

Theory of counterion association in rod-like polyelectrolytes

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Abstract. – A new theory of a polyelectrolyte solution at low densities is proposed. It is shown that below temperature T_{cl} , counterions associate with polyions forming clusters consisting of a polyion and of n counterions. The distribution of cluster sizes is Gaussian, and leads to a strong logarithmic correction to the limiting laws obtained by Manning. Above T_{cl} the limiting laws remain unchanged. Furthermore, unlike some recent suggestions it is demonstrated that counterion condensation is *distinct* from the Kosterlitz-Thouless phase transition.

For almost a century it has been realized that the electrolyte solutions behave in an intrinsically different fashion than the solutions composed of neutral molecules do. In order to understand this unusual behaviour Debye and Hückel (DH) created their, now famous, theory of strong electrolytes [1]. The theory has proved to be even more successful than its creators could have possibly expected. The limiting, low-density laws, for pressure and other thermodynamic functions derived by DH, have been subsequently shown to be the exact consequences of statistical mechanics [2], while the general prediction of the screening inside the electrolyte solution has been proved in a rigorous way through field-theoretic methodology [3]. However, the validity of the DH theory seems to extend far beyond the limiting laws. Thus, it has recently been shown that the full DH theory augmented by Bjerrum's ideas of dipolar formation [4] can account for the observed liquid-liquid and liquid-gas phase separation encountered in the ionic systems [5]. In the case of the Restricted Primitive Model of an Electrolyte (RPM), which consists of a gas of charged hard spheres, the extended Debye-Hückel-Bjerrum theory (DHBj) [6], [7] predicts a coexistence curve in excellent agreement with the most recent Monte Carlo simulations (MC) [8]. Furthermore, the theory can be easily extended to general dimensions [9] and, in particular, reproduces the Kosterlitz-Thouless result [10] of a 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 vapour phase will coexist with a conducting fluid [9], a conclusion which is once again in agreement with the MC [11].

No such fully thermodynamic theory seems to be available in the case of polyelectrolytes. Polyions are molecules which can carry any number of charged groups of the *same* sign. There

are usually charged groups of the order of a thousand on a polyion, the most common examples of which are the DNA and other polyphosphates or polyacrylates.

The most promising approach to the problem of strong polyelectrolytes was developed by Manning [12a] in a pioneering paper published a quarter of a century ago. In order to explain the basis of Manning's approach we shall first define a Primitive Model of Polyelectrolyte (PMP). This model consists of N polyions inside a volume V . The molecules are idealized as long cylinders of cross-sectional diameter a 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 diameter a , equal to that of a cylinder, each carrying a charge q . The solvent is represented as a uniform medium of dielectric constant D . The PMP should best represent stiff polymers such as DNA and polysaccharides [13], while for flexible chains such as polyacrylic and polystyrene sulfonic acids the theory should be at most qualitative. In this respect the recent simulations of flexible charged polymers by Stevens and Kremer [14] are not directly applicable to the PMP.

In the low-density limit, we shall neglect the discrete nature of the charge distribution and assume a uniform charge density, $\sigma = -Pq/L = -q/b$, 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, $\varphi(r) = -2q(\sigma/D) \ln(r/r_0)$, where r_0 is an arbitrary zero point of the potential. Following Onsager, Manning observed that in the limit of a vanishing hardcore size ($a \rightarrow 0$) this potential will result in an infinite contribution to the partition function below a certain temperature T_c [12a]. Namely

$$L \int_a^R \exp \left[\frac{\varphi(r)}{k_B T} \right] d^2 r = \pi L r_0^2 \left((R/r_0)^{2-2\xi} - (a/r_0)^{2-2\xi} \right) / (1-\xi), \quad (1)$$

where $\xi = q^2/Dk_B T b$, will diverge logarithmically as $\xi \rightarrow 1^-$ and $a \rightarrow 0$. Manning then interpreted the divergence above $\xi = 1$ as signifying that a certain number of counterions have condensed onto a polyion. Since the parameter ξ is effectively proportional to the charge density, Manning *assumed* that $P(1 - 1/\xi)$ counterions will condense onto a polyion, thus lowering the effective charge density of a polyion and preventing the integral in eq. (1) from diverging. Using this observation and treating the uncondensed counterions within DH theory, Manning was able to derive a set of limiting laws for the polyelectrolytes, which have since proved to work quite well [12].

Notwithstanding its success, there remain quite a few problems with the theory described above, the most fundamental one being that it is thermodynamically inconsistent, since the number of condensed counterions is *postulated* on the basis of the divergence of the two-body polyion-counterion phase integral, instead of a minimization of the Gibbs free energy for the polyelectrolyte solution. The latter, of course, is equivalent to the law of mass action which governs any association phenomena in nature. Another 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 a proper basis for the theory of counterion condensation [12b]. In fact, one is quite naturally led to observe a similarity between Manning's theory of counterion condensation and the Kosterlitz-Thouless (KT) theory of metal-insulator transition in a two-dimensional hard-disk Coulomb gas [10]. The interaction potential, $\varphi(r)$, between the two oppositely charged Coulombic particles in two dimensions is the same as for polyion-counterion interaction, with a substitution $\sigma \rightarrow -q$. In this case in the limit $a \rightarrow 0$, just as for a polyelectrolyte, the partition function, eq. (1), is singular and the ionic condensation occurs at $k_B T_c D/q^2 = 1$ [15]. For any finite a , however, the transition happens

at $k_B T_{KT} D/q^2 = 1/2$, while at T_c all the thermodynamic functions remain analytic [10]. Could this also be the case for a polyelectrolyte?

In this letter a new theory of a polyelectrolyte solution which addresses all of the above issues will be presented. We find that below temperature T_{cl} counterions will *associate* with the polyions forming clusters consisting of *one* polyion and of n counterions. We find that the distribution of cluster sizes is Gaussian, centred on the value *close* to the one postulated by Manning.

We shall work in the context of the PMP defined above. In general, we expect that a polyelectrolyte solution will be composed of free unassociated polyions of density ρ_0 , of free unassociated counterions of density ρ_+ , and of clusters, consisting of a polyion and of $1 \leq n \leq P$ associated counterions of density ρ_n . We are led to two conservation equations, $\rho = \sum_{n=0}^P \rho_n$, $P\rho = \rho_+ + \sum_{n=0}^P n\rho_n$, where ρ is the *total* density of the polyions, associated or not. The pressure can be expressed as a Legendre transform of the Helmholtz free-energy density, $f = -F/V$, $p(T, \rho_+, \{\rho_n\}) = f(T, \rho_+, \{\rho_n\}) + \sum_s \mu_s \rho_s$, where the chemical potential of a species s is $\mu_s = -\partial f / \partial \rho_s$. The free energy is constructed as a sum of the most relevant contributions, starting with an ideal-gas (entropic) term $\beta f^{\text{Ideal}} = \sum_s \rho_s [1 - \ln(\rho_s \Lambda_s^{3|s|} / \zeta_s)]$, where $\beta = 1/k_B T$, $|s| = n + 1$, Λ_s 's are the thermal wavelengths, and $\zeta_+ = \zeta_0 = 1$, $\zeta_{n \geq 1}(T)$ represent the internal counterion, polyion, and cluster partition functions, respectively. The expression for ζ_1 is given by eq. (1). 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 the experiments on polyphosphates, and has been extensively discussed by Manning [12d]. 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 $\sigma_n = \sigma(P - n)/P$. The internal partition function for the formation of an n -cluster, from an $(n - 1)$ -cluster and a counterion, is then given by an integral in eq. (1) multiplied by $a^{3(n-1)}$, and with a substitution $\sigma \rightarrow \sigma_{n-1}$.

The DH excess electrostatic free energy is calculated in a usual way based on the linearized Poisson Boltzmann equation. The standard argument yields the Debye screening length $\xi_D = 1/\kappa(T, \rho_+)$ via $(\kappa a)^2 = 4\pi\rho_+^*/T^*$, where the reduced density and temperature are $\rho_s^* = \rho_s a^3$, $T^* = k_B T D a / q^2$. In terms of the reduced temperature Manning's condensation parameter is $\xi = a/T^* b$. For convenience, we shall also set $r_0 = a$. Notice that only free, unassociated, counterions contribute to the Debye length, while polyions and clusters are too massive to be polarized, and contribute only to a neutralizing background. The electrostatic free energy of an n -cluster is obtained through the Debye charging process [9]. We find

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

where $K_1(x)$ is a modified Bessel function. The total free-energy density is then $f(\rho_+, \{\rho_n\}) = f^{\text{Ideal}}(\rho_+) + \sum_{n=0}^P f^{\text{Ideal}}(\rho_n) + \sum_{n=0}^P f_n^{\text{DH}}(\rho_+, \rho_n)$. In this expression, we do not include the electrostatic free energy due to counterion-counterion and polyion-polyion interactions, since it can be easily shown that in the limits of low densities, these will not contribute to the limiting laws. The law of mass action then states that $\mu_n = \mu_0 + n\mu_+$, which reduces to

$$\rho_n^* = K_n(T) \rho_0^* (\rho_+^*)^n \exp[\beta \mu_0^{\text{Ex}} + n\beta \mu_+^{\text{Ex}} - \beta \mu_n^{\text{Ex}}], \quad (3)$$

where the equilibrium constant is $K_n(T) = \zeta_n(T)/a^{3n}$, and the excess chemical potentials are $\mu_s^{\text{Ex}} = -\partial f^{\text{Ex}} / \partial \rho_s$, with $f^{\text{Ex}} = \sum_{n=0}^P f_n^{\text{DH}}$. In general, solving the coupled set of equations (3),

under the constraint of conservation equations, is a very difficult task, not to say impossible, in particular when P is very large. In the limit of small densities, the problem, however, simplifies dramatically. We first observe that

$$\beta\mu_n^{\text{Ex}} = -\frac{(P-n)^2}{P}\xi\left[\frac{2\gamma_E-1}{2} + \ln(\kappa a)\right] + O(\rho_+); \quad \beta\mu_+^{\text{Ex}} = -\sum_{n=0}^P \frac{(P-n)^2\rho_n^*}{2P\rho_+^*}\xi + O(\rho_+), \quad (4)$$

where γ_E is the Euler constant, $\gamma_E = 0.577215664\dots$. Inserting these expressions into eq. (3) and using the explicit form for κa , it becomes evident that in the limit of large dilution the densities of n -clusters are ordered in 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 Manning's assumption that for $\xi > 1$, $P(1 - 1/\xi)$ counterions condense onto a polyion! For $\xi < 1$, $n_c = 0$. Equivalently, we can say that in this limit the distribution of cluster sizes approaches a delta-function form, $\rho(n) = \rho\delta(n - n_c)$.

The limiting laws for the osmotic pressure are found to be $\beta p = (1 - \frac{\xi}{2})P\rho + O((P\rho)^{2-\xi+\xi/2P})$ for $\xi < 1$, and $\beta p = P\rho/2\xi + O((P\rho)^{1+\xi/2P})$ for $\xi > 1$, where the corrections come from the next dominant clusters. The leading-order terms in these equations are the same as the ones obtained by Manning based on the assumption of counterion condensation [12a]. The limiting law for $\xi < 1$ should work quite well for reasonably small densities, since the corrections will indeed be sufficiently small. We are, however, led to observe that in practice the *mathematical limit* $\rho_+ \rightarrow 0$ will be impossible to take for $\xi > 1$, since it would require $(P\rho)^{\xi/2P} \ll 1$, or equivalently $|\ln(P\rho^*)| \gg P$. This, of course, is impossible for realistic densities, since P is assumed to be of an order of a thousand groups. The implication of this result is that at *realistic* densities other clusters besides n_c are important as well. In fact from eqs. (3), (4), it can be shown that in the *realistic* low-density limit, $1 < |\ln(P\rho^*)| \ll P$, the distribution of cluster size densities, instead of being a delta-function, assume a Gaussian form:

$$\rho(n) = \frac{\rho}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(n - n^*)^2}{2\sigma^2}\right], \quad (5)$$

where $n^* = P - \rho_+^*/\rho^*$, $\sigma^2 = -P/\xi(\ln\rho_+^* + c(T^*) - 1/2)$, and the density of free counterions ρ_+^* is determined by the solution of $\rho_+^* = P\rho^* \ln\rho_+^*/\xi(\ln\rho_+^* + c(T))$, where $c(T) = 2\gamma_E - 1/2 + \ln(\pi/T^*)$. The peak in the distribution function is now found to shift from its zero-density limit to $n^* = P(1 - 1/\xi) + Pc(T)/\xi d(\rho) + O(1/d^2(\rho))$, where $d(\rho) = \ln(P\rho^*/\xi)$. The temperature at which the clusters begin to form, $n^*(T_{\text{cl}}) = 0$, is given as a function of the total density of polyions by the solution of $\ln(P\rho^*) = c(T_{\text{cl}}^*)a/(T_{\text{cl}}^*b - a)$. The pressure can now be calculated straightforwardly by replacing all the sums by the integrals over the cluster distribution. For $T < T_{\text{cl}}$, to leading order in density we find

$$\beta p = \rho_+ \left(1 - \frac{\xi\rho_+}{2P\rho}\right) + O(P^0\rho) \approx \frac{P\rho}{2\xi} \left(1 - \frac{c^2(T)}{d^2(\rho)} + \frac{2c^3(T)}{d^3(\rho)} + O\left(\frac{1}{d^4(\rho)}\right)\right) + O(P^0\rho). \quad (6)$$

Thus, for $T < T_{\text{cl}}$ Manning's limiting law for the pressure will have a strong logarithmic correction. It is also interesting to note that, for *large* P , the limiting law is independent of the equilibrium constant, implying that the exact mechanism of binding is not of importance.

The most striking difference between a simple electrolyte and a polyelectrolyte is that in the case of the former, the clusters, such as dipoles, quadrupoles etc., are diluted away as the density of solute is decreased. This is a realization of the fact that at low densities the increase in entropy, due to the break-up of clusters, outweighs the increase in the electrostatic energy, due to the separation of oppositely charged ions, and thus helps to reduce the *overall* free energy of solution. On the other hand, the electrostatic interaction between a polyion and a

counterion 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! The DHBj theory captures this fundamental property of a polyelectrolyte solution.

Although the DHBj theory is intrinsically mean field, we do expect that just as in the case of the pure DH theory and the primitive model of electrolyte, the limiting laws obtained on its basis will be exact for the PMP. Finally, a crucial distinction between the KT transition in a two-dimensional Coulomb gas and a polyelectrolyte should be made. While the KT transition is a real thermodynamic transition characterized by a diverging Debye length, this is not the case for a polyelectrolyte for which a fraction of counterions remains unassociated, producing a finite screening length, all the way down to zero temperature. In principle, however, the counterion association can be compared to the micellar formation in amphiphilic systems [16].

From metal-insulator transitions in two dimensions, to electrolytes and polyampholytes [17], the DHBj theory has proved to be successful in explaining a wide range of complex behaviours found in the systems where Coulombic interaction plays the dominant role. For polyelectrolytes it gives a novel, and dramatically different picture of the low-density state, which from a theoretical perspective, at least, is an improvement over the previously available theories. In a future work the experimental ramifications of the new theory will be addressed [18].

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