Exact partition functions of a polymer on a square lattice up to chain length 38

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Abstract. Collapse transition of the lattice polymer on a square lattice is studied by calculating the exact partition functions up to chain length 38; they are obtained by enumerating the number of possible conformations for each energy value. We observe that the locus of partition function zeros approaches the positive real axis as the chain length increases, providing evidence of the collapse transition. The crossover exponent and the transition temperature are estimated from the scaling behavior of the first partition function zeros with increasing chain length.

1. Introduction

A flexible polymer chain in a dilute solution is influenced by both hydrophobic interactions between the monomers and the excluded volume effect. The attractive interactions are neglected at high temperatures or in a good solvent, but become significant as the temperature T is lowered. As T reaches a special temperature θ, the linear polymer undergoes an abrupt change from an expanded conformation for $T > \theta$ to a fully compact conformation for $T < \theta$ [1, 2, 3]. A long polymer in a good solvent is a critical system, and the collapse transition at $T = \theta$ has been identified as a tricritical transition [3, 4]. The θ point behavior is well-described by self-avoiding walks with attractive interaction energy assigned for each pair of nonbonded nearest-neighbor (NN) monomers. The tricritical exponents take the mean-field values for $d > 3$, and there are logarithmic corrections at $d = 3$ [3, 4, 5, 6, 7, 8, 9]. A great deal of studies have been performed to understand the nature of the collapse transition in two dimensions, which is expected to exhibit much more non-trivial behavior than its higher dimensional counterparts.

In this work, we calculate the exact partition function of a polymer on a square lattice with chain length 38 for the first time, and obtain the crossover exponent and the tricritical temperature by examining their scaling behavior of the partition function zeros with increasing chain length.

2. Number of conformations

By using self-avoiding walks on a square lattice, conformations of a polymer chain with N monomers are modeled. The position of a monomer i is expressed as $\mathbf{r}_i = (a, b)$ with integer

values of the coordinates a and b. Chain connectivity requires bond length is unity, $|\mathbf{r}_i - \mathbf{r}_{i+1}| = 1$, and the excluded volume effect does allow only one monomer on each lattice, $\mathbf{r}_i \neq \mathbf{r}_j$ for $i \neq j$.

We consider the Hamiltonian with the nearest-neighbor interaction:

$$\mathcal{H} = -\epsilon \sum_{i<j} \Delta(\mathbf{r}_i, \mathbf{r}_j), \tag{1}$$

where

$$\Delta(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} 1 & \text{if } |i-j| > 1 \text{ and } |\mathbf{r}_i - \mathbf{r}_j| = 1, \\ 0 & \text{otherwise}, \end{cases} \tag{2}$$

and ϵ is set to a positive value to incorporate the attractive interaction between the monomers.

Assuming that the polymer chain has an intrinsic direction, the conformations with reverse labels $i \leftrightarrow N - i + 1$ for all $(i = 1, 2, \cdots, N)$ are considered distinct. The total number of conformations generated by rotations and reflections from a given two-dimensional conformation is 8, since the rigid rotations and reflections in two dimensions form an 8-fold symmetry. The straight chain is an exception, however, a one-dimensional conformation invariant with respect to reflection perpendicular to the chain, where the total number of conformations generated by rotations and reflections is 4. Here, we define the reduced number of conformations $\omega_N(K)$, where conformations related by rigid rotations, reflections, and translations are regarded as equivalent, and counted only once. Consequently, the number of conformations with rigid rotations and reflections considered distinct, denoted by $\Omega_N(K)$, can be easily obtained by

$$\Omega_N(K) = \begin{cases} 8\omega_N(K) - 4 & \text{if } K = 0, \\ 8\omega_N(K) & \text{otherwise}. \end{cases} \tag{3}$$

Thus, one can achieve about 8-fold reduction in the computing time by enumerating the reduced number of conformations $\omega_N(K)$ instead of $\Omega_N(K)$ [10, 11]. We obtained $\omega_N(K)$ up to $N = 38$ by the help of a parallel algorithm classifying conformations by sizes of rectangles they span [12]. The number of conformations $\Omega_N(K)$ for $N = 38$ is presented in table 1.

3. Partition function zeros in the complex temperature plane

Partition function zeros have been the subject of interest as a sensitive indicator of a phase transition [10, 11, 13, 14, 15, 16]. Partition function zeros were introduced by Yang and Lee in the complex fugacity plane of a fluid system and the complex magnetic-field plane of the nearest-neighbor Ising ferromagnet (Yang-Lee zeros), to study the phase transition driven by the fugacity or the magnetic field [17]. Later, Fisher [18] used the partition function zeros in the complex temperature plane (Fisher zeros) of the square-lattice Ising model, to study the temperature driven transition. In the thermodynamic limit, the locus of zeros forms a continuous curve which crosses the real axis if a transition exists. Thus, the theory of partition function zeros provides the explanation on how the partition function, which is an analytic function of thermodynamic parameters at a finite size, acquires the singularities necessary for a phase transition in the thermodynamic limit. In the case of Fisher zeros, the transition temperature in the thermodynamic limit is the intersection point of the locus of zeros with the real temperature axis. Therefore, the conjugate pair of zeros closest to the positive real axis, called the *first zeros*, determine the leading singular behavior of the partition function. Since the behavior of the first zeros can be analyzed separately from the other zeros, the phase transition can be analyzed more accurately by computing the partition function zeros than studying real-valued quantities such as the specific heat which includes the effect from all the zeros [11].

The partition function of our model is

$$Z = \sum e^{-\beta\mathcal{H}} = \sum_{K=0}^{K_{\max}(N)} \Omega_N(K) y^K, \tag{4}$$

Table 1. The number of conformations $\Omega(K)$ on a square lattice as a function of the number of contacts K for chain length 38.

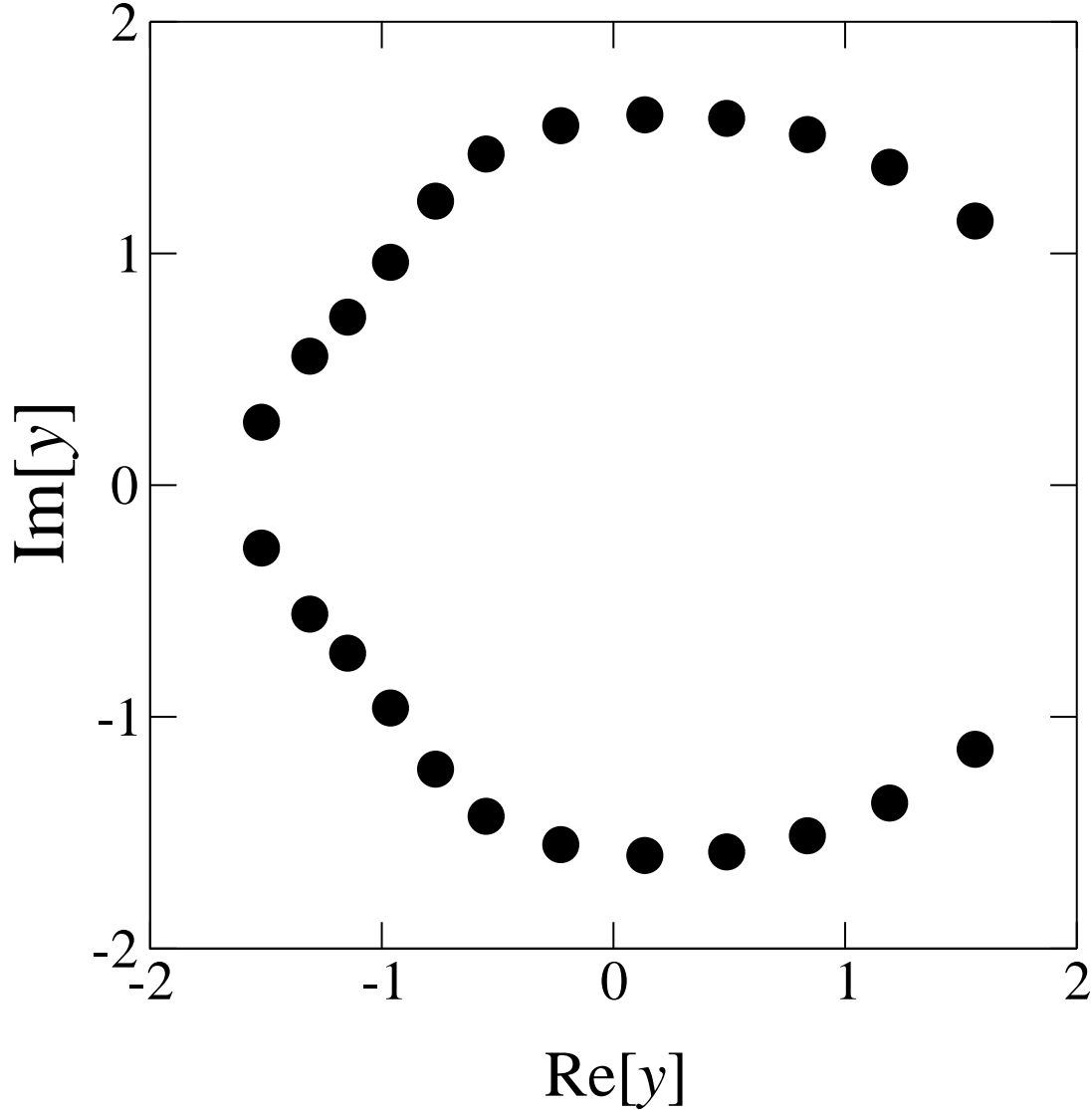| K	$\Omega(K)$
0	128296079455572
1	515427549335840
2	1128115046251464
3	1756218784960648
4	2184512179070336
5	2306182278125992
6	2144957763099744
7	1799694003510208
8	1385401931446192
9	990209382129048
10	663137244947784
11	418840297796560
12	250761159690416
13	142813585256872
14	77560661732336
15	40218582883856
16	19921507091832
17	9413632521400
18	4236279016096
19	1807558226256
20	725595746792
21	271663920168
22	93029010016
23	28148212408
24	7210320464
25	1082656960
26	45293464
Total	15968852281708724

where $y \equiv \exp(\beta\epsilon)$, $\beta \equiv 1/k_B T$, and $K_{\max}(N)$ is the maximum number of possible contacts for polymer length N [19],

$$K_{\max}(N) = \begin{cases} N - 2m & \text{for } m^2 < N \leq m(m+1), \\ N - 2m - 1 & \text{for } m(m+1) < N \leq (m+1)^2, \end{cases} \tag{5}$$

where m is a positive integer. Then, the partition function becomes a $K_{\max}$-th order polynomial of y and can be expressed in the form,

$$Z(y) = A(y) \prod_i (y - y_i), \tag{6}$$

where $A(y)$ is a function which is analytic in the whole complex plane and the partition function zeros y_i $(i = 1, 2, \cdots, K_{\max})$ are obtained by solving the polynomial equation $Z(y) = 0$ with MATHEMATICA. Figure 1 shows the partition function zeros for $N = 38$ in the complex temperature plane. One can realize that the first zeros approach the positive real axis in the complex temperature plane as polymer length increases (figure 2).

Figure 1. Positions of the partition function zeros in the complex temperature ($y = e^{\beta\epsilon}$) plane for $N = 38$. The first zeros are the ones closest to the positive real axis.
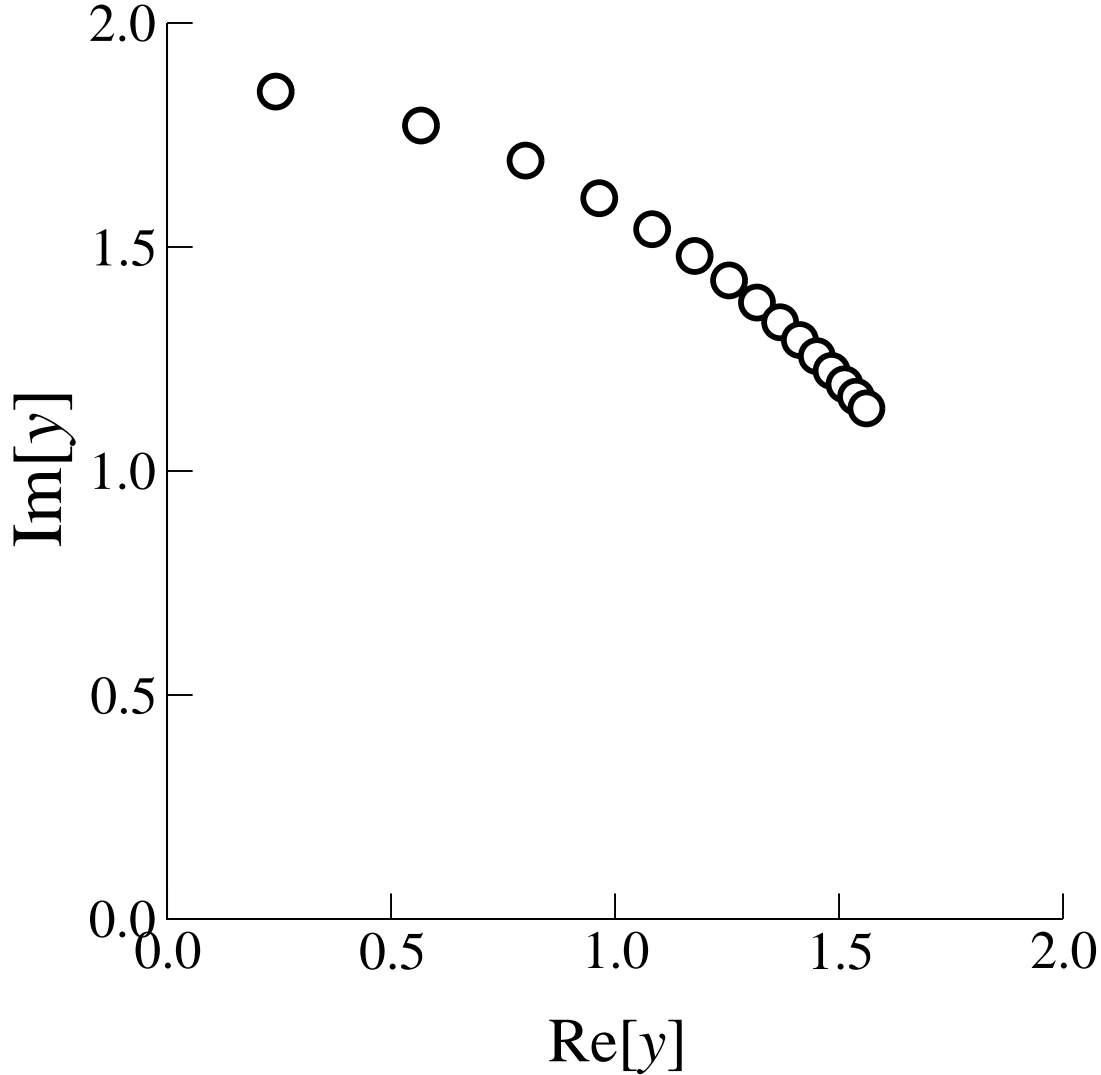
4. Crossover exponent and tricritical temperature

The crossover exponent ϕ, introduced in the Introduction, also describes how rapidly the first zeros approach the positive real axis as N increases [11, 13],

$$\text{Im}[y_1(N)] \sim N^{-\phi}, \tag{7}$$

where $y_1(N)$ is a first zero for a polymer chain with N monomers. In finite-size systems ($N = $ even), the crossover exponent is approximated as

$$\phi(N) = -\frac{\ln\{\text{Im}[y_1(N+2)]/\text{Im}[y_1(N)]\}}{\ln\{(N+2)/N\}}, \tag{8}$$

which reduces to the exact value of ϕ in $N \to \infty$ limit, estimated by using the Bulirsch-Stoer (BST) extrapolation [20]. We obtain $\phi = 0.430(29)$ from the data for even N with $N \geq 22$, where

Figure 2. Positions of the first zeros in the first quadrant of the complex temperature ($y = e^{\beta\epsilon}$) plane for even lengths $N = 10, 12, 14, \cdots, 38$ from left to right. The first zeros approach the positive real axis as N increases.

the estimated error can be further reduced by removing unreliable data obtained from $N < 22$. The error is estimated by examining the robustness of the extrapolated value with respect to perturbations of the data points, but it is not a statistically rigorous confidence level [11, 20]. The value of ϕ we obtained agrees quite well with the exact value $3/7$ obtained by analytic calculation on the polymers on the hexagonal lattice [8], which is believed to be in the same universality class as those on the square lattice.

With the value of ϕ, the tricritical temperature can be obtained by estimating the point on the positive real axis where the first zeros approach in the limit of $N \to \infty$,

$$\text{Re}[y_1(N)] - y_c \sim N^{-\phi}. \tag{9}$$

The value of $y_c = 2.15(30)$, which corresponds to $\theta = 1.31(32)$, is obtained by extrapolating the data for even N with $N \geq 22$. In table 2, our results given in the first line are compared with those from the earlier works.

Table 2. The tricritical temperature θ and the crossover exponent ϕ obtained in the current work, displayed in the first line, are compared with those in the literature. θ is displayed only for the model of the current work.

Method	lattice	$N_{\max}$	θ	ϕ
Exact partition function zeros	square	38	1.31(32)	0.430(29)
Field theory [5]	N/A	N/A	-	$\frac{7}{11}$ (≈ 0.64)
Monte Carlo [6]	square	160	1.31(6)	-
Renormalization group [21]	N/A	N/A	-	$\frac{19}{22}$ (≈ 0.86)
Monte Carlo [22]	square	200	1.55(15)	0.6(1)
Transfer matrix [7, 23]	square	N/A	1.42(4)	0.48(7)
Series expansion [24]	triangular	16	-	0.64(5)
Coulomb gas method [8]	hexagonal	N/A	-	$\frac{3}{7}$ (≈ 0.43)
Monte Carlo and RG [25]	square	40	1.54(7)	0.52(7)
Monte Carlo [26]	hexagonal	300	-	0.5(1)
Scanning simulation [27]	square	240	1.52(1)	0.530(4)
Recursive enrichment method [28]	square	2048	1.504(5)	0.435(6)
The pruned-enriched Rosenbluth method [29]	square	256	1.4993(23)	-
Interacting growth walk [30]	square	2000	-	0.419(3)
Monte Carlo [31]	square	1600	1.50	0.545(4)
Monte Carlo [32]	square	300	1.505(18)	-
Monte Carlo [33]	square	3200	1.4986(11)	0.46(3)
Exact enumeration [34]	square	26	1.515(47)	-
Monte Carlo [34]	square	71	1.529	-

5. Discussion

With the number of all possible conformations obtained by exhaustive enumeration up to chain length $N = 38$, we studied the collapse transition of a polymer on a square lattice by calculating the partition function zeros. We observed that the first zeros tend to approach the positive real axis as the chain length increases, and we measured the crossover exponent ϕ and the tricritical temperature θ by the BST extrapolation.

The maximum chain length in our study is so much shorter in contrast to Monte Carlo approaches with polymer lengths up to several hundreds or thousands. According to the exactness of our data, however, we could use a powerful extrapolation method and then estimated reasonably accurate values of the crossover exponent and the tricritical temperature. Furthermore, the partition function zeros allow us to carry out much more accurate analysis of the collapse transition than examining the radius of gyration or specific heat.

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