

Dressed polyions, counterion condensation, and adsorption excess in polyelectrolyte solutions

(Poisson–Boltzmann)

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ABSTRACT The phenomenon of Manning–Oosawa counterion condensation is given an explicit statistical mechanical and qualitative basis via a dressed polyelectrolyte formalism in connection with the topology of the electrostatic free-energy surface and is derived explicitly in terms of the adsorption excess of ions about the polyion via the nonlinear Poisson–Boltzmann equation. The approach is closely analogous to the theory of ion binding in micelles. Our results not only elucidate a Poisson–Boltzmann analysis, which shows that a fraction of the counterions lie within a finite volume around the polyion even if the volume of the system tends towards infinity, but also provide a direct link between Manning’s θ —the number of condensed counterions for each polyion site—and a statistical thermodynamic quantity, namely, the adsorption excess per monomer.

Although our understanding of the structure of simple and molecular liquids has increased dramatically over the past two decades, the dynamics and the equilibrium properties of polyelectrolytes are fundamental and major unsolved problems. Biopolymers are usually charged under physiological conditions, and their biological functions are dictated by their polyelectrolyte’s behavior. A vast amount of experimental data indicates that polyelectrolytes are characterized by several universal or semiuniversal features as follows (1–4). (i) For a rod-like configuration, there is a critical value of the dimensionless linear charge density (3) $\xi_{\text{crit}} = 1/|z|$, where $\pm z$ is the valence of the counterion.[§] For $\xi > \xi_{\text{crit}}$, counterions would condense in a region near the polyion (3). (ii) For $\xi_{\text{crit}} > 1$, the number of condensed counterions, for each polyion site, is $1 - 1/\xi$. The fraction of polyelectrolyte charge not compensated by the associated counterions is found to be invariant to salt concentrations, even as large as 0.1 M or higher (3, 5). (iii) Dynamical properties such as tracer diffusion coefficient (6), low frequency conductivity (7), and electrophoretic mobility (8) show a discontinuity at or near ξ_{crit} . (iv) The scattering vector of the coulomb peak q_m scales as $c^{1/2}$, where c is the concentration of polyions (9).

The characteristics of polyelectrolytes and oligoelectrolytes have been studied by various researchers by the Manning–Oosawa counterion condensation approach to ionic solutions (2–18). In this approach, if the linear charge density ξ of the polyion is larger than unity, then as the Debye screening length κ^{-1} increases towards infinity,[¶] counterions would condense on the polyions to reduce ξ to unity (3–5). The uncondensed counterions are treated in the Debye–Huckel approximations (2, 3, 19). It is generally regarded, though not universally, that the condensed counterions are “territorial” or delocalized and not site-bound (3, 20, 21). In this report, a synthesis is made of a dressed polyelectrolyte picture of polyions with statistical mechanical techniques and the nonlinear Poisson–Boltzmann

equation to investigate the following question: How are the characteristics of counterion condensation connected with the adsorption excess of the ions about the polyion through the topology of the electrostatic free energy surface? Evans *et al.* (22) have already shown how the thermodynamics of ion binding in micelles emerges without evoking the concept of Stern layers (23–26).^{**}

We consider a polyelectrolyte chain of contour length L to be a cylinder of radius R . A uniform linear charge density $\xi = Q_B/I_b$ is assigned to the chain, where $I_b = L/P$ is the average linear charge spacing, Q_B is the Bjerrum length, and P is the number of charged groups. The polyion is immersed in a 1:1 electrolyte solution (Fig. 1). For sufficiently high linear charge densities, one anticipates that ions are “bound” to the polyion. It is therefore useful to recast the system as a bare polyion plus the bound ions (22–26). The solution is then an ideal mixture formed by the free ions and the dressed chains (22, 23). Due to charge neutrality, the species in solution interact by a Donnan potential (22, 23). This was exploited by Evans and coworkers (22, 23) to express the fraction of bound ions in terms of a thermodynamic quantity—namely, the adsorption excess. Observe that in the picture there is no actual binding of the ions. The dressed polyion formalism will be valid if it emerges that the fraction of counterions that are bound to it is invariant to salt concentration over a range and agrees with experiments.

Due to cylindrical symmetry, the ionic distribution around the polyion depends on the radial distance r from the center of the cylinder. We introduce scaled distance $x = \kappa r$, and potential $y = e\Psi/k_B T$. Ψ is the electrostatic potential which satisfies the nonlinear Poisson–Boltzmann equation (15, 27). The boundary condition is that as x approaches infinity, both the potential y and its slope, dy/dx , approach zero. Gauss’ flux theorem enables us to relate the surface charge density σ and the potential gradient (27).

$$\sigma = - \left(\frac{dy}{dx} \right)_{x=x_0=\kappa R} = 2\xi/x_0. \quad [1]$$

We now show how the dressed polyion picture emerges from the nonlinear Poisson–Boltzmann equation through a statistical mechanical quantity—the so-called adsorption excess.

[§] ξ is the ratio of the Bjerrum length $Q_B = e^2/\epsilon k_B T$ to spacing between the negatively charged phosphate charges, ϵ is the dielectric constant of the solvent, k_B is Boltzmann’s constant, and e is the electronic charge.

[¶]For a 1:1 electrolyte, the Debye length $\kappa^{-1} = \lambda (c_e + 2c_s)$, where $\lambda = 4\pi e^2/k_B T$ and T is the absolute temperature. c_s and c_e are the salt and the equivalent polymer concentrations, respectively.

^{||}The counterions translate and mix in a region of volume $V_p \approx 8\pi e N_{av} (\xi - 1) I_b^3$, where N_{av} is Avogadro’s number and e here is base of the natural logarithm (3).

^{**}The innermost region of the double layer is called the Stern layer. The hydrodynamic shear surface separates the Stern layer from the Gouy layer.

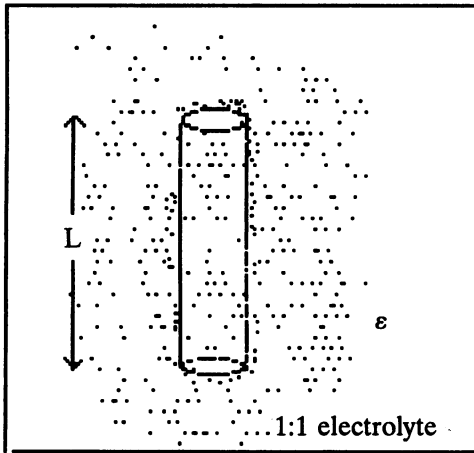


FIG. 1. A rod-like polyion. The dielectric constant of the solvent is ϵ . If one ignores coulombic end effects, Gauss' flux theorem (27) enables us to use a cylindrical surface to relate the surface charge density to the potential gradient.

The electrostatic free-energy per monomer for charging the polyion is $\beta g_{\text{elec}} = 1/\sigma \int_0^{\sigma} y_0(\sigma') d\sigma'$, where $y_0 = y(x_0)$ (22, 23, 28). The adsorption excess per monomer $\gamma = -\beta\kappa/2 (\partial g_{\text{elec}}/\partial \kappa)$ about the polyion is related to the local surface slope of the electrostatic free energy (22, 23, 28). Our viewpoint is that to elucidate the observed limiting law in polyelectrolytes, what is required is the construction of accurate slopes of the electrical free energy, not the solution of the entire nonlinear Poisson-Boltzmann equation for the potential in terms of charge densities (22, 23, 28).

It is useful to introduce the surface charge density via the Poisson-Boltzmann equation as

$$\sigma^2 = 4 \sinh^2(y_0/2) - 2 \int_0^{y_0} \left(\frac{dy}{dx} \right) \frac{dy}{x}. \quad [2a]$$

Since the main contribution to the integrand comes from the region around $y = y_0$, one approximates the integrand as $2/x_0 \int_0^{y_0} (dy/dx) dy$ (22, 23, 28). To proceed further, we evaluate σ by a self-consistent renormalization (22, 23, 28) based on the known result for a planar surface—i.e., by choosing dy/dx

$$dy/dx \approx -\sigma \sinh(y/2)/\sinh(y_0/2), \quad [2b]$$

such that dy/dx also satisfies Eq. 1. Substituting Eq. 2b in Eq. 2a and carrying out the integral we obtain

$$\sigma^2 = 4 \sinh^2(y_0/2) + 4\sigma/x_0 \sinh(y_0/2) [\cosh(y_0/2) - 1]. \quad [2c]$$

An explicit expression for the surface charge density is obtained by solving Eq. 2c

$$\sigma = 2/x_0 \{ \cosh(y_0/2) - 1/\cosh(y_0/2) + 1 \}^{1/2} [1 + (1 + w^2)^{1/2}], \quad [2d]$$

where $w = x_0(z+1)/2$ and $z = \cosh(y_0/2)$.

Since the Gibbs free energy per monomer for charging the polyion, βg_{elec} , can be expressed as (22, 28)

$$\beta g_{\text{elec}} = y_0 - (2/x_0\sigma) \int_{x_0}^w [1 + (1 + w^2)^{1/2}] dw/w, \quad [3]$$

one obtains the adsorption excess per monomer

$$\gamma = (2/x_0\sigma) [(1 + w^2)^{1/2} - (1 + x_0^2)^{1/2}]. \quad [4]$$

Arguments based on the Mayer cluster expansion show that if $\kappa L \gg 1$, counterion condensation occurs for a rigid cylindrical polyion (13). In this limit, and for large z , we find that the adsorption excess per monomer is

$$\gamma = 1 - \frac{1}{\xi} + O\left(\frac{1}{(\kappa L)^2}\right), \quad \xi > 1. \quad [5]$$

Consequently, for $\xi > 1$, γ is identical to θ —the number of condensed counterions for each polymer site as assigned by the counterion condensation formalism (3). Our results not only elucidate a Poisson-Boltzmann analysis that shows that a fraction of the counterions lie within a finite volume around the polyion even if the volume of the system tends towards infinity (14) but also provide a direct link between θ and a statistical thermodynamic quantity—namely, the adsorption excess per monomer.

The dressed polyion formalism is constructed to describe the case when the counterions condense on the polyion. Observe that Eq. 4 is identical in form to the ion binding adsorption equation in micelle solutions by Hayter (28). Evans and coworkers (22, 23) showed, without resorting to Stern layers, how an ion binding picture emerges. These authors took into account both the opposing interfacial forces at the micelle-water interface and the free energies to transfer the hydrocarbon tails from water to an interior region that is nonpolar (22, 23). If the micelle is a sphere of radius R and N is the aggregation number (22, 23), then the scaled distance x_0 and scaled potential y_0 play the same role as in the polyelectrolyte system. Further, the degree of ionization, defined as $1 - \gamma$, in micelle (22, 23, 28) and polyelectrolyte systems is invariant to salt concentrations in the limit of infinite dilution (3, 4, 22, 23).

How accurate is the joining of the planar and the cylindrical solutions? This point has been analyzed in detail by Hayter (28) and by Evans and coworkers (22, 23) for ion binding in micelles by using Poisson-Boltzmann analysis. Hayter (28) finds that it is inconsistent to directly use the exact planar curvature $dy/dx = -2 \sinh(y/2)$ instead of Eq. 2b. Use of the exact planar curvature would lead to failure under conditions of low screening (28).

The formalism proposed here can accommodate a description of the association constants (29) for chemical binding of ions, such as H^+ , to the polyion in a univalent electrolyte. We accomplish this by a synthesis of a "charging" process (29) and theories of liquid state (30) with the dressed polyion picture via the nonlinear Poisson-Boltzmann equation. Eqs. 1–4 can also be generalized to deal with asymmetric electrolytes (unpublished data). In this case, however, there is an additional subtlety and one must replace the classical Debye length κ^{-1} by the real Debye length λ since the two quantities are not equal (31).^{††} This would enable us to study the important effects due to pH and charge regulation.

Our analysis of counterion condensation via the Poisson-Boltzmann equation is in agreement with various Monte Carlo simulations. By including dielectric saturation effects and the helical nature of DNA phosphate backbone, Jayaram and coworkers (32, 33) showed via detailed Monte Carlo simulations that the salt dependence of the associated counterions are in agreement with Manning's counterion condensation formalism. In another Monte Carlo study, Mills *et al.* (34) find that the number of counterions enclosed within 2.4 nm of the center of an atomistically detailed $d(AT)_6d(AT)_5$ is independent of the various conformations of the polyion. Pack and coworkers (35) have defined the bound ions in DNA as those whose electrostatic potential energy is less than the negative of the thermal fluctuation energy. By carrying out Poisson-Boltzmann and Monte Carlo simulations of atomistically de-

^{††}For a 2:1 electrolyte at 0.1 M, λ is 18% smaller than κ^{-1} (31).

tailed and cylindrical models of DNA, they find that the fraction of bound ions are in agreement with counterion condensation (35). Although Rosky and coworkers (36, 37) do not find evidence of a singularity at or near $\xi = 1$, they do find qualitative agreement between the hypernetted chain integral equation description of rod-like DNA and predictions of counterion condensation. A recent molecular dynamics simulation on salt-free polyelectrolytes was carried out by Stevens and Kremer (38). By explicitly including the full coulombic interactions between the monomers and between the counterions and the monomers, these authors find the osmotic pressure to be in good agreement with experimental data (38). However, with an increase in the density of monomers a change in the conformation from stretched to coil is observed (38).

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