework of thermodynamics and statistical mechanics. In particular, no unphysical limit of a vanishing hardcore size was necessary in order to reach our conclusions. The law of mass action, properly applied to the polyelectrolyte solution, leads to the fundamental prediction that in the limit  $\rho \rightarrow 0$ , the distribution of the cluster sizes approaches a delta-function centered on the value postulated by Manning,

$$\rho(n) = \rho\delta(n - n_c). \quad (23)$$

Thus, although Manning's underlying assumptions might appear to be in violation of the law of mass action, his conclusion is consistent with this fundamental law. For  $\xi < 1$  no clusters will form and  $n_c = 0$ .

We conclude that in the limit  $\rho \rightarrow 0$ , only the clusters of size  $n_c$  will exist and contribute to the osmotic pressure of the solution. Inserting equations (18, 21, 22) into the expression for pressure (7), in the limit of vanishing density, we find

$$\beta p = \left(1 - \frac{\xi}{2}\right) P\rho + O((P\rho)^{2-\xi+\xi/2P}); \quad \xi < 1, \quad (24a)$$

$$\beta p = \frac{P\rho}{2\xi} + O((P\rho)^{1+\xi/2P}); \quad \xi > 1, \quad (24b)$$

where the corrections come from the next dominant clusters.  $n_c \pm 1$ , ( $n_c + 1$  in the case of Eq. (24a)). These equations, up to the correction terms, are the same as the ones obtains by Manning based on the assumption of counterion condensation [2]. The first of these equations should work quite well in the limit of reasonably small densities if  $\xi < 1$ , since the corrections will indeed be small. We are, however, lead to observe that in practice the mathematical limit  $\rho_+ \rightarrow 0$ , will be impossible to take in the case of the equation (24b), since it would require  $(P\rho)^{\xi/2P} \ll 1$  or  $|\ln(P\rho^*)| \gg P$ , which is, of course, impossible for realistic densities, since  $P$  is assumed to be of an order of a thousand groups. The implication of this result is that other clusters besides  $n_c$  are important at the realistic densities and must be accounted for. One can then attempt to construct a perturbation theory in the size of the clusters. This procedure, however, seems to be quite complicated since a large number of clusters would have to be considered to get a reasonable accuracy. Instead of pursuing a perturbative route, we observe that in the limit of small densities equation (19) can be cast into a Gaussian form in terms of  $n$ . This is possible because for large  $P$ , the equilibrium constant, in the vicinity of  $n_c$ , is quasi-independent of the cluster size,

$$K_{n_c+\delta} = \frac{2\pi L \ln R}{a} \frac{1}{a} + O\left(\frac{\delta - 1}{P}\right). \quad (25)$$

All the dependence on  $n$  is, then, contained in the chemical potentials (21, 22). We can,

therefore, try the following ansatz,

$$\rho(n) = \frac{\rho}{\sqrt{2\pi\sigma^2}} e^{-\frac{(n-n^*)^2}{2\sigma^2}} \quad (26)$$

The conservation equations can now be written in an integral form

$$\int_0^P \rho(n)dn = \rho, \quad (27)$$

$$P\rho = \rho_+ + \int_0^P n\rho(n)dn. \quad (28)$$

Since the distribution function is Gaussian, peaked around  $n^*$ , to simplify the calculations we can extend the limits of integration to  $(-\infty, +\infty)$ . The first of the conservation equation (4) is satisfied trivially, while the second one (5) leads to a relation between the density of unassociated counterions and the peak value of the distribution function,

$$n^* = P - \rho_+/\rho. \quad (29)$$

All the sums can now be easily evaluated by replacing them by the integrals over the cluster distribution. In particular the excess chemical potential of unassociated counterions (Eq. (22)), reduces to,

$$\beta\mu_+^{\text{Ex}} = -\frac{(P-n^*)^2 + \sigma^2}{2P(P-n^*)}\xi. \quad (30)$$

The maximum and the standard deviation can now be obtained by completing the square in equation (19), justifying our ansatz. We find

$$n^* = P \left( 1 - \frac{\ln\rho_+^*}{\xi(\ln\rho_+^* + c(T^*))} \right) + O(P^0) \quad (31)$$

and

$$\sigma^2 = -\frac{P}{\xi(\ln\rho_+^* + c(T^*) - 1/2)}, \quad (32)$$

where  $c(T^*) = 2\gamma_E - 1/2 + \ln(\pi/T^*)$ . Combining equations (29) and (31) we obtain a self-consistent equation for the density of the unassociated counterions,

$$\rho_+^* = \frac{P\rho^* \ln\rho_+^*}{\xi(\ln\rho_+^* + c(T^*))}. \quad (33)$$

Equations (31-33) are the central results of this paper, with their help all the thermodynamic functions of a polyelectrolyte solution at low densities can be obtained.

Solving equation (33) we observe that, the maximum of the density distribution is shifted from its zero density limit to,

$$n^* = P \left( 1 - \frac{1}{\xi} \right) + \frac{P}{\xi} \left( \frac{c(T^*)}{d(\rho^*)} - \frac{c^2(T^*)}{d^2(\rho^*)} + O(1/d^3(\rho^*)) \right), \quad (34)$$

where  $d(\rho^*) = \ln(P\rho^*/\xi)$ . The success of Manning's theory can be attributed to the fact that his postulate for the number of condensed counterions is close to the peak value of the Gaussian distribution, which he effectively replaced by a delta function. Finally, it is interesting to note

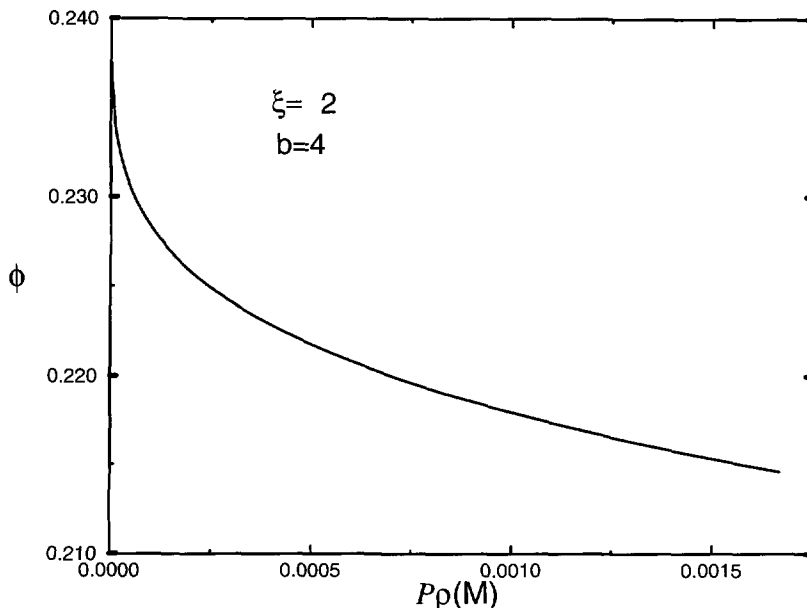


Fig. 2. — The osmotic coefficient of a salt free polyelectrolyte solution. Note that the limiting value is approached logarithmically from below.

that in the limit  $a \rightarrow 0$ , the distribution of cluster sizes will once again approach a delta function centered on  $n = n_c$ . The reason for this unusual behavior, is due to the fact that the corrections to the leading order (Manning), behavior are only dependent on the reduced density  $\rho^* = \rho a^3$ , which vanishes in the limit  $a \rightarrow 0$ . Thus Manning's result is indeed exact for the line of charge model in which polyion is approximated by a straight line, and the counterions are treated as point particles.

Returning to the PMP, we observe that the temperature at which the clusters begin to form,  $n^*(T_{cl}) = 0$ , is given by the solution of

$$\ln(P\rho^*) = \frac{c(T_{cl}^*)a}{T_{cl}^*b - a} \quad (35)$$

Notice that the cluster formation temperature,  $T_{cl}^*$ , is lower than the Manning condensation temperature  $T_M^* = a/b$ .

The pressure can now be calculated straightforwardly by replacing all the sums appearing in equations (7, 22) by an integrals over the cluster distribution. For  $T < T_{cl}$ , to leading order in density and  $P$  we find,

$$\beta p = \rho_+ \left( 1 - \frac{\xi \rho_+}{2P\rho} \right). \quad (36)$$

The value of the counterion density  $\rho_+$  is given by the solution of the self consistent equation (33). In Figure 2 we present a plot of the dependence of the osmotic coefficient  $\phi_0(\rho) \equiv \beta p / P\rho$ , on the density of counterions. From the solution of equation (33) we find,

$$\beta p \approx \frac{P\rho}{2\xi} \left( 1 - \frac{c^2(T^*)}{d^2(\rho^*)} + \frac{2c^3(T^*)}{d^3(\rho^*)} + O\left(\frac{1}{d^4(\rho^*)}\right) \right) \quad (37)$$

Thus, for  $T < T_{cl}$  Manning's limiting laws will have strong logarithmic corrections. Finally, it is important to note that the value of the equilibrium constant has not explicitly entered into our final results. This implies that the exact mechanism of the counterion association is unimportant for the determination of low density properties of a polyelectrolyte solution. Explicitly this is a result of the fact that the equilibrium constant is quasi-independent of the cluster size. This, however, is only true in the limit of large  $P$ . In particular the variation of the equilibrium constant leads to the shift in the peak value of the cluster distribution. For large  $P$  we find that the maximum possible shift in the peak value is  $n_s^* = n^* + 2\xi \ln(R/a)\sigma^2/P$ , where  $R = 2a < \xi_D$ . From equations (31, 32), it is evident that both  $n^*$  and  $\sigma^2$  are of order  $O(P)$ , the shift in the peak value of the cluster distribution is, therefore, of order  $O(1)$  and can be ignored. This once more justifies our ansatz for the density distribution of the cluster sizes.

Motivated by our discussion of the PMP we are now ready to explore the properties of a polyelectrolyte solution in a presence of a simple 1:1 salt.

### 3. PMP in the Presence of Salt

For concreteness we shall assume that polyions are negatively charged, as is the case for the DNA molecules. To simplify the presentation we shall then take the positively charged particles of salt to be identical with the counterions. The overall density of salt ions is  $\rho_+^{\text{salt}} = \rho_-^{\text{salt}} = \rho_s$ . As before, we denote the density of  $n$ -cluster by  $\rho_n$ . We are then lead to three conservation equations. The total density of the polyions as before is given by,

$$\rho = \sum_{n=0}^P \rho_n. \quad (38)$$

Since the negatively charged ions of salt do not participate in the association, their density remains unchanged,

$$\rho_- = \rho_s. \quad (39)$$

The density of unassociated positive ions is,

$$\rho_+ = P\rho + \rho_s - \sum_{n=0}^P n\rho_n. \quad (40)$$

As before, the polyions and the clusters are too massive to be polarized by the fluctuating electric field inside the polyelectrolyte solution and contribute only to the neutralizing background. The counterions and the ions of salt, on the other hand, are light and mobile and can be easily polarized. As before, assuming a Boltzmann distribution for  $g_{+-}(r)$  leads to a NLPBE, which upon linearization of the exponential reduces to the Helmholtz equation (11), with the inverse Debye length,  $1/\xi_D = \kappa$ , now given by,

$$(\kappa a)^2 = \frac{4\pi\rho_1^*}{T^*}, \quad (41)$$

where.  $\rho_1 = \rho_+ + \rho_-$ . The electrostatic free energy of an  $n$ -cluster is now found to be,

$$\beta f_n^{\text{DH}}(\rho_1, \rho_n) = \frac{\rho_n^*(P-n)^2}{2\pi L a^2 \rho_1^*} \ln(\kappa a K_1(\kappa a)). \quad (42)$$

The leading contributions to the total free energy are,

$$f(\rho_+, \rho_-, \{\rho_n\}) = f^{\text{Ideal}}(\rho_+) + f^{\text{Ideal}}(\rho_-) + \sum_{n=0}^P f^{\text{Ideal}}(\rho_n) + \sum_{n=0}^P f_n^{\text{DH}}(\rho_1, \rho_n). \quad (43)$$

The law of mass action leads to the interdependence of the densities of clusters and of unassociated ions and polyions, expressed by equation (19). We find that at low temperatures the cluster densities are once again Gaussianly distributed with

$$n^* = P - \frac{\rho_+ - \rho_s}{\rho}, \quad (44)$$

$$\sigma^2 = -\frac{P}{\xi(\ln \rho_1^* + c(T^*) - 1/2)}, \quad (45)$$

and the density of free unassociated positive ions is given by the solution of,

$$\rho_+^* = \rho_s^* + \frac{P\rho^* \ln \rho_+^*}{\xi(\ln \rho_1^* + c(T^*) - \rho_s^*/\rho_1^*)}. \quad (46)$$

Above  $T_{cl}$ , such that  $n^*(T_{cl}, \rho^*, \rho_s^*) = 0$ ,

$$\frac{T_{cl}^* b}{a} = \frac{\ln(P\rho^* + 2\rho_s^*) + c(T_{cl}^*) - \rho_s^*/(P\rho^* + 2\rho_s^*)}{\ln(P\rho^* + \rho_s^*)} \quad (47)$$

the cluster formation will be exponentially suppressed, and the polyelectrolyte-salt solution will once again be composed of only free polyions, counterions, and salt. It should be noted that the temperature at which clusters begin to form is shifted down from that of a solution in the absence of salt. For  $T > T_{cl}(\xi < \xi_{cl})$ , the leading order contribution to the osmotic pressure of the solution is found to be,

$$\beta p = 2\rho_s + \left(1 - \frac{\xi}{2}\right) P\rho. \quad (48)$$

Below  $T < T_{cl}(\xi > \xi_{cl})$ , the pressure and other thermodynamic functions can be easily calculated by replacing all the sums by the integrals over the cluster distribution. In particular, to leading order in density and  $P$ , the pressure of a polyelectrolyte-salt solution is,

$$\beta p = \rho_1 - \frac{(\rho_+ - \rho_s)^2}{2P\rho} \xi, \quad (49)$$

where  $\rho_+$ , is determined from the solution of equation (46). For the purpose of comparing our results with experiments, it is convenient to define the osmotic coefficient in the presence of salt,  $\phi_s(T; \rho, \rho_s)$ , so that  $\beta p \equiv (P\rho + 2\rho_s)\phi_s$ . In Figure 3, the value  $\phi_s$  is plotted for various fixed values of  $\rho_s$ .

In the mathematical limit,  $(\rho_s \rightarrow 0, \rho \rightarrow 0)$ , the number of unassociated positive ions is,

$$\rho_+ = \rho_s + \frac{P\rho}{\xi} + O(P\rho/\ln(\rho_s^* + P\rho^*/\xi)). \quad (50)$$

Defining the ratio of counterions to salt,  $X = P\rho/\rho_s$ , the osmotic coefficients in the mathematical limit of low densities takes a particularly simple form,

$$\phi_s = 1 - \frac{\xi X}{2(X+2)}; \quad \xi < 1, \quad (51a)$$

$$\phi_s = \frac{2 + X/2\xi}{X+2}; \quad \xi > 1. \quad (51b)$$

These are the same expressions as obtained by Manning [2]. The logarithmic corrections to this equations will, once again, vanish in the limit  $a \rightarrow 0$ . The equations (51) are the exact limiting laws for the line of charge model in the presence of point like ions of salt. As before, however, neither the line of charge model nor the mathematical limit of extremely low densities is very realistic, and the above equations should be taken with a grain of salt.

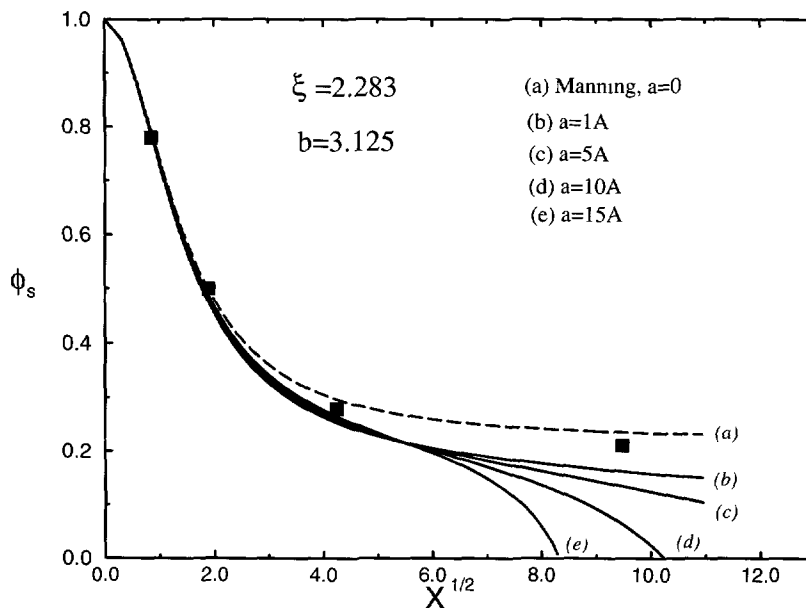


Fig. 3. — Dependence of the osmotic coefficient on the effective diameter of the excluded volume cylinder for  $\rho_s = 0.001$  M. The circles depict the experimental values found in reference [26]. For small  $X$  the osmotic coefficient is quite insensitive to the variations in  $a$ . For larger  $a$ , however, strong deviations are observed when  $\sqrt{X} > 6$ . This is the result of the breakdown in our approximations which have stipulated densities such that  $\kappa a \ll 1$ . For large  $a$  this condition is violated and the expansions (21) and (22) are no longer valid, see also Table I. In this case the full set of equation (19) has to be solved in order to determine the cluster distribution. We do, however, observe that in practice the small values of  $a$  provide an excellent fit to the experimental data. Also note that the presence of hardcore produces a shift towards the lower values of the osmotic coefficient, as compared to the Manning's limiting law ( $a \rightarrow 0$ ) represented by the dashed curve, and in the direction of a better agreement with experiment.

#### 4. Discussion

We have presented a new theory of polyelectrolyte solutions at low densities. Unlike earlier theories our approach is firmly imbedded in thermodynamics and statistical mechanics. We find that at low temperature the polyelectrolyte solution is composed of clusters consisting of one polyion and of  $n$  associated counterions. The distribution of cluster sizes is Gaussian. This view of the polyelectrolyte solution is fundamentally different from the previously available theories, which assumed that all the polyions will have an equal number of counterions condensed onto them. Although, the DHBj theory is intrinsically mean field, we do expect that just as in the case of pure DH theory and simple electrolytes, the limiting, low density laws, obtained on its basis will be exact for the PMP.

The fundamental property of the polyelectrolyte clusters is that they cannot be diluted away by lowering the concentration of solute, or increasing the amount of solvent. This is intrinsically different from any other association phenomena in nature. As the density is lowered, the resulting increase in entropy per particle, always favors the distraction of clusters for systems whose entities interact through short range forces. Even in the case of a simple electrolyte, for which the interaction potential is long ranged, at sufficiently low density the increase in

entropy due to the break up of clusters such as dipole, tripoles, quadrupoles *etc.*, overwhelms the increase in the electrostatic energy due to the unfavorable separation of oppositely charged ions. The overall free energy for the electrolyte solution is, then, minimized by the break up of the clusters. For the rodlike polyelectrolytes, however, the electrostatic interaction between the polyion and the counterions is so strong as to prevent the break up of the clusters even as the density of solute is reduced all the way down to zero. This fundamental property of the polyelectrolyte solution is captured by the DHBj theory. Furthermore, unlike a somewhat metaphysical concept of condensation, counterion association is comparatively simple. The clusters behave as a new species, the densities of which are governed by the law of mass action. For large  $P$ , we have found that the exact mechanism of association is inconsequential, since the density of the clusters is independent of the equilibrium constant. The unusual characteristics of a logarithmic potential, produced by a linear superposition of electric fields for individual monomers, suggest that one should be very careful in trying to extend the formulas derived on the basis of PMP to the flexible polyions [24] which might not have rodlike structure even locally [15].

Recently there have appeared some suggestions that the counterion condensation is a special case of a Kosterlitz-Thouless-like phase transition [25]. Our theory clearly demonstrates that this is not the case. In the low density limit, association occurs at a temperature  $T_{cl}$  about twice the value of the equivalent metal-insulator transition temperature for the two-dimensional hard disk Coulomb gas. Furthermore, while the Kosterlitz-Thouless transition is a real thermodynamic phase transition, characterized by a diverging Debye screening length, nothing like this happens in a polyelectrolyte solution. In fact we have found that for all temperatures  $T > 0$ , there will remain a finite fraction of unassociated polyions and counterions, leading to a finite Debye length. There is, however, a similarity between the two dimensional dipoles below  $T_{KT}$ , and the polyelectrolyte clusters below  $T_{cl}$ , as a result of the logarithmic potential, neither dipoles nor the clusters can be diluted away.

Although from a theoretical point of view the new theory provides an improvement over the previously available approaches, its experimental ramifications are much harder to assess. Thus, for example, while the experiments are in agreement with the general prediction that in the absence of salt the osmotic coefficient asymptotes to its zero density value,  $\phi_0(0) = 1 - \xi/2$  for  $\xi < 1$ , and to  $\phi_0(0) = 1/2\xi$  for  $\xi > 1$ , the way the latter one of this limits is approached disagrees with the theory. Thus while the experiments suggest that the limit is reached from above [26] our calculations predict that the osmotic coefficient is a decreasing function of density, see Figure 2. A partial resolution of these conflicting results may lie in the fact that the experiments have not been conducted at a sufficiently low density. Furthermore at low density, the PMP is not a very true representation of a solution of DNA molecules. On large length scales DNA is not "rodlike". In general we expect that PMP will be sufficiently true representation of a stiff polyion if the screening length due to the counterions,  $\xi_D$ , is shorter than the persistence length  $L_p$  over which the DNA molecule is rodlike. Only in this case the expression (17) will be a good approximation for the electrostatic free energy, since only then will all the contributions to the electrostatic free energy from the length scales larger than  $L_p$  be screened away. It is evident that in the low density limit this condition is violated, namely as  $\rho \rightarrow 0$ ,  $\xi_D \rightarrow \infty$  and clearly  $\xi_D > L_p$ .

In the presence of salt the Debye length will always stay finite and even for very low densities of the polyelectrolyte the condition  $\xi_D < L_p$  can be satisfied. Thus, we do expect that in the presence of salt the PMP will be a good representation of a polyelectrolyte solution at low densities [27]. Indeed this expectation is realized, see Figure 3. At very low concentrations, we find that the value of the osmotic coefficient is not very sensitive to the distance of closest approach,  $a$ . For moderate densities, however, the best agreement with experiment is found

Table I. — *The variation of the osmotic coefficient with the diameter of exclusion cylinder,  $a$ , and with the concentration of polyelectrolyte, for a fixed density of salt  $\rho_s = 0.001$  M. For small  $X$ , the value of the osmotic coefficient is insensitive to  $a$ . For large  $X$  and a strong deviations from the limiting value ( $a \rightarrow 0$ ) are observed. These are the result of the breakdown in our approximation  $\kappa a \ll 1$ , see also Figure 4.*

$a$	$X^{1/2}$	$\phi$	$\kappa a$
1	8	0.176874	0.0495466
1	6	0.205642	0.037288
1	4	0.264046	0.0256733
1	2	0.454977	0.0155026
5	8	0.162574	0.252072
5	6	0.2034	0.187033
5	4	0.268538	0.127422
5	2	0.460551	0.0767528
10	8	0.13572	0.517822
10	6	0.200514	0.37552
10	4	0.272894	0.252886
10	2	0.464766	0.152186
15	8	0.0595288	0.82376
15	6	0.196331	0.566452
15	4	0.27733	0.376103
15	2	0.468158	0.22645

when the distance of closest approach is quite small,  $a \approx 1$  Å (Fig. 3). It is important to remember that our calculations were done in the limit  $\kappa a \ll 1$ , the increase in the distance of closest approach,  $a$ , leads to the violation on this condition and to the breakdown of our approximations, which in turn results in a poor agreement with experiments for higher concentrations, see Table I. Once again we would like to emphasize that the strong deviations from the Manning's limiting law ( $a = 0$ ) observed for larger densities and values of  $a$  are not necessarily the true properties of the PMP, but only the result of the breakdown in our approximation,  $\kappa a \ll 1$ , leading to equations (21, 22). When this condition is violated the full set of equation (19) should be solved numerically in order to calculate the values of the osmotic coefficient for larger  $X$ . In practice, however, this will be quite difficult to do since equation (19) corresponds to  $P \approx 10^3$  coupled nonlinear equations. Nevertheless, it would not be too surprising that if this was accomplished, one might find that  $\phi_s$  is not very sensitive to  $a$  up to much larger values of  $X$ . Figure 4.

The somewhat mixed results obtained when one tries to make the models more realistic is not new for the theory of polyelectrolyte solutions. Thus, in order to make his line of charge model more faithful to reality, Manning extended his calculations to allow for the discrete nature of the charge distribution consistent with that of a real double-helical B-DNA [16]. Surprisingly instead of improving his agreement with experiment, which was quite good for the uniform line of charge model, strong deviations were found. Only the introduction of a



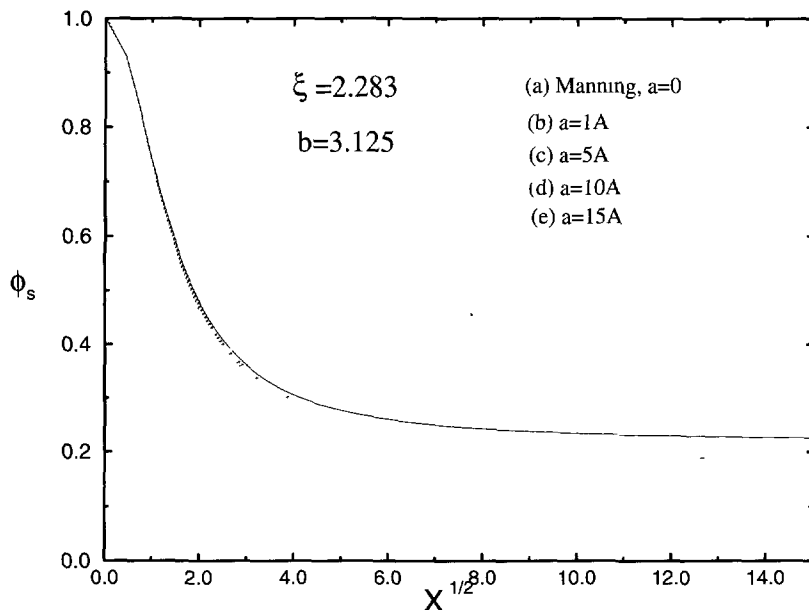


Fig. 4. — Dependence of the osmotic coefficient on the effective diameter of the excluded volume cylinder for  $\rho_s = 0.0001$  M. No experimental data are available for this density of salt. Note, however, the high degree of independence of the osmotic coefficient from the value of  $a$ . For this  $\rho_s$  our approximation  $\kappa a \ll 1$ , holds over the full extent of plotted  $X$ .

distance-dependent dielectric constant could restore the original agreement with experiment. It is hard to understand why the solvent mediated short range forces should exactly compensate for the deviation from uniformity existing in a charge distribution of a real DNA.

The intrinsic complexity of a polyelectrolyte solution and the ability of the simplest possible models to produce a very good agreement with the experiments seems to raise more questions than these theories are able to answer. As is common with many models of a complicated phenomena, our solution contains both simplification of the physical reality abstracted into the PMP and the mathematical approximations which are needed to solve even this comparatively simple model. It, therefore, remains unclear whether the possible flaws of the theory reside in the simplifications imbedded into the PMP, or in the mathematical methods used to solve it. To understand which ones of our assumptions are really fundamental we need a control over input which the real experiments are not able to provide. At this point in the development of the full theory of polyelectrolyte solutions Monte Carlo simulations are essential [28]. Only MC will allow us to say if the approximations used to solve the most basic model of a polyelectrolyte, such as PMP, are sufficient or if more work is required. Only then will we be able to explore further the true complexity of real polyelectrolytes.

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- [22] This assumption is highly non trivial. Thus, for example, if the condensed counterions would not interact with each other the internal partition function for the  $n$ -cluster would be  $\zeta_n = \zeta_1^n/n!$ . Within our theory the counterions, however, interact with each other through the renormalization of the effective charge of the polyion. Even though, it remains unclear to what extent the form presented in text will remain valid for real polyelectrolytes such as

DNA. Clearly in such a complicated molecule the nature of the binding mechanism will be dictated by the details of the intermolecular interactions. In practice, however, since the simple Manning approach seems to work quite well for real polyelectrolytes, we suppose that the proposed form of the internal partition function, and therefore of the equilibrium constant which is related to it through equation (20), can not be too far from reality. We do indeed find that our results are quite insensitive to the exact form of the equilibrium constant. See the discussion following equation (37).

- [23] More careful calculations in (a) Onsager L., *Ann. N. Y. Acad. Sci.* **51** (1949) 627; (b) Stigter D., *Biopolymers* **16** (1977) 1435; (c) Fixman M. and Skolnick J., *Macromolecules* **11** (1978) 863; (d) Odijk T., *J. Chem. Phys.* **93** (1990) 5172, suggest that the polyion-polyion contribution to free energy density scales as  $\beta f_{pp} \approx (P\rho)^{3/2} \ln(P\rho)$ .
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- [29] A Monte Carlo simulation of *one* rodlike polyion and counterions was done by Bratko D. and Vlachy V., *Chem. Phys. Lett.* **90** (1982) 434. However to explore the properties of a polyelectrolyte solution addressed in this paper, it is essential to have simulations of the full PMP, with more than one polyion.