Counterions at Charged Cylinders: Criticality and universality beyond mean-field

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The counterion-condensation transition at charged cylinders is studied using Monte-Carlo simulation methods. Employing logarithmically rescaled radial coordinates, large system sizes are tractable and the critical behavior is determined by a combined finite-size and finite-ion-number analysis. Critical counterion localization exponents are introduced and found to be in accord with mean-field theory both in 2 and 3 dimensions. In 3D the heat capacity shows a universal jump at the transition, while in 2D, it consists of discrete peaks where single counterions successively condense.

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Many biopolymers, such as DNA, actin, tubulin, fd-viruses, are charged and stiff. On length scales smaller than the persistence length, they can be represented by straight, charged cylinders and oppositely charged ions (counterions) are attracted via an electrostatic potential that grows logarithmically with radial distance. As the ion confinement entropy also exhibits a logarithmic dependence, it was suggested early by Onsager that a counterion delocalization transition occurs at a critical cylinder charge (or equivalently at a critical temperature) \( \tilde{\tau} \). This argument is strictly valid only for a single ion since it neglects cooperativity due to inter-ionic repulsions. Nevertheless, it was corroborated by mean-field (MF) studies \( \ref{1}, \ref{2}, \ref{3} \), which demonstrate that below a critical temperature, a fraction of counterions stays bound or condensed in the vicinity of the central cylinder even in the limit of infinite system size: while above the critical temperature, all counterions de-condense to infinity. This counterion-condensation transition (CCT) dramatically affects a whole number of static and dynamic quantities for charged polymers \( \ref{1} \). It has been observed with different polymers by varying the medium dielectric constant \( \varepsilon \) or the polymer charge density \( \sigma \); the counterion distribution around DNA strands has been directly measured recently using anomalous scattering techniques \( \ref{4} \). Since its discovery, the CCT has been at the focus of numerical \( \ref{4}, \ref{5} \) and analytical \( \ref{6} \) studies. Under particular dispute has been the connection between CCT and the celebrated Kosterlitz-Thouless transition of logarithmically interacting particles in 2 dimensions \( \ref{11} \). Also, the precise location of the CCT critical point remains subject of ongoing experimental investigations \( \ref{7}, \ref{8} \).

As is well known from bulk critical phenomena, fluctuations and correlations typically make non-universal and universal quantities deviate from mean-field theory (MFT) below the upper critical dimension \( \ref{12} \). Surprisingly, the MFT prediction for the CCT critical temperature has not been questioned in literature and apparently assumed to be exact. Likewise, the existence of scaling relations and critical exponents associated with the CCT has not been considered, neither on the MFT level and (consequently) also not in the presence of correlations.

In this paper we pose the questions: i) what is the critical temperature of the CCT, and ii) what are the associated relevant critical exponents? We employ Monte-Carlo simulations, which are performed in rescaled logarithmic coordinates in order to handle very large systems (where the criticality actually occurs) with tractable equilibration times. A combined finite-size and finite-ion-number analysis yields the desired critical temperature and exponents. To enhance the effects of fluctuations, we also study a (within MFT equivalent) 2D system of logarithmically interacting charges, as applicable to an experimental system of oriented cationic and anionic polymers (e.g. DNA with polylysine \( \ref{13} \)). Surprisingly, MFT is demonstrated to be accurate both in 3D (charged cylinder with point-like counterions) and in 2D (charged cylinder with cylindrical counterions). The critical exponents associated with the inverse counterion localization length (which plays the order parameter of the CCT) and the universal behavior of the heat capacity are determined; both quantities are experimentally accessible.

In the 3D simulations, we consider a central cylinder of radius \( R \) and uniform surface charge density \( \sigma_s \) (linear charge density \( \tau = 2\pi R\sigma_s \)) with \( N \) neutralizing point-like counterions of valency \( q \) confined laterally in an outer cylindrical box of radius \( D \) (see Fig. \( \ref{4} \) for snapshots projected along the \( z \)-axis). Periodic boundary conditions in \( z \)-direction are handled using summation methods for long-range interactions \( \ref{14} \). Rescaling all spatial coordinates by the Gouy-Chapman length, \( \mu = 1/(2\pi q\ell_B\sigma_s) \), as \( \tilde{x} = x/\mu \), we obtain the Hamiltonian \( \mathcal{H} = 2\xi \sum_{i} [\ln(\tilde{r}_i/R) + \Xi \sum_{(ij)} 1/|\tilde{x}_i - \tilde{x}_j|] \) for \( \ell_B T \), where \( \ell_B = e^2/(4\pi \varepsilon \varepsilon_0 k_B T) \) is the Bjerrum length, and \( \tilde{r} \) is the radial distance from the cylinder axis. The coupling parameter, \( \Xi = 2\pi q^3 \ell_B^2 \sigma_s \), is an indicator for the importance of ionic correlations: in the limit \( \Xi \to 0 \), correlations are unimportant and MFT becomes exact; in the converse strong-coupling limit \( \Xi \to \infty \), MFT breaks down \( \ref{13} \). The so-called Manning parameter (rescaled inverse temperature), \( \xi = q\ell_B\tau \), regulates the CCT and is a measure of counterion binding: According to MFT \( \ref{1}, \ref{2}, \ref{3} \), the CCT occurs for \( \Delta = \ln(D/R) \to \infty \) at the MF critical threshold.
\( \xi^\text{MF} = 1 \), above which a fraction \( 1 - 1/\xi \) of counterions condenses. To investigate the critical limit for large lateral system size, we introduce a (centrifugal) sampling method by mapping the radial coordinate to the logarithmic scale as \( y = \ln(r/R) \). The partition function transforms as \( Z \sim \int \prod_i d\tilde{r}_i d\tilde{z}_i d\phi_i \exp(-\mathcal{H}) \sim \int \prod_i dy_i d\tilde{z}_i d\phi_i \exp(-\mathcal{H}_{\text{MC}}) \), where the “Hamiltonian”

\[
\mathcal{H}_{\text{MC}} = 2(\xi - 1) \sum_{i=1}^N y_i + \Xi \sum_{i<j} 1/|\tilde{x}_i - \tilde{x}_j| \tag{1}
\]

is used for Monte-Carlo sampling; it features a linear potential (first term) acting on counterions from competing energetic (\( \sim 2\xi y \)) and entropic or centrifugal (\( \sim 2y \)) contributions associated with the cylindrical boundary.

In Fig. 1a, we show the snapshot-topviews from our simulations for \( \Delta = \ln(D/R) = 100 \). De-condensation phase is reproduced for small Manning parameter, \( \xi = 0.7 \), as counterions gather at the outer boundary; while for \( \xi = 3 \), a fraction of counterions accumulates or condenses around the central cylinder. The transition regime for intermediate values exhibits strong finite-size e eects. As seen for \( \xi = 1 \) in Figs. 1b and b, only for large logarithmic system size, \( \Delta \gg 1 \), does de-condensation occur. This is also demonstrated by vanishing radial distribution function of counterions, \( p(\tilde{r}) \), for growing \( \Delta \) in Fig. 1c. For small coupling parameter \( \Xi = 0.1 \), the data for \( p(\tilde{r}) \) compare well with the normalized MFT profile (solid curves) \( p_{\text{MF}}(\tilde{r}) = \frac{\beta^2}{2\pi \xi^2} \sin^{-2} \left[ \beta \ln \frac{\tilde{r}}{R} + \cot^{-1} \left( \frac{\xi - 1}{\beta} \right) \right] \), \( \tag{2} \)

where \( \xi \geq \Delta/(1 + \Delta) \) and \( \beta \) is given by \( \xi = (1 + \beta^2)/(1 - \beta \cot(-\beta\Delta)) \) \( \tag{3} \). Conversely, for large coupling \( \Xi \to \infty \), strong-coupling (SC) theory \( \tag{4} \) becomes valid and yields

\[
p_{\text{SC}}(\tilde{r}) = \frac{2(\xi - 1)}{2\pi^2} \int_0^\Lambda dy e^{-ny} \sin^{-2} \left[ \beta y + \cot^{-1} \left( \frac{\xi - 1}{\beta} \right) \right] \tag{4}
\]

while in the strong-coupling limit, we have from Eq. \( \tag{5} \)

\[
S_n^{\text{MF}} = \frac{\beta^2}{\xi^{n+1}} \int_0^\Lambda dy e^{-ny} \sin^{-2} \left[ \beta y + \cot^{-1} \left( \frac{\xi - 1}{\beta} \right) \right] \tag{5}
\]

The data for \( S_1 \) (the mean inverse localization length) in Fig. 1d exhibit the condensation (\( S_1 > 0 \)) and de-condensation (\( S_1 = 0 \)) phases for a wide range of couplings, \( \Xi \). To locate the critical Manning parameter, \( \xi_c \), a finite-size analysis is required since criticality is masked both by finite system size, \( \Delta \), and finite particle number,
$N$, in the simulations (i.e. $S_1$ does not vanish and saturates at a small value at critical point). To this end, we study the singular behavior of rescaled energy $E = \langle \mathcal{H} \rangle / (Nk_B T)$ and heat capacity $C = (\langle \delta \mathcal{H} / k_B T \rangle^2) / N$, where $\delta \mathcal{H} = \mathcal{H} - \langle \mathcal{H} \rangle$. Simulation results for $E$ and $C$ (Figs. 2a, b) show a non-monotonic behavior that can be understood for large systems, $\Delta \to \infty$ (solid line). Simulation results for $E$ and $C$ (Figs. 2a, b) show a non-monotonic behavior that can be understood for large systems, $\Delta \to \infty$ (solid line).

We now turn to the near-threshold scaling behavior of the order parameter. In the thermodynamic infinite-dilution limit ($N \to \infty, \Delta \to \infty$), $S_n$ exhibits a power-law behavior as $S_n \sim \xi^\gamma$ (close to and above $\xi_c$), where $\xi = 1 - \xi_c / \xi$ is the reduced Manning parameter (reduced temperature). Within MFT, we obtain $\chi_{MF} = 2$ for all $n$ from Eq. 14. At criticality, $\xi = 0$, one expects the scaling $S_n \sim \Delta^{-\gamma}$ for $N \to \infty$ but finite $\Delta$ (within MFT, we obtain $\gamma_{MF} = 2$); while for $\Delta \to \infty$ but finite $N$, one expects $S_n \sim N^{-\nu}$ ($\nu$ is not defined in MFT). These relations indicate that close to criticality, $S_n(\xi_c, \Delta)$ takes a homogeneous scale-invariant form, i.e. for $\Delta > 0$,

$$S_n(\lambda \xi_c, \lambda^{-b} \Delta, \lambda^{-c} N) = \lambda^a S_n(\xi, \Delta, N)$$

where $a, b, c$ are related to the exponents $\gamma, \nu, \chi$. Choosing the scale factor as $\lambda = N^{1/c}$, one finds $S_n(\xi_c, \Delta, N) = N^{-a/c} S_n(\xi, \Delta, N = 1)$. For large $\Delta N^{-b/c}$, as is the case in our simulations, and at the transition, $\xi = 0$, we have $S_n \sim N^{-a/c}$ and thus obtain $\nu = a/c$. For $N \to \infty$, a similar argument leads to $S_n \sim \xi^a$, which gives $\chi = a$. In Fig. 2 we plot the rescaled order parameter $N^{a/c} S_n$ as a function of $\xi N^{1/c}$ for various $N$ and fixed large $\Delta$. By choosing the scaling exponents as $\nu = a/c = 2 \pm 0.1$ and $\gamma = a = 2 \pm 0.4$, we obtain excellent data collapse both for small coupling $\Xi = 0.1$ and increasing $N$. The MF prediction asymptotically tends to the MF threshold $\xi^{MF} = 1$ according to $\xi^{MF} = \xi^{E, MF}(\Delta) \sim 1/\Delta$ as $\Delta \to \infty$. The location of the energy peak (and also the heat capacity jump) shows no dependence on the coupling parameter within error bars (Fig. 2 inset). We thus find a universal counterion-condensation threshold as $\xi_c = 1 \pm 0.002$.

We now turn to the near-threshold scaling behavior of the order parameter. In the thermodynamic infinite-dilution limit ($N \to \infty, \Delta \to \infty$), $S_n$ exhibits a power-law behavior as $S_n \sim \xi^\gamma$ (close to and above $\xi_c$), where $\xi = 1 - \xi_c / \xi$ is the reduced Manning parameter (reduced temperature). Within MFT, we obtain $\chi_{MF} = 2$ for all $n$ from Eq. 14. At criticality, $\xi = 0$, one expects the scaling $S_n \sim \Delta^{-\gamma}$ for $N \to \infty$ but finite $\Delta$ (within MFT, we obtain $\gamma_{MF} = 2$); while for $\Delta \to \infty$ but finite $N$, one expects $S_n \sim N^{-\nu}$ ($\nu$ is not defined in MFT). These relations indicate that close to criticality, $S_n(\xi_c, \Delta)$ takes a homogeneous scale-invariant form, i.e. for $\Delta > 0$,
for $\gamma = a/b = 2 \pm 0.6$ both at small (main figure) and large $\Xi$ (inset), which also demonstrates approximate independence from the scaling argument $N\Delta^{-c/b}$. Our numerical results give the same critical exponents, $\gamma$, $\nu$ and $\chi$, for all $n$ and agree with MFT predictions (for $\gamma$ and $\chi$). The exponents appear to be universal, i.e., independent of the coupling parameter, $\Xi$.

Deviations from MFT in general grow with diminishing dimension [12]. The two-dimensional analogue of the counterion-cylinder system consists of logarithmically interacting mobile counterions and a central charged disk. The 2D Hamiltonian reads $\mathcal{H}_N = 2\xi \sum_{i=1}^{N} \ln \tilde{x}_i - 2 \Xi \sum_{i<j} \ln(|\tilde{x}_i - \tilde{x}_j|)$. Unlike in 3D, $\xi$ and $\Xi$ are related due to electroneutrality as $\Xi = \xi/N$. Thus the striking feature in 2D is that for a given Manning parameter, $\xi$, the coupling parameter tends to zero, $\Xi \to 0$, in the limit of many counterions, $N \to \infty$, and MFT should become exact. Fig. 3a shows the simulated order parameter $S_1$ in 2D. For $N = 1$, the data trivially follow the SC prediction [11], dashed curve, and for increasing $N$, they tend to the MF prediction [11], solid curve. Accordingly, scaling analysis of the condensation threshold and the critical exponents for $N \to \infty$ gives identical results as in 3D and thus no deviations from MFT. However, closer inspection of the 2D data in Fig. 3a reveals a peculiar set of cusp-like singularities for finite $N$. In fact, these singularities correspond to delocalization events of individual counterions, which give rise to a sawtooth-like structure for mean energy and a series of discrete peaks for heat capacity (Figs. 3b, c). This can be understood by a simple analysis of the 2D partition function: Suppose that $N - m$ counterions are firmly bound to the central cylinder (disk), while $m - 1$ counterions have evaporated to infinity ($m = 1, \ldots, N$). Neglecting the delocalized ions, the partition function can be written as $Z_N = \int \prod_{i=m+1}^{N} d^2 \tilde{x}_i \exp(-\mathcal{H}_N - m) \times Z_N^{(m)}$, where $Z_N^{(m)} = \int d^2 \tilde{x} \exp[-2\xi \ln \tilde{x} + 2\xi \sum_{i=m+1}^{N} \ln(|\tilde{x}_i - \tilde{x}|)]$ is the contribution from the $m$-th counterion which is assumed to be weakly localized. It is thus de-correlated from the firmly bound ions and $Z_N^{(m)}$ approximately factorizes as $Z_N^{(m)} \approx \int d^2 \tilde{x} \exp[-2\xi \ln \tilde{x} + (2\xi/N) \sum_{i=m+1}^{N} \ln |\tilde{x}_i|] \sim e^{(2-2m\xi/N)\Delta}$. In the limit $\Delta \to \infty$, $Z_N^{(m)}$ diverges for Manning parameters $\xi \leq N/m$. For $N$ counterions this gives a discrete set of singularities at $\xi_m = N/m$ with diverging heat capacity $C \sim (\xi - \xi_m)^{-2}$, and in agreement with our simulations (Fig. 4). For a Manning parameter range $N/(m+1) < \xi < N/m$, there are $m$ de-condensed ions. In the thermodynamic limit $N \to \infty$, the fraction of de-condensed ions, $m/N$, becomes a smooth function and tends to the MF prediction [11], i.e., $m/N \to 1/\xi$.

In summary, both in 2D and 3D the location and critical exponents of the counterion-condensation transition at charged cylinders are correctly described by mean-field theory. The heat capacity is experimentally accessible: in 2D (parallel charged polymers), it consists of a discrete set of peaks at which single counterions condense, and in the limit $N \to \infty$, it converges to the 3D shape with a universal jump at the condensation threshold.

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