Manning condensation in two dimensions

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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.

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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 escape to infinity: The ion density at any finite distance from the charged cylinder is zero.

The existence of a critical temperature, above which all ions decondense is predicted within mean-field (MF) theory [1–5]. We consider here the equivalent two-dimensional (2D) problem where ion-ion interactions, as well as ion–macroion interactions, are logarithmic. We show that some thermodynamic properties can be evaluated exactly in this case, without resorting to the MF approximation. In particular, the decondensation temperature is the same as that predicted by MF theory—strongly suggesting that a similar conclusion may hold in the three-dimensional (3D) case, where ion correlation effects are expected to be weaker than in two dimensions. Very recently, this conclusion was also pointed at by Monte Carlo (MC) simulations in two and three dimensions [6], in which no deviation from the MF decondensation temperature was found numerically. Beyond the threshold for ion concentration, we obtain exact results for the contact density and electrostatic energy, showing a series of discrete binding transitions, in agreement with the recent MC simulations, and in striking difference from the MF theory prediction.

We begin by briefly discussing the MF theory for a charged cylinder of radius a in three dimensions, confined in a cylindrical cell of radius R. The electrostatic potential depends only on the radial coordinate r and obeys the Poisson–Boltzmann equation [7]

$$-\frac{1}{4\pi}\nabla^2\phi = \tilde{\lambda}\theta(\tilde{r})e^{-\phi} - \frac{\xi}{2\pi}\delta(\tilde{r}-1) \qquad (1)$$

in which $\mathbf{r}$, the spatial coordinate, was rescaled by the cylinder radius: $\tilde{\mathbf{r}}=\mathbf{r}/a$, and ϕ 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 $\xi=l_B\rho$, the so-called Manning parameter [8], 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, $\phi'(\tilde{r}=R/a)=0$, enforces charge neutrality. Finally, $\tilde{\lambda}$ is a rescaled fugacity, which does not have any physical consequence since changing its value merely shifts the MF solution ϕ by a constant. The only dimensionless parameters in the problem are thus ξ and R/a.

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

$$-\frac{1}{4\pi}\frac{d^2\varphi}{du^2} = \tilde{\lambda}e^{-\varphi} \qquad (2)$$

for $0\le u\le L$ with boundary conditions

$$\left.\frac{d\varphi}{du}\right|_{u=0} = 2(\xi-1) \qquad \left.\frac{d\varphi}{du}\right|_{u=L} = -2, \qquad (3)$$

where $L=\log(R/a)$. Equations (2) and (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

$$\sigma_{u=0} = -\frac{1}{2\pi}(\xi-1); \sigma_{u=L} = -\frac{1}{2\pi} \qquad (4)$$

(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 ξ: for $\xi<1$ ions are repelled from the positively charged surface, and escape to infinity as $L\rightarrow\infty$; for $\xi>1$ a finite fraction of the ions remain bound, so as to neutralize the negatively charged surface at $u=0$.

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The mapping from a 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 $\mathcal{H}_n = 2qq'\Sigma_{i=1}^n \log(r_i/a) - q'^2 \Sigma_{i \neq j} \log|\mathbf{r}_i - \mathbf{r}_j|$, which describes n pointlike ions of charge q' interacting with a central disc of charge q and radius a in two dimensions. In analogy with the 3D model, we assume that ions are confined to the radial coordinates $a \leq r \leq R$. 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 $Z_n = (1/n!)\Pi_i \int_a^R dr_i r_i \int_0^{2\pi} d\theta_i \exp(-\beta H)$, where $\beta = 1/kT$. We define a Manning parameter $\xi = \beta qq'$ so that

$$\beta \mathcal{H}_n = 2\xi \sum_{i=1}^n \log(r_i/a) - \frac{\xi}{n} \sum_{i \neq j} \log|\mathbf{r}_i - \mathbf{r}_j|, \quad (5)$$

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. [9])

$$Z_\Lambda = \sum_{n=0}^\infty \frac{\tilde{\lambda}^n}{n!} \exp(-\mathcal{H}_n) \propto \int \mathcal{D}\varphi \exp\left\{-\frac{1}{q'^2} \int d\tilde{\mathbf{r}}\right.$$
$$\left. \times \left[\frac{1}{8\pi}(\nabla\varphi)^2 - i\varphi \frac{\xi}{2\pi}\delta(\tilde{r} - 1) - \tilde{\lambda}\theta(\tilde{r})\exp(-i\varphi)\right]\right\}. \quad (6)$$

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 ξ, 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 ξ and n (or, alternatively, q and q'). To proceed, we note that

$$Z_n = \frac{\zeta}{n!} \int du_i \int d\theta_i \exp(-\tilde{\mathcal{H}}), \quad (7)$$

where $u_i = \log(r_i/a)$, $\zeta = \exp[(n-1)\xi \log a]$,

$$\tilde{H} = (\xi - 2 + \xi/n)\sum_i u_i - \frac{q'^2}{2}\sum_{i \neq j} v(u_i - u_j, \theta_i - \theta_j), \quad (8)$$

and

$$v(u, \theta) = -\log[2\cosh u - 2\cos\theta]. \quad (9)$$

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 θ interval, exerts an exactly linear potential,

$$\frac{-q}{2\pi}\int_0^{2\pi} d\theta \log[2\cosh u - 2\cos\theta] = -q|u|. \quad (10)$$

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 $-q'(q_0 - q_1) = \xi - 2 + \xi/n$. Adding the same constant to q_0 and
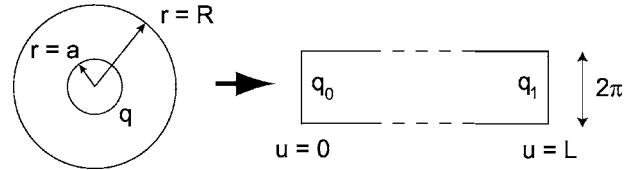

FIG. 1. The transformation from cylindrical geometry to a problem defined on the (u, θ) strip (schematic representation).

q_1 does not influence the force exerted on the ions, and we are free to choose 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,

$$q'q_0 = -\xi + 1 - \frac{\xi}{2n}; \quad q'q_1 = -1 + \frac{\xi}{2n}, \quad (11)$$

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 θ is periodic (see Fig. 1). On the (u, θ) strip, ions interact with each other through a potential of the form $-q'^2|u_1 - u_2|$, 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 2π. 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 [10].

In the 1D model, the partition function is $Z_{1D} = (1/n!)\Pi_{i=1}^n \int_0^L dx_i \exp(-H_{1D})$ where

$$H_{1D} = \frac{1}{2}\int_0^L dx q(x)\psi(x) - \frac{1}{4}\int_0^L dx\left(\frac{d\psi}{dx}\right)^2, \quad (12)$$

$q(x)$ 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 $d\psi/dx = 0$ 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 $d\psi/dx$ 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

$$Z_{1D} = \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{n-1}}^L dx_n$$
$$\times \exp[-\alpha_0 x_1 - \alpha_1(x_2 - x_1)\cdots - \alpha_n(L - x_n)], \quad (13)$$

where $\alpha_i = (q_0 + iq')^2$. Note that this expression could have also been obtained directly by writing the partition function

(7), with a linear electrostatic potential $v(x, \theta) \approx -|x|$ obtained from (9) in the limit $L \rightarrow \infty$.

It follows from Eq. (13) that $Z_{1D} = f_0 \circ f_1 \circ \cdots \circ f_n(L)$ is the convolution of $f_0, \ldots, f_n$, 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

$$\mathcal{Z}_{1D}(s) = \prod_{k=0}^{n} \frac{1}{\alpha_k + s}, \tag{14}$$

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 α_k or c_k depend on L.

In the limit $L \rightarrow \infty$, Z_{1D} is dominated by the term $k = k^*$ having the smallest α_k. When the Manning parameter $\xi = 0$, this dominating term is $k^* = 0$; with increase of ξ, 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.

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

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

where

$$k^* = \begin{cases} 0, & \xi < 1 \\ \lfloor 1 + n(1 - \xi^{-1}) \rfloor, & \xi \geq 1 \end{cases}. \tag{19}$$

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 ξ_k. However, the derivative of $n(0)$ with respect to ξ 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 $n \rightarrow \infty$, the contact density (18) approaches the MF theory prediction, $\rho(a) \rightarrow (\xi - 1)^2/(2\pi a^2 \xi)$.

An exact sum rule, similar to the contact theorem for the planar electric double layer [11], 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. (18)]. This relation is ob-
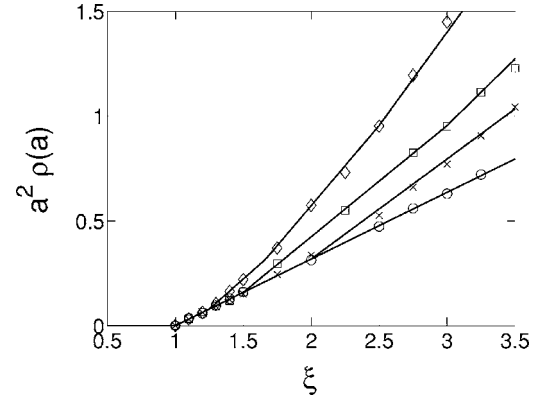

FIG. 2. The contact density, $a^2 \rho(a)$, as obtained from Eq. (18) (lines), compared with MC simulation results [6] ($L=300$): $n=1$ (circles), 2 (crosses), 3 (squares), and 5 (diamonds). When $\xi < 1$ the contact density vanishes.

tained 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. (18), is exact.

To evaluate the density at $u > 0$, 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 mth 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

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

The Laplace transform of the total particle density is thus

$$\mathcal{N}(s) = \frac{\gamma_1}{s + \gamma_1} \left\{ 1 + \frac{\gamma_2}{s + \gamma_2} \left[1 + \ldots \left(1 + \frac{\gamma_{k^*}}{s + \gamma_{k^*}} \right) \ldots \right] \right\}. \tag{22}$$

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

$$\langle r^{-k} \rangle = \frac{2\pi}{n} \int_a^\infty r dr r^{-k} \rho(r) = \frac{a^{-k}}{n} \int_0^\infty du \exp(-ku) n(u)$$

$$= \frac{a^{-k}}{n} \mathcal{N}(k), \tag{23}$$

where $\rho(r) = n(u)/(2\pi r^2)$ is the ion density in the cylindrical coordinates. Figure 3 shows $(a/\xi)\langle 1/r \rangle$, obtained from Eq. (23) (solid lines). Rescaling with $\mu = a/\xi$ is used to facilitate comparison with MC simulation results from Ref. [6] (symbols). The agreement is good but not perfect—deviations reflect the effect of using the 1D model as an approximation to
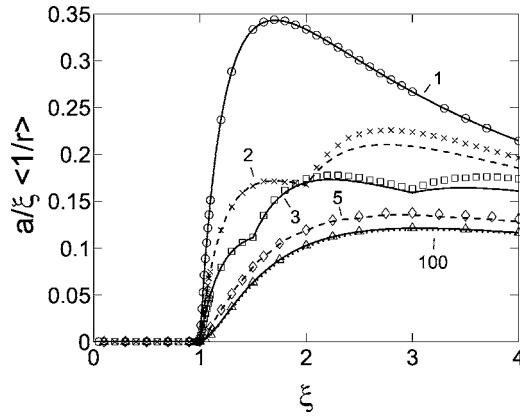
FIG. 3. $(a/\xi)\langle r^{-1}\rangle$ as calculated from Eq. (23) for $n=1$, 2, 3, 5, and 100 (alternating solid and dashed lines). The symbols show MC simulation results [6] for the same quantity ($L=300$). The dotted line shows the prediction of MF theory.
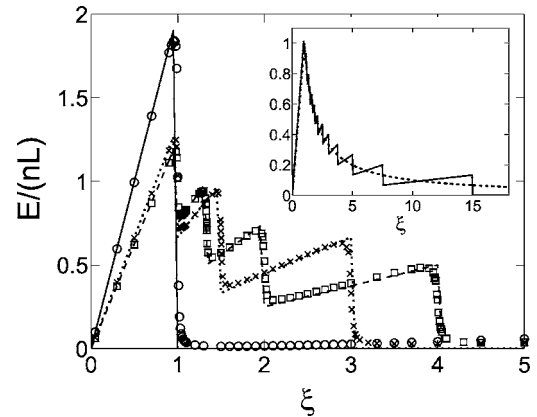

FIG. 4. Leading (large L) term in $E/(nL)$ [Eq. (24), lines], compared with MC simulation data from Ref. [6] ($L=300$, symbols): solid line and circles, $n=1$; dotted line and crosses, $n=2$; dashed line and squares, $n=4$. The inset shows $E/(nL)$ for $n=15$ (solid line), together with the MF prediction $E/(nL)=\xi^{-1}$ for $\xi>1$ (dotted line).

the 2D model on the strip. As should be expected, agreement is perfect in the MF limit ($n\to\infty$) as well as in the opposite limit, $n=1$.

We next evaluate the electrostatic energy. To leading order in L, the free energy in the 1D model is $-\log Z_{1D}=\alpha_{k^*}L$, which corresponds to a free energy $(\alpha_k^*-q_1^2)L$ in the original cylindrical problem. The mean electrostatic energy E is found by taking a derivative $\xi(d/d\xi)$, which is equivalent to $\beta(d/d\beta)$ by virtue of Eq. (5), and yields

$$E = \frac{\xi}{n}(n-k^*)(n-k^*+1)L. \tag{24}$$

One may expect to find $E=q'^2(n-k^*)^2L$, the electrostatic energy of a cylindrical capacitor having charges $\pm q'(n-k^*)$ on its inner and outer surfaces. Equation (24) is similar to this expression, but there is a correction (second parentheses, third term), whose contribution goes to zero only in the limit of large n. We expect Eq. (24) to be the exact leading term in the electrostatic energy for $L\to\infty$. A comparison with MC simulation data ($L=300$) [6] is shown in Fig. 4.

Finally, close to each one of the transition points $\xi=\xi_k$, α_k approaches α_{k-1} and, as seen from Eq. (15), both c_k and c_{k-1} diverge. Concentrating only on their divergent contribution to the free energy, we find that

$$E \simeq E_0 + \frac{\xi}{|\xi-\xi_k|} \tag{25}$$

on both sides of the transition, where E_0 is the leading term in L [Eq. (24)]. The leading divergence in the heat capacity $\partial E/\partial T$ follows as $\xi_k^2/(\xi-\xi_k)^2$. Scaling arguments, previously presented in Ref. [6], are thus in agreement with the analytical result.

In summary, the counterion condensation problem in two dimensions is treated here analytically, taking ion-ion correlations into account. A series of single-ion condensation transitions is found with increasing ξ, in agreement with recent MC simulations [6], the first of these occurring at the MF theory transition, $\xi=1$. A possible experimental realization of this problem may be obtained with parallel, rodlike polyelectrolytes. Being an analog of the 3D problem with lower dimensionality, the 2D model suggests that the Manning transition temperature in three dimensions is exact even in the presence of ion-ion correlations.

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