Manning condensation in two dimensions

Yoram Burak

Kavli Institute for Theoretical Physics, UCSB, Santa Barbara, California 93106, USA

Henri Orland

Service de Physique Théorique, CE-Saclay, 91191 Gif sur Yvette, France

(Dated: May, 2005)

We consider a macroion confined to a cylindrical cell and neutralized by oppositely charged counterions. Exact results are obtained for the two-dimensional version of this problem, in which ion-ion and ion-macroion interactions are logarithmic. In particular, the threshold for counterion condensation is found to be the same as predicted by mean-field theory. With further increase of the macroion charge, a series of single-ion condensation transitions takes place. Our analytical results are expected to be exact in the vicinity of these transitions and are in very good agreement with recent Monte-Carlo simulation data.

Properties of charged polymers in solution are intimately related to the distribution of small ions around them. A key theoretical model for studying this distribution is that of an infinite charged cylinder, immersed in a solution containing counterions, and confined to a cylindrical cell of finite size. When the cell size increases to infinity only some of the counterions remain bound at a finite distance from the cylinder. The remaining ions escape to infinity, leaving behind a distribution of ions that compensates only part of the cylinder’s charge. Furthermore, below a critical linear charge density (or, equivalently, above a critical temperature), all the counterions condense and obey the Poisson-Boltzmann equation

\[ \nabla^2 \varphi = \lambda \theta(\tilde{r}) e^{-\varphi} - \frac{\tilde{\xi}}{2\pi} \delta(\tilde{r} - 1) \]  

in which \( \tilde{r} \), the spatial coordinate, was rescaled by the cylinder radius: \( \tilde{r} = r/a \), and \( \varphi \) is the reduced electrostatic potential, in units of the thermal energy \( kT \). We assume that counterions carry a positive charge \( e \) and the cylinder is negatively charged, with a linear charge density \( -e \rho \). This charge density enters Eq. (1) via \( \tilde{\xi} = l_B \rho \), the so-called Manning parameter \( \tilde{\xi} \), and \( l_B = e^2/kT \) is the Bjerrum length. The step function \( \theta(\tilde{r}) \) is equal to unity for \( 1 < \tilde{r} < R/a \) and to zero elsewhere, and the boundary condition, \( \varphi(\tilde{r} = R/a) = 0 \), enforces charge neutrality. Finally, \( \lambda \) is a rescaled fugacity, which does not have any physical consequence since changing its value merely shifts the MF solution \( \varphi \) by a constant. The only dimensionless parameters in the problem are thus \( \tilde{\xi} \) and \( R/a \).

By defining \( u = \log(\tilde{r}) = \log(r/a) \) and \( \varphi = \phi - 2u \), Eq. (1) becomes

\[ -\frac{1}{4\pi} \frac{d^2 \phi}{du^2} = \tilde{\lambda} e^{-\varphi} \]  

for \( 0 < u \leq L \) with boundary conditions

\[ \left. \frac{d\phi}{du} \right|_{u=0} = 2(\tilde{\xi} - 1) , \quad \left. \frac{d\phi}{du} \right|_{u=L} = -2 , \]  

where \( L = \log(R/a) \). Equations (2)–(3) can be interpreted as describing an ionic solution confined between two parallel planar surfaces – one at \( u = 0 \), another at \( u = L \), having surface charges

\[ \sigma|_{u=0} = -\frac{1}{2\pi}(\tilde{\xi} - 1) ; \quad \sigma|_{u=L} = -\frac{1}{2\pi} \]  

(\text{using units such that } l_B = 1.) In this equivalent planar problem, the surface at \( u = L \) is negatively charged and thus always attracts the positively charged counterions. On the other hand, the surface at \( u = 0 \) may be positively or negatively charged, depending on \( \tilde{\xi} \). For \( \tilde{\xi} < 1 \) ions are repelled from the positively charged surface, and escape to infinity as \( L \to \infty \); For \( \tilde{\xi} > 1 \) a finite fraction of the ions remain bound, so as to neutralize the negatively charged surface at \( u = 0 \).

The mapping from cylindrical geometry to a planar one provides an instructive way to understand the behavior of the MF solution (1), but is valid only on the MF level. On the other hand, in the 2d case we show that a similar transformation is exact, on the Hamiltonian level.

We begin with the Hamiltonian \( \mathcal{H}_n = 2qd' \sum_{i=1}^{n} \log(r_i/a) - q^2 \sum_{i,j} |\log| \mathbf{r}_i - \mathbf{r}_j| \), which describes \( n \) point-like ions of
charge \( q' \) interacting with a central disc of charge \( q \) and radius \( a \) in 2d. By analogy with the 3d model, we assume that ions are confined to the radial coordinates \( r \leq R \). Charge neutrality requires \( q/q' = n \) so that, in contrast to the 3d case, the number of ions is finite. The partition function is given by
\[
Z_n = \frac{1}{n!} \int d\phi \exp(-\beta H) \prod_i \int \frac{d\psi}{2\pi} \exp(-\beta \theta_i \phi \langle i \phi \rangle)
\]
where charge-neutrality is assumed. For convenience, in the following we set \( \beta = 1 \).

In the grand-canonical ensemble, the partition function can be transformed into a field-theory form (as outlined in Ref. [3]):
\[
Z = \frac{\lambda^n}{n!} \int d\phi \exp(-\beta H) \exp \left\{ -\frac{1}{q^2} \sum_{i \neq j} \int d\phi \left[ \frac{\xi}{2\pi} \delta_{ij} - 1 - \beta \theta \langle \phi \rangle \exp(-i\phi) \right] \right\}
\]
As \( q^2 \to 0 \) the prefactor inside the exponential tends to infinity. Hence, MF theory [Eq. (1)] becomes exact, for any fixed value of \( \xi \), in the thermodynamic limit \( n \to \infty \). In the following, we analyze the canonical partition function \( Z_n \) for finite \( n \), characterized by the two parameters \( \xi \) and \( n \) (or, alternatively, \( q \) and \( q' \)). To proceed, we note that
\[
Z_n = \frac{\lambda^n}{n!} \int du \int d\theta_i \exp(-\beta H)
\]
where \( u_i = \log(r_i/a) \), \( \xi = \exp[(n-1)\xi \log a] \),
\[
H = (\xi - 2 + \xi/n) \sum_i u_i - \frac{q^2}{2} \sum_{i \neq j} \Theta(u_i - u_j, \theta_i - \theta_j)
\]
and
\[
v(u, \theta) = -\log[2\cosh u - 2\cos \theta]
\]
The potential \( v \) is linear for \( |u| \gg 1 \) being then equal, approximately, to \( -|u| \). We note that, since \( 0 \leq \theta < 2\pi \) is a compact coordinate, the correction to this linear potential is short-ranged.

A charge \( q \), evenly smeared over the \( \theta \) interval, exerts an exactly linear potential:
\[
-\frac{q}{2\pi} \int_0^{2\pi} d\theta \log |2\cosh u - 2\cos \theta| = -q|u|
\]
It is thus convenient to interpret the linear term in (8) as coming from an interaction of the ions with a smeared charge \( q_0 \) at \( u = 0 \) and a smeared charge \( q_1 \) at \( u = L \), which requires \( -q' \langle q_0 - q_1 \rangle = \xi - 2 + \xi/n \). Adding the same constant to \( q_0 \) and \( q_1 \) does not influence the force exerted on the ions, and we are free to chose this additive constant such that the system is overall charge-neutral, in the following sense:
\[
nq' = -(q_0 + q_1)
\]
With this requirement there is a unique choice of \( q_0 \) and \( q_1 \):
\[
q' q_0 = -\xi + 1 - \xi \frac{2}{2n}; \quad q' q_1 = -1 + \xi \frac{2}{2n}
\]
which bears some resemblance to Eq. (4).

So far, we made an exact transformation of the problem from cylindrical coordinates into a problem defined on a strip: the coordinate \( u \) goes from 0 to \( L \), and the coordinate \( \theta \) is periodic (see Fig. 1). On the \( (u, \theta) \) strip, ions interact with each other through a potential of the form \(-q'^2|u - u'|\), augmented by a short-range contribution. They also interact with two smeared charges, \( q_0 \) at \( u = 0 \) and \( q_1 \) at \( u = L \), and the system is overall charge-neutral. Note that any critical property of the system should be exactly captured by the long-range linear potential term.

Since we are interested in the behavior when \( L \to \infty \), we next introduce an approximation, treating the 2d strip as a one-dimensional (1d) domain, with a purely linear ion-ion interaction. This can be thought of as the result of coarse-graining on a scale of order \( 2\pi \). Scaling analysis of the partition function shows that in the 1d model, the value of some observables is the same, when \( L \to \infty \), as in the 2d problem – for example, the number of ions between \( u = 0 \) and \( u = \alpha L \), for any \( 0 \leq \alpha \leq 1 \). Therefore we expect the number of bound ions, evaluated in the 1d approximation, to be the same as in the 2d problem.

In the 1d model, the partition function is
\[
Z_{1d} = \frac{1}{n!} \int dx \exp(-H_{1d})
\]
where
\[
H_{1d} = \frac{1}{2} \int_0^L dx q(x) \psi(x) - \frac{1}{4} \int_0^L dx \left( \frac{d\psi}{dx} \right)^2
\]
\( q(x) \) is the one-dimensional charge density, including the boundary charges at 0 and \( L \), and \( d^2\psi/dx^2 = -2q(x) \). Charge neutrality ensures that \( dq/dx = 0 \) outside the interval \([0, L]\). To evaluate \( Z_{1d} \), the \( n \) particles can be ordered according to their position (canceling the \( 1/n! \) in \( Z_{1d} \)). The derivative \( dq/dx \) is then equal to \(-2q_0 \) between 0 and \( x_1 \) and decreases in a stepwise fashion by \( 2q' \) at each ion position \( x_i \), so that
\[
Z_{1d} = \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{n-1}}^L dx_n \exp\left[-\alpha_0 x_1 - \alpha_1(x_2 - x_1) \cdots - \alpha_{n-1}(L - x_n)\right]
\]
where \( \alpha_i = (q_0 + iq') \). Note that this expression could have also been obtained directly by writing the partition function.
with a linear electrostatic potential \( v(x, \theta) \approx -|x| \) obtained from (9) in the limit \( L \to \infty \).

It follows from Eq. (14) that \( Z_{1d} = f_0 \circ f_1 \circ \cdots \circ f_n(L) \) is the convolution of \( f_0, \cdots, f_n \), evaluated at \( u = L \), where \( f_i(u) = \exp(-\alpha_i u) \) are defined for \( u \geq 0 \). The Laplace transform of \( Z_{1d}(L) \) is thus

\[
Z_{1d}(s) = \prod_{k=0}^{n} \frac{1}{\alpha_k + s}, \tag{14}
\]

so that, performing the inverse Laplace transform,

\[
Z_{1d} = \sum_{k=0}^{n} c_k \exp(-\alpha_k L) \ ; \ c_k = \prod_{j \neq k} \frac{1}{\alpha_j - \alpha_k}. \tag{15}
\]

Note that neither \( \alpha_k \) or \( c_k \) depend on \( L \).

In the limit \( L \to \infty \), \( Z_{1d} \) is dominated by the term \( k = k^* \) having the smallest \( \alpha_k \). When the Manning parameter \( \xi = 0 \), this dominating term is \( k^* = 0 \); with increase of \( \xi \), \( k^* \) increases in a stepwise fashion, changing by unity at \( n \) threshold values (where \( \alpha_k = \alpha_{k-1} \)).

\[
\xi_k = \frac{n}{n+1-k} \tag{16}
\]

Each one of these discontinuities in \( k^* \) corresponds to a thermodynamic transition. In the following, we analyze the behavior of several quantities at these transitions. More details will be presented in a separate publication.

To evaluate the contact density \( n(0) \), it is sufficient to consider the distribution function of \( x_1 \) (an ion at \( x = 0 \) is necessarily the closest to the origin)

\[
n_1(x_1) = (\alpha_0 - \alpha_{k^*}) e^{-(\alpha_0 - \alpha_{k^*}) x_1}. \tag{17}
\]

We thus find that \( n(0) = \alpha_0 - \alpha_{k^*} \) is equal to

\[
n(0) = k^* \left[ -2 + \frac{2 - k^* - 1}{n} \right] \xi, \tag{18}
\]

where

\[
k^* = \begin{cases} 0 & 1 + n (1 - \xi - 1) \\ 1 + n (1 - \xi - 1) & \xi < 1
\end{cases} \quad \xi \geq 1. \tag{19}
\]

Below the first threshold at \( \xi_1 = 1 \), \( n(0) \) vanishes, whereas above this threshold it is finite. Therefore the threshold for ion condensation is the same as predicted by MF theory. Note that the contact density is continuous at \( \xi = \xi_1 \). This is true also at each one of the other transitions \( \xi_k \). However the derivative of \( n(0) \) with respect to \( \xi \) is discontinuous.

In the original, cylindrical problem, our result for \( n(0) \) translates into an ion concentration \( \rho(a) = 1/(2\pi a^2) n(0) \). In Fig. 2 we compare this result with \( a^2 \rho(a) \), as obtained from MC simulation of the full 2d problem. Although we used the approximate 1d model, the agreement between the analytical prediction and simulation is very good. In the limit \( n \to \infty \), the contact density approaches the MF theory prediction, \( \rho(a) \to (\xi - 1)^2/(2\pi a^2 \xi) \).

An exact sum rule, similar to the contact theorem for the planar electric double layer \( [17] \), relates the contact density in the 2d strip to the number of bound ions: \( n(0) = q_0^2 - (q_0 + k^* q)^2 \) [in agreement with Eq. (15)]. This relation is obtained by comparing the pressure across the plane \( u = 0 \) to the pressure acting across a plane \( u = u_0 \), where \( u_0 \) is chosen to be far away from both \( u = 0 \) and \( u = L \). Since the sum rule is exact in both the 2d problem and the 1d approximation, equality in the number of bound ions implies that \( \rho(a) \) in the cylindrical problem, as calculated from Eq. (15), is exact.

To evaluate the density at \( a > 0 \), the distribution of all ions \( x_2, x_3, \ldots \) must be evaluated. We find that \( k^* \) [Eq. (19)] is equal to the number of bound ions, and that for the \( m \)-th bound ion, the Laplace transform of the distribution function is

\[
\mathcal{N}_m(s) = \prod_{j=1}^{m} \frac{\gamma_j}{s + \gamma_j}, \tag{20}
\]

where

\[
\gamma_m = (k^* - m + 1) \left[ -2 + \frac{2(n+1) - m - k^*}{n} \right]. \tag{21}
\]

The Laplace transform of the total particle density is thus

\[
\mathcal{N}(s) = \frac{\gamma_1}{s + \gamma_1} \left[ 1 + \frac{\gamma_2}{s + \gamma_2} \left[ 1 + \frac{\gamma_3}{s + \gamma_3} \left[ \cdots \right] \right] \right]. \tag{22}
\]

This result provides a particularly simple expression for all moments of the single-ion distribution in the cylindrical coordinates, because the \( (-k) \)-th moment,

\[
\langle r^{-k} \rangle = \frac{2\pi}{n} \int_a^\infty \rho(r) r^{k-1} dr = \frac{a^{-k}}{n} \int_0^\infty \langle u \rangle u^{k-1} du \mathcal{N}(k) \tag{23}
\]

where \( \rho(r) = n(u)/(2\pi r^2) \) is the ion density in the cylindrical coordinates. Figure 3 shows \( (a/\xi)/(1/r) \), obtained from Eq. (23) (solid lines). Rescaling with \( \mu = a/\xi \) is used to facilitate comparison with MC simulation results from Ref. [10].
energy of a cylindrical capacitor having charges
by virtue of Eq. (5), and yields
the mean electrostatic energy
by taking a derivative
which corresponds to a free energy
the 2d model on the strip. As should be expected, agreement
= \ln n \left(1 - \frac{1}{a \xi} - \frac{\xi}{a} + \frac{1}{a} \right)
\frac{\partial E}{\partial T} \text{ follows as } \frac{\xi^3}{(\xi - \xi_k)^2}. 
Scaling arguments, previously presented in Ref. [6], are thus in agreement with the
analytical result.

In summary, the counterion condensation problem in 2d is
treated here analytically, taking ion-ion correlations into ac-
count. A series of single-ion condensation transitions is found
with increasing \( \xi \), in agreement with recent MC simulations
\( \xi \), the first of these occurring at the MF theory transition,
\( \xi = 1 \). A possible experimental realization of this problem
may be obtained with parallel, rod-like polyelectrolytes. Be-
ing an analogue of the 3d problem with lower dimensionality,
the 2d model suggests that the Manning transition temperature
in 3d is exact even in the presence of ion-ion correlations.

We acknowledge discussions with A. Naji and R. R Netz,
and thank them for sharing with us their simulation data prior
to publication. This research was supported in part by the
National Science Foundation under Grant No. PHY99-07949.

* Electronic address: yorambu@kitp.ucsb.edu

[1] R. M. Fuoss, A. Katchalsky, and S. Lifson, Proc. Natl. Acad. Sci.
(USA) 37, 579 (1951); T. Altfrey, P. W. Berg, and H. Morawetz,
J. Polym. Sci. 7, 543 (1951).

[2] M. Le Bret and B. H. Zimm, Biopolymers 23, 287 (1984).

[3] R. R. Netz and H. Orland, Eur. Phys. J. E 1, 203 (2000).

[4] D. Andelman, in Handbook of Physics of Biological Systems,
edited by R. Lipowsky and E. Sackmann (Elsevier, Amsterdam,
1994).

[5] G. S. Manning, J. Chem. Phys. 51, 924 (1969).

[6] A. Naji and R. R. Netz, cond-mat/0504447 (2005).

[7] S. L. Carnie and D. Y. C. Chan, J. Chem. Phys. 74, 1075 (1981); J.
Israelachvili, Intermolecular and Surface Forces (Academic,
New York, 1991).

[8] Preliminary data obtained by A. Naji and R. R. Netz, private
communication.

[9] The ion-ion potential, Eq. (9), is divergent when
\( u_i = u_2 \) and
\( \theta_1 = \theta_2 \), but this does not lead to a divergence in the partition
function since the corresponding Boltzmann weight vanishes.