Painleve III and Manning's Counterion Condensation

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Using results of McCoy, Tracy, and Wu [J. Math. Phys. (N.Y.) **18**, 1058 (1977)] the Manning counterion condensation for rodlike polyelectrolyte solutions in the presence of salt is rigorously proven. It is demonstrated that the Manning condensation belongs to a special case of the Kosterlitz-Thouless-like phase transition in the presence of boundaries.

Recently there has been a renewed interest in various kinds of boundary-related phenomena which involve statistical systems near criticality [1,2]. This is motivated by the necessity to extend the results of conformal theories in the bulk, especially those which involve the exactly integrable models, to the situations where the boundary interactions are present. Although previously some significant results related to the conformal field theories with boundaries were obtained [3], recent developments [1,2] allow one to obtain much more complete information for the same systems.

The two-dimensional Ising model is considered to be exactly integrable. Near criticality its thermodynamics is being fully described by the free two-dimensional Dirac fermions [4]. The quantum correlation functions for this model are described, nevertheless, as solutions of the classical integrable nonlinear differential equations, a feature typical for quantum integrable models [5]. Specifically, the spin-spin correlator for the Ising model can be obtained in terms of solutions of the classical sinh-Gordon equation [4,5]

$$\frac{d^2 y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = \sinh y. \tag{1}$$

The same equation happens to occur in the theory of Manning polyelectrolyte counterion condensation in the presence of excess salt as discussed in Ref. [6]. The polyelectrolyte is a charged macromolecule (e.g., DNA) which in Manning's theory is assumed to have the conformation of a rigid rod. The aqueous solutions of such charged rods could be prepared with or without the added salt. In the last case instead of Eq. (1) one should consider the Liouville-like equation [i.e., one has to replace $\sinh y$ on the right hand side (rhs) of Eq. (1) by $\exp y$]. Since this case has been widely discussed in the literature, e.g., see Ref. [7], we shall discuss only the case of added 1:1 univalent salt. The more general case of a salt mixture can be also considered, in principle, as we shall discuss below.

Equation (1) is the Poisson-Boltzmann (PB) equation written in terms of the reduced dimensionless variables. In physical units we have $r = \kappa R$, where R is the radial distance while $\kappa^2 = 8\pi \ell_B n_0$ is the usual Debye-Hückel parameter with n_0 being an equilibrium salt concentration,

and the Bjerrum length ℓ_B is defined as $4\pi \ell_B = e^2/\varepsilon k_B T$, with $k_B T$ being the temperature factor. The quantity ε is the dielectric constant of the solution (assumed to be unaffected by the presence of charged polymers [8,9]), and e is the electric charge. The PB equation, Eq. (1), is written for the single polyelectrolyte chain (the infinite dilution limit [8]) and the presence of a chain in solution is reflected in the boundary condition

$$r\frac{dy}{dr}\bigg|_{r=a} = -2\xi, \tag{2}$$

where $\xi = \ell_B/\ell$, ℓ is the characteristic spacing between the charges along the chain [3], and a is the characteristic radius of a rigid rod polyelectrolyte.

The essence of Manning's theory of condensation lies in the following two statements. It is expected that for $r \to \infty$ the solution of the PB equation [Eq. (1)] acquires the following asymptotic form:

$$y(r) \cong 2\xi' K_0(r), \tag{3}$$

where $K_0(r)$ is the modified Bessel function of zeroth order and the parameter ξ' (the effective charge) is expected to depend on ξ in such a way that, for $\xi \leq 1$, ξ' is some function of ξ, while for $\xi > 1$, ξ' remains constant independent of ξ. For $\xi > 1$ it is anticipated that a portion of the counterions floating in solution will be absorbed at the surface of the polyelectrolyte chain (counterion condensation) so that the effective charge ξ' remains constant independent of ξ.

These statements were tested analytically for the Liouville-like PB equation in [7] and numerically in [6]. No rigorous analytic results explicitly supporting the above statements have been reported in the literature.

In this Letter, using the results of McCoy, Tracy, and Wu [10] for the Ising model correlators, we demonstrate explicitly the correctness of both statements made above. Biological applications of these results could be found, for example, in Ref. [11]. In order to use the results of Ref. [10], it is necessary to bring Eq. (1) to the standard Painleve III form. This is accomplished by introducing new variables w and x, so that $w = \exp(-y/2)$ and $x = r/2$. In terms of these variables, Eq. (1) acquires the form

$$\frac{d^2 w}{dx^2} + \frac{1}{w}\left(\frac{dw}{dx}\right)^2 + \frac{1}{x}\frac{dw}{dx} = w^3 - \frac{1}{w}. \tag{4}$$

Comparison between this equation and Eq. (1.3) of Mc-Coy, Tracy, and Wu [10] indicates that Eq. (4) is a special case of Eq. (1.3), where one needs to require $\nu = 0$ to reach an agreement with our Eq. (4). For $x \to 0$ and $\nu = 0$, Ref. [10] provides the following asymptotic result for w:

$$w(x/2, \lambda) \cong Bx^{\sigma}\left[1 - \frac{1}{16}B^{-2}(1 - \sigma)^{-2}x^{2-2\sigma}\right] + O(x^2),$$

$$(5)$$

where, according to Theorem 3 of Ref. [10], we have

$$B = 2^{-3\sigma}\Gamma\left(\frac{1-\sigma}{2}\right)\bigg/ \Gamma\left(\frac{1+\sigma}{2}\right), \qquad (6)$$

with $\Gamma(x)$ being the usual gamma function. The parameter σ entering Eq. (5) is connected with the parameter λ via

$$\sigma(\lambda) = \frac{2}{\pi}\arcsin(\pi\lambda), \qquad (7)$$

for $0 \le \lambda \le 1/\pi$. The parameter λ enters into the large x asymptotic solution for w as an integrating constant,

$$w(x/2, \lambda) \cong 1 - \lambda\sqrt{\frac{2\pi}{x}}e^{-2x} \quad \text{for } x \to \infty. \qquad (8)$$

Equations (6) and (7) relating λ to the constants B and σ of the small x asymptotic solution, Eq. (5), were obtained in Ref. [10] and independently in [12]. Using the fact that for $x \to \infty$, $K_0(x) \cong \sqrt{\pi/2x}\,e^{-x}$ and the above result, Eq. (8), can be rewritten as

$$w(x/2, \lambda) \cong 1 - 2\sqrt{2}\lambda K_0(2x). \qquad (9)$$

Equation (9) can be reexpressed in terms of the original variable y as follows:

$$y(r) \cong 2\sqrt{2}\lambda K_0(r). \qquad (10)$$

If σ in Eq. (7) is known, then we obtain from this equation

$$\lambda = \frac{1}{\pi}\sin\left(\frac{\pi\sigma}{2}\right), \qquad (11)$$

so that comparison between Eqs. (3) and (10) produces $2\sqrt{2}\lambda = \xi'$.

In order to determine σ, we have to use the boundary condition, Eq. (2), along with the asymptotic result given in Eq. (5). For $\sigma < 1$ and $a \to 0$ we obtain $\sigma \cong \xi$. Therefore, in this regime

$$\xi' = \frac{2\sqrt{2}}{\pi}\sin\left(\frac{\pi\xi}{2}\right), \quad \text{for } \xi < 1. \qquad (12)$$

For $\sigma \to 1$ and nonzero a, Eq. (5) becomes singular. The nature of this singularity can be best understood in terms of the Kosterlitz-Thouless- (KT-) like argument [13]. For this purpose, in the spirit of the original Manning theory [8], it is sufficient to calculate the total charge $Q(r)$ per unit length for all ions that lie between the distance of the closest approach a and some distance r,

$$Q(r) = \int_a^r 2\pi r\rho(r)\,dr, \qquad (13)$$

where, according to the electrolyte theory [14], $\rho(r) = \sinh y(r)$. Since $y(r)$ is not known exactly for all r, we

are forced to restrict our analysis to the values of r which are close to a. In this case Eq. (5) can be used so that approximately

$$y(r) = 2\xi\ln r + \text{const}. \qquad (14)$$

The explicit form of const is unimportant for our calculation. Using Eq. (14) in Eq. (13) and retaining only the most potentially divergent part of the total expression for $Q(r)$ produces

$$Q(r) \propto \frac{a^{-2(\xi-1)} - r^{-2(\xi-1)}}{2(\xi - 1)}, \quad r > a. \qquad (15)$$

In order to analyze Eq. (15), we have to convert it into original system of units in which $r = \kappa R$. By writing $R = \hat{r}/\alpha$, where α is a parameter which we choose to be equal to κ, we obtain $R \to \infty$ for $\kappa \to 0$. This limit coincides with that considered in the KT paper [13]. Alternatively, one can put $a \to 0$ and keep r constant. This would be in accord with Manning's original treatment [8]. In the vicinity of the rod there is no screening and, for finite rod radius, we can neglect the first term on the rhs of Eq. (15) for $\kappa \to 0$. Then, for $\xi \to 1^-$, we obtain $Q(r) \to \infty$.

Consider therefore more closely the equation $\xi = 1$ or $\ell_B = \ell$. This result produces the critical temperature T_c given by

$$k_B T_c = \frac{1}{2}\frac{e^2}{2\pi\varepsilon\ell}. \qquad (16)$$

In the original KT paper the factors like 2π (characteristic for two-dimensional Coulomb problems), etc. are omitted; the dielectric constant ε is taken to be 1 and the dimensionality of charge, e, is two dimensional rather than three dimensional as in our calculations. If we denote $q^2 = e^2/2\pi\varepsilon\ell$, then Eq. (16) produces *exactly* the KT result for T_c at the mean field level. Hence Manning's condensation is just another application of KT general results.

Let us now discuss the case $\lambda > 1/\pi$, which effectively corresponds to $\xi > 1$ as shown below. For this case McCoy, Tracy, and Wu [10] have obtained for $x \to 0$ and $\nu = 0$ the following asymptotic result:

$$w(x/2, \lambda) \cong -\frac{1}{4\mu}x\sin\left(2\mu\ln\frac{x}{8} + 2\phi(\mu)\right), \qquad (17)$$

where μ is defined through $\sigma = 1 + 2i\mu$, provided that

$$\lambda = \cosh(\mu\pi), \qquad (18)$$

and the phase $\phi(\mu)$ is defined according to

$$\Gamma(i\mu) = |\Gamma(i\mu)|e^{i\phi(\mu)}.$$

Using Ref. [15] it can be shown that

$$\phi(\mu) = c_1\mu - c_3\mu^3 - c_5\mu^5 - \cdots, \qquad (20)$$

with c_1, c_3, etc. being known numerical coefficients. Since at large distances the result given by Eq. (10) still holds, then, in view of Eqs. (3) and (18), we obtain

$$\xi' = \frac{2\sqrt{2}}{\pi} \cosh\mu\pi. \tag{21}$$

In order for the charge ξ' to remain constant for $\xi > 1$ we must require that μ is independent of ξ. At the same time, the solution given by Eq. (17) should still obey the boundary condition given by Eq. (2). Substitution of Eq. (17) into Eq. (2) produces the following self-consistency result for μ:

$$\mu = (\xi - 1)\tan\left(2\mu \ln\frac{a}{8} + 2\phi(\mu)\right). \tag{22}$$

In view of Eq. (20), the result $\mu \rightarrow 0^+$ is an acceptable solution for Eq. (22). Substitution of this solution into Eq. (21) produces for the effective charge ξ' the result $\xi' = 2\sqrt{2}/\pi$, independent of ξ. This provides a rigorous proof of Manning's conjecture discussed above.

The above proof is based, however, on our initial assumption that our polyelectrolyte chain is dissolved in 1:1 ionic salt solution. If we would have a salt mixture, e.g., of 1:1 and 2:2 salts, the resulting equation, which replaces Eq. (1), would be the double sinh-Gordon. This equation cannot be reduced to the Painleve type and, therefore, its solution would require a perturbative treatment [16]. At the same time, for salt solutions made of asymmetric electrolytes of the form $M^{+m}N^{-n}$, Eq. (1) should be replaced by [6]

$$\frac{d^2y}{dx^2} + \frac{1}{r}\frac{dy}{dx} = \frac{1}{2}[\exp(my) - \exp(-ny)]. \tag{23}$$

The above equation can be reduced to one of the "complete" third Painleve equations [6]. The theory of such equations was recently developed in Ref. [17] and, hence, can be used for polyelectrolytes.

Finally, the above treatment is valid only for a single rodlike polyelectrolyte chain. Finite concentrations of such chains would require us to consider equations like Eq. (1) in the multiply connected (punctured) planar domains. As is was discussed in Ref. [18], the Laplace operator acting on such multiply connected planes can be treated equivalently on Riemannian surfaces (without punctures) of the appropriate genus determined by the polyelectrolyte concentration. Physical applications of these ideas can be found in Ref. [19]. In addition, for the case of no added salt, the sinh-Gordon equation is reduced to the Liouville equation. For punctured planar domains

such an equation was considered in connection with the nonperturbative treatment of quantum gravity in Ref. [20]. It remains to apply the same ideas to polyelectrolytes.

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