

Ensemble equivalence for counterion condensation on a two-dimensional charged disk

Anoop Varghese,^{*} Satyavani Vemparala,[†] and R. Rajesh[‡]

The Institute of Mathematical Sciences, C.I.T. Campus, Taramani, Chennai 600113, India

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We study the counterion condensation on a two-dimensional charged disk in the limit of infinite dilution, and compare the energy–temperature relation obtained from the canonical free energy and microcanonical entropy. The microcanonical entropy is piecewise linear in energy, and is shown to be concave for all energies. As a result, even though the interactions are long-ranged, the energy–temperature relation and hence the counterion condensation transition points are identical in both the ensembles.

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I. INTRODUCTION

Polyelectrolytes are polymers that release counterions into a polar solvent, making the polymer backbone charged [1–3]. They are ubiquitous in biological systems (examples include DNA [4], F-actin, microtubules, and the tobacco mosaic virus [5]). On increasing the linear charge density of the polymer backbone beyond a threshold value, counterions start condensing onto the polymer [6,7]. The interactions due to the condensed counterions lead to complex phase diagrams [1,2,8,9], and phenomena such as the collapse of an extended polyelectrolyte chain [10–12], and aggregation of similarly charged polyelectrolyte chains [4,13,14]. This counterion condensation transition (CCT) has been mostly studied in the mean field limit, for idealized systems like the cylinder [6,15,16], planes [17–19], and spheres [18] due to the analytical intractability of real polyelectrolyte systems. In recent work, the partition function of a two-dimensional system of counterions around a charged disk was evaluated in the limit of infinite dilution [20]. The theoretically obtained critical points of CCT and the dependence of energy on temperature matched with results from Monte Carlo simulations [15,16].

Electrostatic interactions are examples of long-ranged interactions (i.e., in d dimensions, they decay as $r^{-d-\sigma}$ at large distances r , with $\sigma < 0$). For interactions with $\sigma > 0$, the thermodynamic limit exists, though the exponents may depend on σ (see Refs. [21,22] for a discussion). When $\sigma \leq 0$, energy may be nonadditive, resulting in the inequivalence of different statistical ensembles [23,24]. This inequivalence may be manifested as negative specific heat or magnetic susceptibility in the microcanonical ensemble, different order of phase transitions, and different critical points [23–25]. As systems that show CCT are long-ranged, it would be of interest to know if CCT is the same in different ensembles. However, almost all such models are only studied in the canonical ensemble. In this paper, we solve the model of CCT in Ref. [20] of a system of counterions condensing onto an oppositely charged disk in two dimensions in the microcanonical ensemble to address the question of the ensemble equivalence of CCT. We first obtain the expression for entropy and show that it is piecewise linear in energy. This entropy is then shown to be concave everywhere in energy. The CCT temperature and the energy-temperature rela-

tions obtained in the microcanonical ensemble are shown to be identical to those obtained from the calculation in the canonical ensemble [20]. Thus CCT, at least in this solvable case, is shown to be equivalent in the canonical and microcanonical ensembles, despite the interactions being long-ranged.

Examples of nonadditive long-ranged systems that show ensemble inequivalence include spin systems [26,27], self-gravitating systems [28–30], plasma [31,32], two-dimensional hydrodynamic systems [33,34], and other model systems [35–37]. In the last decade there have been various attempts to compare the solutions of long-ranged systems obtained in the microcanonical and canonical ensembles [24]. However, the number of exactly solvable models where one can pinpoint the equivalence or inequivalence are limited since the calculation of microcanonical entropy is difficult, even for systems with short-ranged interactions. The solution presented in this paper will add to this list of exactly solvable models.

II. MODEL

Consider a uniformly charged disk of charge q and radius a . N counterions, each carrying a charge $-q'$, are distributed in the annular region between the charged disk and a circular boundary of radius R . Overall charge neutrality is achieved by choosing $q = Nq'$. Let \mathbf{r}_i be the position of counterion i in a coordinate system with origin at the center of the disk. The Hamiltonian of the system is

$$H = 2\chi \sum_{i=1}^N \ln\left(\frac{r_i}{a}\right) - \frac{\chi}{N} \sum_{i \neq j} \ln\left(\frac{r_{ij}}{a}\right), \quad (1)$$

where $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The parameter $\chi = qq' = Nq'^2$ measures the strength of the electrostatic interaction. The permittivity ϵ has been set equal to $1/(4\pi)$. The thermodynamics of this system was studied in the canonical ensemble in Ref. [20]. We now obtain the expression for the partition function following closely the steps in Ref. [20].

The Hamiltonian can be rewritten in terms of $u_i = \ln(r_i/a)$ as

$$H = \chi \left(1 + \frac{1}{N}\right) \sum_{i=1}^N u_i - \frac{\chi}{2N} \sum_{i \neq j} \ln[2 \cosh(u_i - u_j) - 2 \cos \theta_{ij}], \quad (2)$$

where $\cos \theta_{ij} = \mathbf{r}_i \cdot \mathbf{r}_j / (r_i r_j)$. This Hamiltonian is analytically intractable. However, some simplifications occur when the

^{*}anoop@imsc.res.in

[†]vani@imsc.res.in

[‡]rajesh@imsc.res.in

limit of infinite dilution, $N/R^2 \rightarrow 0$, is considered. This corresponds to the limit of a finite number of counterions in infinite volume, similar to the limit considered in the Manning condensation [6]. In this limit, counterions are far away from each other. Thus, $|u_i - u_j| \gg 1$, and the summand in the second term of Eq. (2) may be approximated by $|u_i - u_j|$ since $2 \cosh(u_i - u_j) \approx \exp(|u_i - u_j|)$. In this limit, the partition function of the system was calculated by the authors of Ref. [20] and is given by (in slightly different notation)

$$Z = \sum_{k=0}^N \prod_{\substack{m=0 \\ m \neq k}}^N \left[\frac{\xi(k, m)}{2(k-m)\chi \left[\beta - \frac{\xi(k, m)}{\chi} \right]} \right] \times \exp \left[\frac{-2(N-k)\chi L}{\xi(N, k)} \left(\beta - \frac{\xi(N, k)}{\chi} \right) \right], \quad (3)$$

where $L = \ln(R/a)$, β is the inverse temperature and

$$\xi(k, m) = \frac{2N}{2N - k - m + 1}. \quad (4)$$

In the limit $L \rightarrow \infty$ keeping N fixed, the sum in Eq. (3) is dominated by the largest summand. Given a value of $\beta\chi$, the k corresponding to the largest summand is obtained by solving $\beta\chi = N/(N - k + 1)$ for k and taking the integer part [20]. As $\beta\chi$ is increased, k changes by unity, resulting in nonanalytic behavior of the free energy. These critical points occur at

$$(\beta\chi)_c = \frac{N}{N - k + 1} = \xi(k - 1, k), \quad k = 1, 2, \dots, N. \quad (5)$$

The first transition is at $\beta\chi = 1$ ($k = 1$), corresponding to the Manning condensation temperature on cylinders [6].

III. THE MICROCANONICAL ENSEMBLE

To show the ensemble equivalence, we now compute the entropy in the microcanonical ensemble from the canonical partition function in Eq. (3). We then show that the entropy is concave everywhere and the CCT temperatures coincide in both the ensembles.

The density of states $g(E)$ is defined as

$$g(E) = \frac{1}{N!} \int \prod_{i=1}^N dr_i r_i d\theta_i \delta(E - H). \quad (6)$$

$g(E)$ is obtained from the partition function Z by performing an inverse Laplace transform, that is,

$$g(E) = \frac{1}{2\pi i} \int_{-i\infty+c}^{+i\infty+c} d\beta Z(\beta) \exp(\beta E), \quad (7)$$

where the constant c is to be chosen such that the path of integration lies to the right of all the poles of $Z(\beta)$. This corresponds to $\xi(k, m)/\chi < c$ for all k and m . We evaluate the above integral by the method of residues, by closing the contour of integration with a semicircle that is either to the left or right, such that the contribution to the integral from the semicircle is zero. If E and k do not satisfy the condition

$$E - \frac{2(N-k)\chi L}{\xi(k, N)} > 0, \quad (8)$$

then the contour of integration is closed to the right in the complex plane. The closed contour does not enclose any of

the poles of the partition function, and hence, the contribution to $g(E)$ from such k is zero. On the other hand, if E and k satisfy the condition in Eq. (8), the contour is closed to the left, and $g(E)$ is the sum of the residues of the partition function, and is given by

$$g(E) = \sum_{k=k^*}^N \sum_{\substack{l=0 \\ l \neq k}}^{k^*-1} \frac{\xi(k, l)}{2(k-l)\chi} \exp \left[\frac{(N-k)(N-l)\xi(k, l)L}{N} + \frac{\xi(k, l)E}{\chi} \right] \prod_{\substack{m=0 \\ m \neq k \\ m \neq l}}^N \left[\frac{N}{(k-m)(l-m)\xi(k, l)} \right], \quad (9)$$

where k^* is the smallest value of k , given E , that satisfies Eq. (8). In writing Eq. (9), we have used the relation

$$\xi(l, k) - \xi(m, k) = \frac{(l-m)\xi(l, k)\xi(m, k)}{2N}, \quad (10)$$

derived from Eq. (4). The terms in the summation with $l \geq k^*$ do not contribute to $g(E)$ because the summand is antisymmetric in k and l . This leads to an upper bound $k^* - 1$ for l . Also, the maximum possible value of the energy of the system is $(N+1)\chi L$, corresponding to $u_i = L$ for all i . It then follows from Eq. (8) that the lowest value of k^* is 1.

The density of states $g(E)$ in Eq. (9) is a sum of exponentials of the form $\exp[f(k, l, E/L)L]$, where the function f is derivable from Eq. (9). In the limit $L \rightarrow \infty$, keeping N fixed, the sum is dominated by that k, l which maximize the function f . E is implicitly dependent on L and we make this dependence explicit by converting the inequality in Eq. (8) into an equality by replacing k by $k^* - \delta$, where $0 < \delta < 1$. Thus, eliminating E , f becomes a function of k, l , and k^* . It is then easy to show that f increases with l for $k \geq k^*$, and decreases with k for $l \leq k^*$. As a result, the dominant contribution to $g(E)$ comes from the term with $k = k^*$ and $l = k^* - 1$.

By considering only the largest term, we obtain the entropy $S = \ln[g(E)]$ to be

$$\lim_{L \rightarrow \infty} \frac{S}{NL} = 1 - \frac{k^*}{N} + \frac{\xi(k^*, k^* - 1)}{\chi} \frac{E}{NL}, \quad (11)$$

where $\xi(k^*, k^* - 1) = N/(N - k^* + 1)$. In Fig. 1, we show the dependence of entropy on energy, obtained by considering all the terms in $g(E)$ [see Eq. (9)], and compare it with the entropy in Eq. (11). On increasing L , $S/(NL)$ approaches the limiting curve with N linear portions, determined by Eq. (11).

IV. ENSEMBLE EQUIVALENCE

We now show that the entropy is concave in energy E . In Eq. (11), k^* , though a function of E , takes on integer values and is a constant over a range of E . As E increases from 0 to its maximum value, k^* decreases from N to 1, in steps of unity. Thus, the entropy curve consists of N linear segments of slope $\xi(k^*, k^* - 1)/\chi$, $k^* = 1, \dots, N$, where the segment with larger energy has smaller slope, thereby implying that the curve is concave. The piecewise linear character of microcanonical entropy has its origin in the first-order poles of the canonical

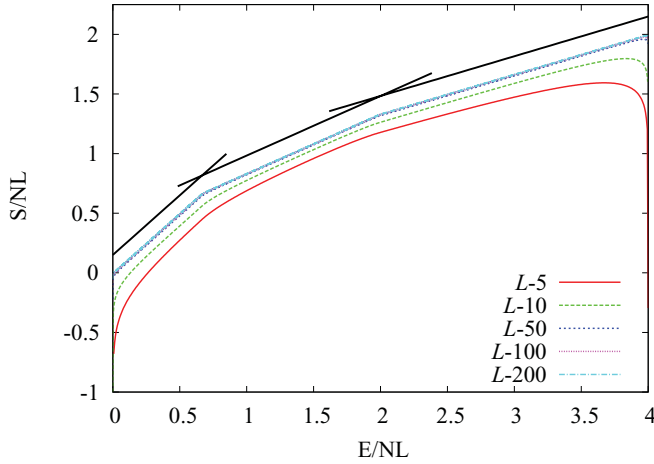


FIG. 1. (Color online) The variation of microcanonical entropy S with energy E is shown for different L . The data are for $N = 3$ and $\chi = 3$. The solid black lines correspond to the limiting curve obtained from Eq. (11). They have been shifted upward and extended to the left and right for clarity since the unshifted lines are indistinguishable from the curve for $L = 200$.

partition function, with the slopes being equal to the strength of the poles [38].

The energy–temperature relation in the microcanonical ensemble is obtained from the thermodynamic relation $\beta = \frac{\partial S}{\partial E}$. This gives $\beta\chi = \xi(k^*, k^* - 1)$, implying that $\beta\chi$ takes on N distinct values, corresponding to the N transition points, which coincide with those obtained from the canonical partition function [see Eq. (5)]. In Fig. 2(a), we show the energy–temperature relation in the microcanonical ensemble for finite L by considering all the terms in $g(E)$. As L is increased we obtain the limiting step function determined by the relation $\beta\chi = \xi(k^*, k^* - 1)$. The corresponding data for the canonical partition function from Eq. (3) are shown in Fig. 2(b). Thus, in the thermodynamic limit ($L \rightarrow \infty$), we obtain the same limiting curve in both the ensembles.

We can further quantify the energy–temperature relation shown in Fig. 2. The energies of the plateaus are obtained by solving Eq. (8) as an equality, and are given by $E_{\text{plateau}} = \chi N^{-1}(N - k)(N - k + 1)L$, $k = 0, \dots, N$. A simple physical interpretation can be ascribed to these plateaus, as explained below. Consider a scenario when m counterions have condensed onto the disk, while the remaining $N - m$ counterions are at the boundary R . The energy of this configuration, in the limit of large L has contribution from two parts: (1) $q^2 L(N - m)^2$ corresponding to interaction between a disk of charge $(N - m)q'$ and $N - m$ counterions and (2) $q^2 L(N - m)(N - m - 1)/2$ corresponding to interaction between counterion pairs. The total energy of this geometry is thus $\chi N^{-1}(N - m)(N - m + 1)$. Comparing this energy with the energy of a plateau, it is clear that the plateau corresponding to a certain value of k corresponds to a case where k counterions have condensed and the remaining ones are at the boundary.

We stress that we have not used the Legendre transformation to evaluate the microcanonical entropy from the canonical free energy. The entropy obtained by the Legendre transformation will always give the concave envelope of the microcanonical

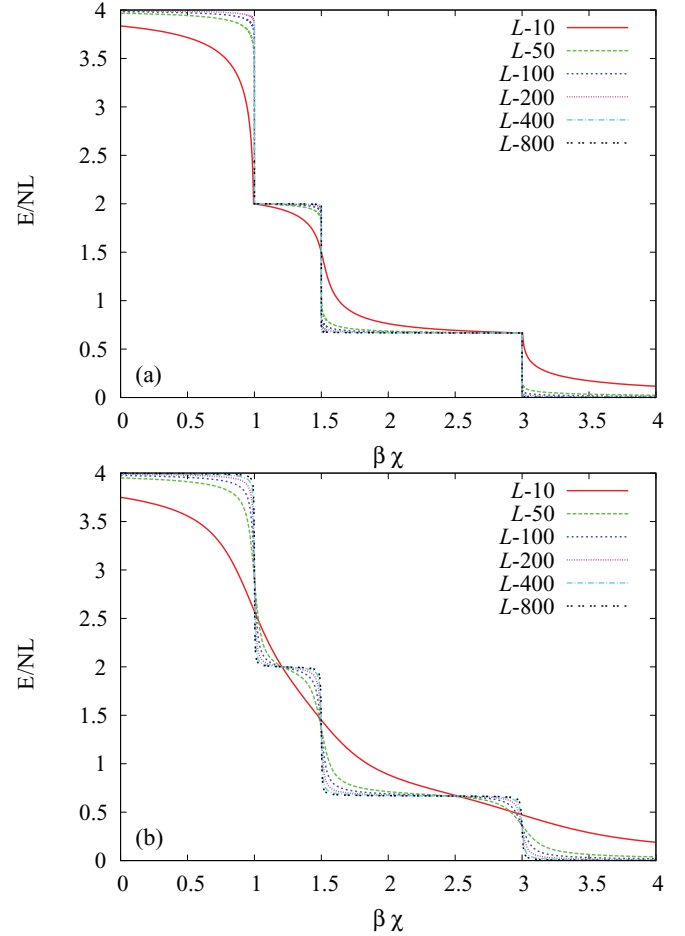


FIG. 2. (Color online) The energy–temperature relation for $N = 3$, $\chi = 3$ for different L in the (a) microcanonical ensemble and (b) canonical ensemble. For large values of L , the transition points are given by $(\beta\chi)_c = \xi(k^*, k^* - 1)$.

entropy [27,39]. Since the entropy that we have calculated directly from the density of states is concave, we should be able to obtain the same by a Legendre transform of the free energy, $S(E) = \beta E - \beta F(\beta)$, where β is to be eliminated using the energy–temperature relation $E = \frac{\partial}{\partial \beta}(\beta F)$. In the thermodynamic limit, it is straightforward to do so for this model.

V. CONCLUSIONS

To summarize, we studied counterion condensation transition on a two-dimensional charged disk in the microcanonical ensemble. In the limit of infinite dilution, we obtained an expression for the microcanonical entropy, and showed that the entropy–energy curve consisted of linear segments with decreasing slope, and hence that the entropy is concave with respect to energy. This implies the equivalence of the microcanonical and canonical ensembles. In particular, the energy–temperature relation and the transition points of CCT obtained from the microcanonical entropy are shown to be identical with those obtained from the canonical partition function.

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