On exact solutions to the cylindrical Poisson–Boltzmann equation with applications to polyelectrolytes

Craig A. Tracy[a],*, Harold Widom[b],1

[a] *Department of Mathematics and Institute of Theoretical Dynamics, University of California, Davis, CA 95616, USA*
[b] *Department of Mathematics, University of California, Santa Cruz, CA 95064, USA*

Abstract

Using exact results from the theory of completely integrable systems of the Painlevé/Toda type, we examine the consequences for the theory of polyelectrolytes in the (nonlinear) Poisson–Boltzmann approximation.

Dedicated to Benjamin Widom on the occasion of his seventieth birthday

1. Introduction

A polyelectrolyte is a macromolecule with a large number of ionizable groups, which in a solvent becomes highly charged [1,2]. This highly charged structure is referred to as the polyion. If the polyion has charge $Q = Ze$, then in solution, there are Z counterions. (We take the polyion to have negative charge and thus, the counterions have positive charge.) Typically, the solvent also contains a salt and so the total number of counterions is Z plus the number of positive ions from the salt. The negative salt ions are called coions. Typically, the excess salt is a 1–1 salt, e.g. NaCl, though other salts are considered. (MgCl$_2$ is an example of a 2–1 salt.)

One class of polyelectrolytes that is widely studied are those consisting of slender, rod-like particles. For example, the tobacco mosaic virus, a polyelectrolyte, has a diameter of about 18 nm with a length of 300 nm. For such systems, the idealized model is an infinite cylinder of radius a of uniform linear charge density with counterions and coions treated as point particles. This neglects several important effects such as the interaction between polyions, the flexibility degrees of freedom of the polyion, finite size effects, to name but a few. Nevertheless, this model has been

---

*Corresponding author. E-mail: tracy@itd.ucdavis.edu.
1 E-mail: widom@cats.ucsc.edu.

extensively studied (for reviews see [3,4]). In this idealized model there are two additional length scales: the electrostatic length scale (Bjerrum length) $\ell_B = e^2/\varepsilon k_B T$ (ε is the solvent permittivity) and the inverse Debye–Hückel screening parameter $\kappa^2 = 8\pi\ell_B I$, where $I = \frac{1}{2}\sum n_j q_j^2$ is the ionic strength, with n_j the molar concentration of ion j of (integer-valued) charge q_j with the convention that $q_j < 0$ for counterions and $q_j > 0$ for coions. From these two lengths we form the dimensionless *Manning parameter* [5,6] $\xi = \ell_B/b$, where b is the average spacing between charges on the polyion and the dimensionless distance parameter $r = \kappa R$, where R is the cylindrical distance variable.

A mean field theory approach to this model results in the Poisson–Boltzmann (PB) equation, i.e. the electrostatic potential Ψ is assumed to satisfy the Poisson equation of electrostatics with the density of various ions being given in terms of Boltzmann factors [3,4,7–9]. Introducing the reduced potential $y = e\Psi/k_B T$, the PB equation becomes

$$\Delta y = -4\pi\ell_B \sum_j q_j n_j e^{-q_j y}.$$

In terms of r, and for cylindrical geometry the PB equation is, explicitly for the cases of 1–1 and 2–1 "excess of salt" [7],

$$\frac{d^2 y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = \begin{cases} \sinh y, & \text{1–1 salt}, \\ \frac{1}{3}(e^{2y} - e^{-y}), & \text{2–1 salt}. \end{cases} \tag{1.1}$$

One boundary condition for (1.1) is obtained by applying Gauss's Law at the surface of the polyion

$$\lim_{r \to a} r\frac{dy}{dr} = -2\xi. \tag{1.2}$$

(We use the same symbol a for both the polyion radius and the dimensionless polyion radius). The second boundary condition depends upon whether the system is closed or open. For a closed system, one requires that the electric field vanish at some finite distance, whereas, for an open system with a finite concentration of added salt one requires that

$$y(r) \to 0 \text{ as } r \to \infty. \tag{1.3}$$

We will consider only the case of an open system. A further simplification, and one we will also assume, is to take the polyion radius $a \to 0$, which means we model the polyion as a line charge. The mathematical problems that we address in this paper are now well formulated: to solve (1.1) subject to the boundary conditions (1.2) and (1.3).

2. Exact solutions for a 1–1 and 2–1 salt

First, note that the solutions to the linearized versions of (1.1), satisfying (1.2) and (1.3) are in both cases the familiar Debye–Hückel solution

$$y_{DH}(r) = 2\xi K_0(r), \tag{2.1}$$

where K_0 is the modified Bessel function. The exact solution for the 1–1 salt is [10–12]

$$y_{11}(r) = 2 \log \det(I + \lambda K) - 2 \log \det(I - \lambda K)$$

$$= 4 \sum_{j=0}^{\infty} \frac{\lambda^{2j+1}}{2j+1} \operatorname{Tr}(K^{2j+1}), \qquad (2.2)$$

where K is the integral operator on $\mathbf{R}^+$ with kernel

$$\frac{\exp(-r/2(x + 1/x))}{x + y}$$

and

$$\lambda = \frac{1}{\pi} \sin \frac{\pi \xi}{2} \quad \text{for } \xi \leqslant 1.$$

Note that $\operatorname{Tr}(K) = K_0(r)$ and that $\operatorname{Tr}(K^j) = O(e^{-jr})$ as $r \to \infty$. For $r \to 0$ it has been proved that [10, 13]

$$y_{11}(r) = -2\xi \log r + 6\xi \log 2 + 2 \log \frac{\Gamma((1+\xi)/2)}{\Gamma((1-\xi)/2)} + o(1) \quad \text{for } \xi < 1, \qquad (2.3)$$

where Γ is the gamma function.

The exact solution for the 2–1 salt is [12]

$$y_{21}(r) = \log \det(I - \lambda K_3) - \log \det(I - \lambda K_2)$$

$$= \sum_{j=0}^{\infty} \frac{\lambda^j}{j} (\operatorname{Tr}(K_2^j) - \operatorname{Tr}(K_3^j)), \qquad (2.4)$$

where K_j ($j = 2, 3$) are integral operators on $\mathbf{R}^+$ with kernel

$$\omega^{j-2}(1 - \omega) \exp[-(r/2\sqrt{3})((1-\omega)x + (1-\omega^{-1})x^{-1})](-\omega x + y)^{-1}$$

$$+ \omega^{2(j-2)}(1 - \omega^2) \exp[-(r/2\sqrt{3})((1-\omega^2)x + (1-\omega^{-2})x^{-1})]$$

$$\times (-\omega^2 x + y)^{-1}.$$

Here $\omega = e^{2\pi i/3}$ and

$$\frac{\lambda}{\lambda_c} = 2 \sin\left(\frac{2\pi}{3}(\xi + 1/4)\right) - 1, \qquad \lambda_c = \frac{1}{2\sqrt{3}\pi}, \quad \text{for } \xi \leqslant \frac{1}{2}.$$

Again note that

$$\operatorname{Tr}(K_2) - \operatorname{Tr}(K_3) = 6K_0(r). \qquad (2.5)$$

An elementary calculation produces a simpler representation than the definition for the trace of the square of the operators:

$$\operatorname{Tr}(K_2^2) - \operatorname{Tr}(K_3^2) = 9 \int_0^{\infty} \int_0^{\infty} \frac{\exp(-r/2(x_1 + 1/x_1 + x_2 + 1/x_2))}{x_1^2 + x_1 x_2 + x_2^2} \, dx_1 \, dx_2. \qquad (2.6)$$

The computations (2.5) and (2.6) lead one to suspect that for all positive integers n, the quantities $\mathrm{Tr}(K_2^n) - \mathrm{Tr}(K_3^n)$, as functions of r, are monotonically decreasing. Indeed, one can derive an alternative matrix kernel representation of the operators K_j such that the monotonic decay is manifestly clear.

For $r \to 0$, it has been proved that [13, 14]

$$y_{21}(r) = -2\xi \log r + (2\log 2 + 3\log 3)\xi + \log \frac{\Gamma((1+\xi)/3)\Gamma((2+2\xi)/3)}{\Gamma((2-\xi)/3)\Gamma((1-2\xi)/3)}$$

$$+ o(1) \quad \text{for } \xi < 1/2. \tag{2.7}$$

Higher-order terms in both (2.3) and (2.7) can be computed from use of the differential equations and all additional constants appearing can be expressed in terms of the quantities above.

3. Asymptotics at the critical value of ξ-counterion condensation

The Oosawa–Manning arguments [1, 5, 6] for counterion condensation are well known and need not be repeated here. These arguments, when applied to a 1–1 salt and 2–1 salt, predict critical values of ξ at 1 and $\frac{1}{2}$, respectively. Recall that in the theory of counterion condensation, the meaning of $\xi > \xi_c$ is that the average charge spacing b on the polyion is increased by counterion condensation (onto or around the polyion) until $\xi = \xi_c$ is achieved. Thus, one must distinguish between the stoichiometric value of ξ computed using only the charge groups on the polyion and the lower value of ξ achieved through counterion condensation.

Mathematically, the critical value of ξ is seen through the qualitative change in the small r asymptotics (2.3) and (2.7). For the 1–1 salt case we have as $r \to 0$ [10, 13]

$$\exp(-y_{11}(r)/2) = -\frac{r}{2}\Omega_1 - \frac{r^5}{2^{12}}(8\Omega_1^3 - 8\Omega_1^2 + 4\Omega_1 - 1) + O(r^9 \Omega_1^5), \tag{3.1}$$

where

$$\Omega_1 = \Omega_1(r) = \log(r/8) + \gamma$$

and γ is the Euler constant. Thus, the potential $y_{11}(r)$ develops an additional $\log\log r$ singularity at the critical Manning parameter. Similarly for the 2–1 case as $r \to 0$ [13, 14],

$$\exp(-y_{21}(r)) = -\frac{r}{\sqrt{3}}\Omega_2 + \frac{r^4}{81}(\Omega_2^2 - \tfrac{2}{3}\Omega_2 + \tfrac{2}{9}) + O(r^7 \Omega_2^3), \tag{3.2}$$

where

$$\Omega_2 = \Omega_2(r) = \log(r/8) + \gamma + \tfrac{1}{3}\log 2 + \tfrac{3}{2}\log 3.$$

For $\xi > \xi_c$, the above solutions are no longer physically valid. For example, the Boltzmann factor $\exp(-y_{11}(r))$ will become negative for small enough r.

4. Exact electrostatic free energy for 1–1 and 2–1 salt cases

At constant temperature and pressure, the free energy is the work done in placing charges on the polyion. This is the familiar "charging process" and one imagines an increment of charge dq placed at the surface of the polyion so that the infinitesimal work done is $\Psi(a)\,dq$, where the electrostatic potential is evaluated at $R = a$ [15, 16]. Thus,

$$
w^{el} = \int_0^Q \Psi(a)\,dq
$$

is the free energy associated with a single line charge. Our solutions y_{11} and y_{21} are of the form

$$
y(r) = -2\xi \log r + y_0(\xi) + o(1) \text{ as } r \to 0
$$

and are for the limiting case of $a \to 0$. We take, therefore, for the value of the $e\Psi(a)/k_B T$ the quantity $-2\xi \log(\kappa a) + y_0(\xi)$. Re-writing the above expression for w^{el} in terms of dimensionless quantities and multiplying the result by N_p, the total number of polyions in solution of volume V, we obtain for the free energy, W^{el}, of the entire solution [5, 6]

$$
\frac{W^{el}}{V k_B T} = -n_p \left(\log(\kappa a)\xi - \frac{1}{\xi} \int_0^\xi y_0(\xi')\,d\xi' \right)
$$

$$
:= -n_p f(\xi) \,,
$$

where $n_p = N_p/V$ is the polyion concentration. Using the expressions (2.3) and (2.7) we calculate $f(\xi)$ in these two cases

$$
f_{11}(\xi) = (\log(\kappa a) - 3\log 2)\xi + \frac{2}{\xi} \int_0^\xi \log \frac{\Gamma(1/2 - \xi'/2)}{\Gamma(1/2 + \xi'/2)}\,d\xi'
$$

$$
= (\log(\kappa a) - \log 2 + \gamma)\xi - \sum_{n=1}^\infty \frac{\psi^{(2n)}(1/2)}{2^{2n-1}(2n+2)!} \xi^{2n+1}
$$

$$
= (\log(\kappa a) + 1 - 3\log 2) + 2\log \frac{\Gamma((1-\xi)/2)}{\Gamma((1+\xi)/2)}
$$

$$
+ \frac{2}{\xi} \log \frac{\Gamma((1-\xi)/2)\Gamma((1+\xi)/2)}{\Gamma^2(1/2)}
$$

$$
+ \frac{4}{\xi} \log \frac{G((1-\xi)/2)G((1+\xi))/2)}{G^2(1/2)} \,, \tag{4.1}
$$

$$f_{21}(\xi) = (\log(\kappa a) - \log 2 - \tfrac{3}{2}\log 3)\xi$$

$$+ \frac{1}{\xi}\int_0^\xi \log \frac{\Gamma(2/3 - \xi'/3)\Gamma(1/3 - 2\xi'/3)}{\Gamma(1/3 + \xi'/3)\Gamma(2/3 + 2\xi'/3)}\, d\xi'$$

$$= (\log(\kappa a) - \log 2 + \gamma)\xi + \tfrac{1}{18}(\psi^{(1)}(\tfrac{1}{3}) - \psi^{(1)}(\tfrac{2}{3}))\xi^2$$

$$- \tfrac{1}{72}(\psi^{(2)}(\tfrac{1}{3}) + \psi^{(2)}(\tfrac{2}{3}))\xi^3 + O(\xi^4)\,. \tag{4.2}$$

In the above, $\psi(x) = \Gamma'(x)/\Gamma(x)$ and $\psi^{(n)}(x)$ is the nth derivative of ψ. The function $G(s)$ is the Barnes G-function [17] which is an entire function of s and is defined by

$$G(s+1) = (2\pi)^{s/2}\exp(-s/2 - (1+\gamma)s^2/2)\prod_{k=1}^{\infty}\left(1 + \frac{s}{k}\right)^k \exp\left(-s + \frac{s^2}{2k}\right).$$

The G-function satisfies the functional equation $G(s+1) = \Gamma(s)G(s)$ and has the special value $G(1) = 1$. It arises in the present context through the integral

$$\int_0^z \log\Gamma(x+1)\,dx = \frac{z}{2}\log 2\pi - \frac{1}{2}z(z+1) + z\log\Gamma(z+1) - \log G(z+1)\,.$$

(Clearly one can also express f_{21} in terms of the G-function.)

In the small ξ expansion for both f_{11} and f_{21}, the linear term is the contribution from the Debye–Hückel theory. Observe that since the volume dependence resides solely in the $\log \kappa a$ term, such derived quantities as the osmotic pressure (which is
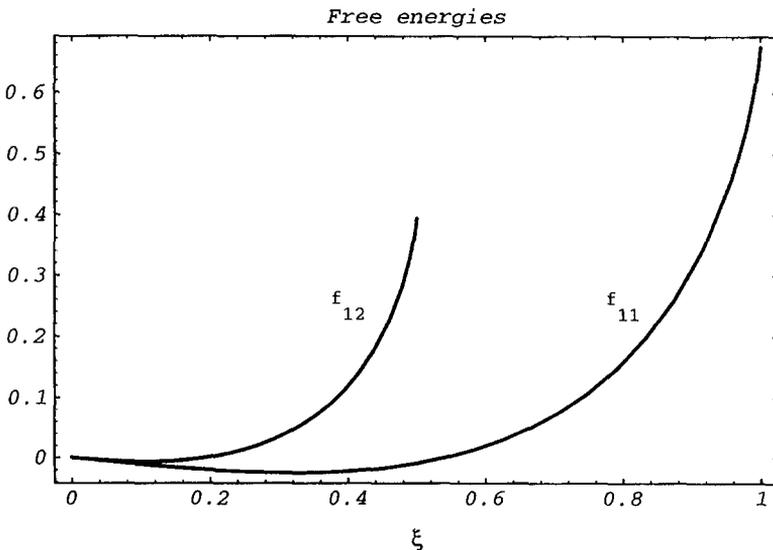
Fig. 1. The free energies f_{11} and f_{21} as functions of the Manning parameter $\xi \leqslant \xi_c$ with $\kappa a = 1$. At the critical value, $f_{11}(1) = \log\kappa a + 0.674563$ and $f_{21}(1/2) = \frac{1}{2}\log\kappa a + 0.393915$.

expressible in terms of a first derivative of W^{el} with respect to V) will be identical to that derived from the Debye–Hückel theory. The mean activity coefficients $\gamma_{\pm}$, expressible in terms of the function f, will have different numerical values from the Debye–Hückel theory, however, their dependence on n_p will be identical. Though this has been understood and used by previous workers, we stress these facts since it emphasizes the wider validity of the linear theory than one might a priori expect.

Both f_{11} and f_{21} are singular at the critical Manning parameter and have leading singularities of the form $(\xi_c - \xi)\log(\xi_c - \xi)$. The graphs of f_{11} and f_{21} are shown in Fig. 1, where for convenience we have set $\kappa a = 1$.

5. Partial equilibrium structure factors

Within the Poisson–Boltzmann approximation, the density distributions of counterions ($+$) and coions ($-$) are given by

$$n_{\pm}(r) = n_{\pm} \exp(\mp q_j y(r)),$$

where $n_{\pm}$ are the concentrations at infinity. Light scatters from the local concentration fluctuations of the counterions and coions and the observed scattering intensity in the static approximation is expressible in terms of the partial structure factors which are, in the cylindrical PB approximation, the (two-dimensional) Fourier transform of $(n_{\pm}(r)/n_{\pm} - 1)$ [18–20]. Thus we examine, for the 1–1 salt,

$$S_{\pm}(q, \xi) = \mathscr{F}(e^{\pm y} - 1) = 2\pi \int\limits_0^{\infty} J_0(qr)(e^{\pm y(r)} - 1)r\,dr, \tag{5.1}$$

where q is the dimensionless wave number and J_0 is the Bessel function of zeroth order. For the 2–1 we replace $e^y \to e^{2y}$ in the above expression.

At $q = 0$,

$$S_+(0, \xi) = \begin{cases} 4\pi\xi(1 + \xi/2), & \text{1–1 salt}, \\ 8\pi\xi(1 + \xi/2), & \text{2–1 salt}, \end{cases} \tag{5.2}$$

$$S_-(0, \xi) = \begin{cases} -4\pi\xi(1 - \xi/2), & \text{1–1 salt}, \\ -4\pi\xi(1 - \xi), & \text{2–1 salt}. \end{cases} \tag{5.3}$$

The differences $S_+(0, \xi) - S_-(0, \xi)$ follow directly from the differential equations (1.1) and the boundary condition (1.2). The individual terms require additional identities (for 1–1 case see Eq. (6) in [11]). In the Debye–Hückel approximation (2.1), $S_{\pm}(0, \xi)$ is $\pm 4\xi$ for the 1–1 salt and similarly for the 2–1 salt. For the 1–1 salt, $S_-(q, \xi) = S_+(q, -\xi)$.

To understand further how these results differ from the Debye–Hückel approximation, we expand the exponentials in (5.1) and use the expansions (2.2) and (2.4) to deduce the expansions

$$S_{\pm}(q,\xi) = \sum_{j=1}^{\infty} \lambda^j S_{\pm,j}(q).\tag{5.4}$$

For the 1–1 salt we find, for example,

$$S_{\pm,1}(q) = \pm \mathscr{F}(4\mathrm{Tr}(K)) = \pm\frac{8\pi}{1+q^2},$$

$$S_{\pm,2}(q) = \pm \mathscr{F}(8\mathrm{Tr}(K)^2) = 8\pi\,\frac{\log(q/2 + \sqrt{(q/2)^2+1})}{(q/2)\sqrt{(q/2)^2+1}},$$

$$S_{\pm,3}(q) = \pm \mathscr{F}(\tfrac{4}{3}(\mathrm{Tr}(K^3) + 8\mathrm{Tr}(K)^3)),$$

$$= \pm\frac{32\pi}{3}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\frac{(x_1 + x_2 + x_3)(1/x_1 + 1/x_2 + 1/x_3)}{(x_1 + x_2)(x_2 + x_3)(x_3 + x_1)}$$

$$\times\frac{(x_1 + 1/x_1 + x_2 + 1/x_2 + x_3 + 1/x_3)}{[4q^2 + (x_1 + 1/x_1 + x_2 + 1/x_2 + x_3 + 1/x_3)]^{3/2}}\,dx_1\,dx_2\,dx_3.$$

From (5.2), it follows that $S_{\pm,3}(0) = \pm 4\pi^3/3$. In general, $S_{\pm,2p+1}$ and $S_{\pm,2p+2}$ will involve the $\mathrm{Tr}(K^{2\ell+1})$ $(\ell = 1, \ldots, p)$ and they will have, in the complex q-plane, branch point singularities at $q = \pm i(2p+1)$, $\pm i(2p+2)$, respectively. Since $\lambda = O(\xi)$, $\xi \to 0$, we see, for $\xi \ll 1$, that the Debye–Hückel approximation of taking the first term in the sum (5.4) is valid for bounded q. Similar expansions can be derived for the 2–1 salt, where we note that $S_{\pm,1}(q)$ will again be the Debye–Hückel term (see (2.5)) but now $S_{\pm,2}(q)$ will contain irreducible "two-particle" effects (see (2.6)).
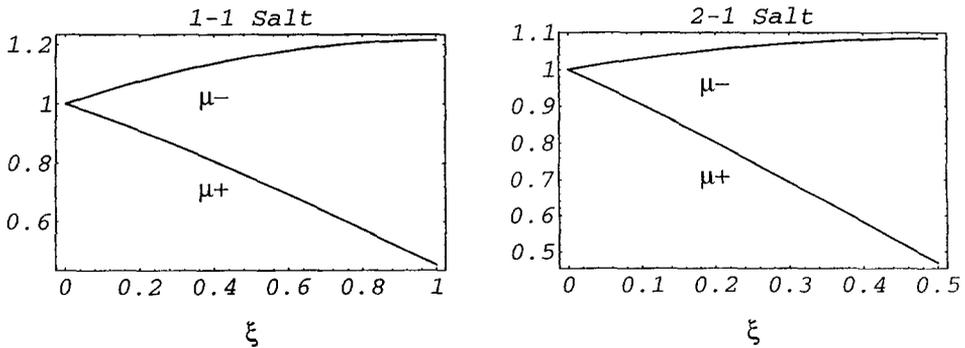
Fig. 2. The normalized moments $\mu_{\pm}$ as functions of the Manning parameter ξ.

For any scattering intensity $I(q)$, one experimentally accessible quantity is the normalized second moment μ in the small q expansion

$$\left[\frac{I(q)}{I(0)}\right]^{-1} = 1 + \mu q^2 + O(q^4).$$

For the partial structure factors $S_\pm$ one similarly defines $\mu_\pm(\xi)$ and in Fig. 2 we graph $\mu_\pm(\xi)$. We have defined the inverse correlation length by the distance to the nearest pole in $S(q)$. (The choice of the dimensionless wave number $q = k/\kappa$ fixes the location to $\pm i$.) For the Debye–Hückel approximation $\mu_\pm \equiv 1$, in contrast with the PB equation, where μ_+ (μ_-) decreases (increases) with increasing ξ. The partial structure functions themselves are shown in Figs. 3 and 4 for various values of ξ. Note that with increasing ξ there is a significant increase in $S_+(q,\xi)/S_+(0,\xi)$ for large q, whereas $S_-(q,\xi)/S_-(0,\xi)$ shows only a slow decrease for increasing ξ.
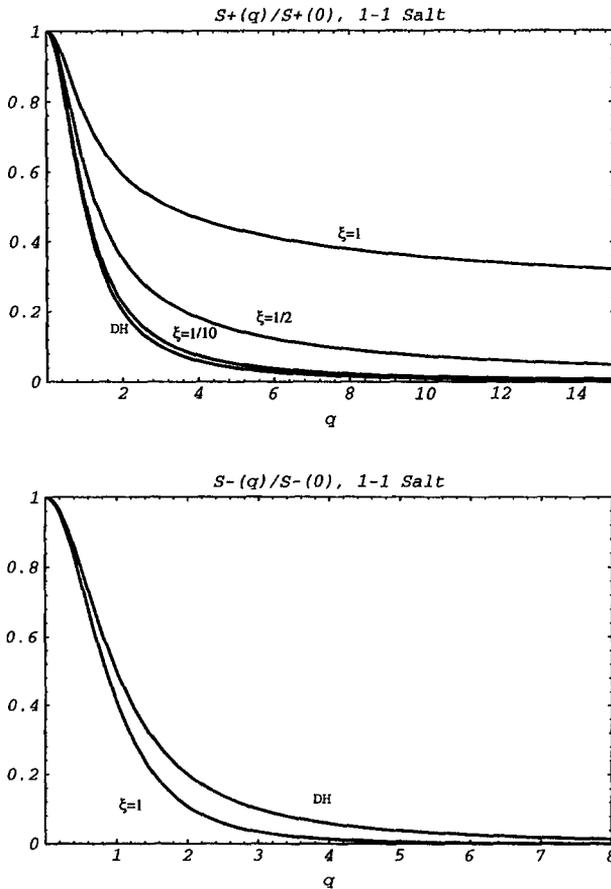
Fig. 3. The structure factors $S_\pm(q,\xi)/S_\pm(0,\xi)$ as functions of q for the 1–1 salt. Also plotted is the Debye–Hückel approximation.
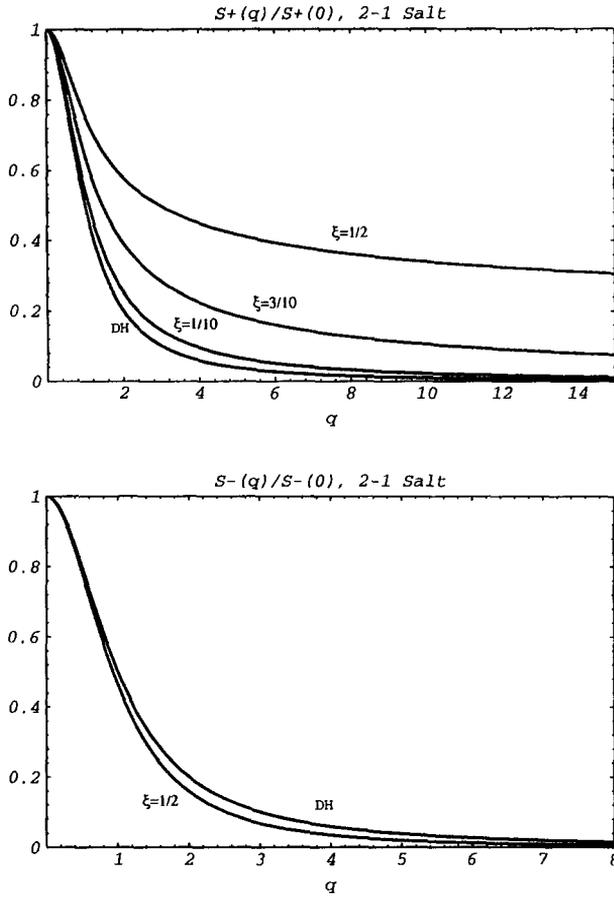
Fig. 4. The structure factors $S_\pm(q,\xi)/S_\pm(0,\xi)$ as functions of q for the 2–1 salt. Also plotted is the Debye–Hückel approximation.

To determine the large q asymptotics of $S_\pm(q,\xi)$, we use the fact that if

$$f(r) \sim r^\lambda \quad \text{as } r \to 0,$$

then

$$\mathscr{F}(f)(q) \sim C(\lambda)q^{-2-\lambda} \text{ as } q \to \infty$$

with $C(\lambda) = -2^{2+\lambda}\sin(\pi\lambda/2)\Gamma(1+\lambda/2)^2$. From (2.3) and the above fact, we deduce for the 1–1 salt that as $q \to \infty$, for fixed $\xi < 1$,

$$S_\pm(q,\xi) \sim \frac{C_\pm}{q^{2 \mp 2\xi}}, \tag{5.5}$$

where $C_{\pm} = \exp(\pm y_0(\xi))C(\mp 2\xi)$. At the critical value $\xi = 1$, the short distance asymptotics of $e^{y_{11}}$ are no longer of the above form (see (3.1)). For this case we find as $q \to \infty$

$$S_+(q,1)/S_+(0,1) = \frac{4}{3}\frac{1}{\log q} - \frac{8\log 2}{3}\frac{1}{\log^2 q} + O\left(\frac{1}{\log^3 q}\right),$$

$$S_-(q,1)/S_-(0,1) = \frac{2\log q}{q^4} + \frac{2(2\log 2 - 1)}{q^4} + \text{lower-order terms}.$$

Similar large q expansions hold for the 2–1 salt.

In critical light or neutron scattering from simple fluid or magnetic systems, the large q behaviour of $S(q)$ defines the critical exponent η [21, 22]. For mean field theories of critical scattering, $\eta = 0$. We remark that even though the PB equation is a mean field theory, we have a nonzero "η" ($\eta = \pm 2\xi$, $\xi < 1$, for the 1–1 salt) which is a reflection of the fact that the short distance potential is the bare Coulomb potential. As the critical value of the Manning parameter is approached, the Poisson–Boltzmann theory predicts an enhanced scattering at large wave numbers from the concentration fluctuations of the counterions, while at the same time predicting little change in the scattering from the concentration fluctuations of the coions. As is the case in critical scattering [23, 24], the measurement of these effects may well prove difficult.

Acknowledgements

References

[1] F. Oosawa, Polyelectrolytes, Marcel Dekker, New York, 1971.
[2] J.L. Barrat, J.F. Joanny, in: I. Prigogine, S.A. Rice (Eds.), Advances in Chemical Physics: Polymeric Systems, vol. 94, Wiley, New York, 1996, p. 1.
[3] C.F. Anderson, M.T. Record, in: B.S. Rabinovitch, J.M. Schurr, H.L. Strauss (Eds.), Annual Review of Physical Chemistry, vol. 33, Annual Reviews, Palo Alto, 1982, p. 191.
[4] C.F. Anderson, M.T. Record, in: Annual Review of Biophysics and Biophysical Chemistry, vol. 19, Annual Reviews, Palo Alto, 1990, p. 423.
[5] G.S. Manning, J. Chem. Phys. 51 (1969) 924.
[6] G.S. Manning, in: E. Sélégny, M. Mandel, U.P. Strauss (Eds.), Polyelectrolytes, Reidel, Dordrecht, 1974, p. 9.
[7] A. Katchalsky, Z. Alexandrowicz, O. Kedem, in: B.E. Conway, R.G. Barradas (Eds.), Chemical Physics of Ionic Solutions, Wiley, New York, 1965, p. 295.
[8] M. Fixman, J. Chem. Phys. 70 (1979) 4995.
[9] H. Qian, J.A. Schellman, Transformed Poisson–Boltzmann equations and ionic distributions around linear polyelectrolytes, preprint.
[10] B.M. McCoy, C.A. Tracy, T.T. Wu, J. Math. Phys. 18 (1977) 1058.

[11] C.A. Tracy, H. Widom, Commun. Math. Phys. 179 (1996) 1.
[12] H. Widom, Some classes of solutions to the Toda lattice hierarchy, Commun. Math. Phys., solv-int/9602001, to appear.
[13] C.A. Tracy, H. Widom, Asymptotics of a class of solutions to the cylindrical Toda equations, solv-int/9701003.
[14] A.V. Kitaev, J. Sov. Math. 46 (1989) 2077.
[15] T.L. Hill, Arch. Biochem. Biophys. 57 (1955) 229.
[16] C. Tanford, Physical Chemistry of Macromolecules, ch. 7. Wiley, New York, 1961.
[17] E.W. Barnes, Quart. J. Pure Appl. Math. 31 (1900) 264.
[18] J.J. Hermans, Rec. des Travaux Chim, des Pays-Bas et de la Belgique, 68 (1949) 859.
[19] B.J. Berne, R. Pecora, Dynamic Light Scattering, ch. 9, Wiley, New York, 1976.
[20] T. Odijk, in: W. Brown (Ed.), Light Scattering: Principles and Development, Clarendon Press, Oxford, 1996, p. 103.
[21] M.E. Fisher, J. Math. Phys. 5 (1964) 944.
[22] J. Zinn-Justin, Quantum Field Theory and Critical Phenomena, 2nd ed., Clarendon Press, Oxford, 1993.
[23] C.A. Tracy, B.M. McCoy, Phys. Rev. B 12 (1975) 368.
[24] R.F. Chang, H. Burstyn, J.V. Sengers, Phys. Rev. A 19 (1979) 866.