Partition function zeros of a square-lattice homopolymer with nearest- and next-nearest-neighbor interactions

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We study distributions of the partition function zeros in the complex temperature plane for a square-lattice homopolymer with nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions. The dependence of distributions on the ratio of NN and NNN interaction strengths R is examined. The finite-size scaling of the zeros is performed to obtain the crossover exponent, which is shown to be independent of R within error bars, suggesting that all of these models belong to the same universality class. The transition temperatures are also computed by the zeros to obtain the phase diagram, and the results confirm that the model with stronger NNN interaction exhibits stronger effects of cooperativity.

I. INTRODUCTION

Conformational transition of a flexible polymer chain in a dilute solution is controlled by both hydrophobic interactions between the monomers and the excluded volume effect. The effects of the attractive and repulsive interactions are dominant in low- and high-temperature regimes, respectively, and the conformation of a linear polymer undergoes a transition from a swollen state to a fully compact one [1–3] at a special temperature θ. The collapse transition at θ has been identified as a tricritical transition [2,4].

The interacting self-avoiding walk on a lattice has been studied as a model for the polymer, where a site visited once is banned and the energy of attractive interactions is defined to be proportional to the number of nonbonded nearest-neighbor (NN) monomer pairs. In three dimensions, the upper tricritical dimension [5], the tricritical behavior follows the mean-field theory prediction with logarithmic corrections [6], and the first-order transition is expected at a temperature lower than θ between liquid-like globule and solid-like phase [7–14]. On the other hand, the nature of the collapse transition of a two-dimensional polymer, which cannot be described by the mean-field theory, has been extensively studied using lattice polymer models with NN interactions [15–35].

In a previous work [36], we studied the critical properties of a homopolymer on a square lattice where the strength of NN and next-nearest-neighbor (NNN) interactions are the same, and the result suggested that the model belongs to the universality class of a polymer with NN interaction only. We extend the investigation in this work to study the partition function zeros for the continuous range of the ratio of NN and NNN interaction strengths. The crossover exponent is computed by the finite-size scaling, which is seen to be independent of relative strengths of NN and NNN interactions, suggesting that all of these models belong to the same universality class. The critical temperature is also estimated to construct a phase diagram in the space of interaction

parameters, which shows the enhancement of cooperative effect by NNN interaction. Although NNN interaction on a hexagonal lattice [18,23,37–40] has been studied, we study NN and NNN interactions on a square lattice with varying ratio of their strengths for the first time, to the best of our knowledge.

II. THE NUMBER OF CONFORMATIONS

Conformations of a polymer chain with N monomers can be modelled by a self-avoiding walk where the position of the ith monomer is given by $\mathbf{r}_i = (k,l)$, with integers k and l, and $\mathbf{r}_i \neq \mathbf{r}_j$ for $i \neq j$ due to the condition that each lattice site is visited only once. By chain connectivity, we have $|\mathbf{r}_i - \mathbf{r}_{i+1}| = 1$. The Hamiltonian is

$$\mathcal{H} = -\epsilon_1 \sum_{i<j} \Delta(\mathbf{r}_i,\mathbf{r}_j) - \epsilon_2 \sum_{i<j} \tilde{\Delta}(\mathbf{r}_i,\mathbf{r}_j), \qquad (1)$$

where

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

and

$$\tilde{\Delta}(\mathbf{r}_i,\mathbf{r}_j) = \begin{cases} 1 & \text{if } |\mathbf{r}_i - \mathbf{r}_j| = \sqrt{2}, \\ 0 & \text{otherwise.} \end{cases} \qquad (3)$$

In this paper, the energies $-\epsilon_1 < 0$ and $-\epsilon_2 < 0$ are assigned to each nonbonded NN and NNN contact between monomers, respectively, to implement the effect of the attractive hydrophobic interaction. The case of $\epsilon_2 = 0$ corresponds to the model where only NN interaction is present [29,33].

The energy of a given conformation can be expressed as $E = -\epsilon_1 K_1 - \epsilon_2 K_2$, where K_1 and K_2 are the number of contacts between NN and NNN monomers, respectively. The partition function Z is then calculated from the number of conformations for given values of K_1 and K_2, $\Omega_N(K_1,K_2)$, as

$$Z = \sum e^{-\beta\mathcal{H}} = \sum_{K_1,K_2} \Omega_N(K_1,K_2)e^{\beta\epsilon_1(K_1+RK_2)}, \qquad (4)$$

where $\beta \equiv 1/k_B T$ and $R \equiv \epsilon_2/\epsilon_1$. Although the total number of conformations $\sum_{K_1,K_2} \Omega_N(K_1,K_2)$ has been computed

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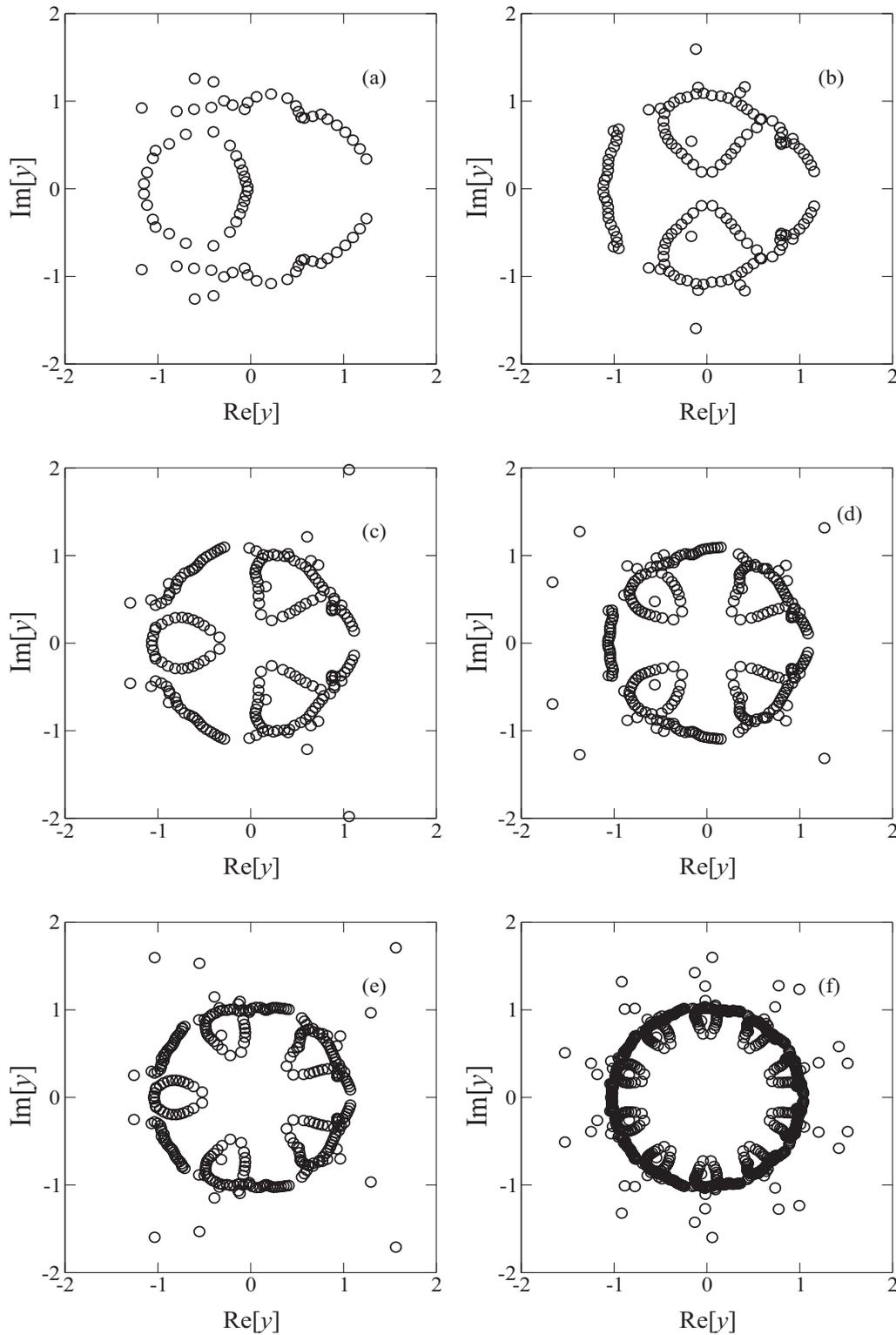
FIG. 1. Partition function zeros in the complex $y = e^{\beta \epsilon_1}$ plane of the square-lattice homopolymer with $N = 38$ for (a) $R = 1$, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 10.

up to $N = 72$ [41], the computation of $\Omega_N(K_1, K_2)$ itself is much more expensive computationally, since the number of NN and NNN interactions has to be checked for each conformation. The number of conformations for a given value

of K_1, $\sum_{K_2} \Omega_N(K_1, K_2)$, was computed in Ref. [33] up to $N = 36$ using an efficient parallel algorithm [42]. Using a slightly modified version of the same algorithm, we compute $\Omega_N(K_1, K_2)$, up to chain length $N = 38$ in the current work.

III. PARTITION FUNCTION ZEROS IN THE COMPLEX TEMPERATURE PLANE

The partition function zeros were introduced by Yang and Lee [43], in the complex fugacity plane of a fluid system and the complex magnetic-field plane of the NN Ising ferromagnet (Yang-Lee zeros), in order to explain the mechanism for the occurrence of phase transitions in the thermodynamic limit. Fisher [44] later studied the partition function zeros of the square-lattice Ising model in the complex temperature plane (Fisher zeros).

The distribution of Fisher zeros forms a simple locus in the thermodynamic limit, and intersects positive real axis at a transition temperature if a transition exists, thus explaining the origin of the singularity of the free energy, which is absent for a finite-size system [45,46]. The *first zeros*, the zeros closest to the positive real axis, determine the singular behavior of the free energy in the thermodynamic limit. Since the behavior of the first zeros can be studied separately from other zeros, the partition function zeros are a much more sensitive indicator of a phase transition than the real-valued quantities, such as the specific heat where effects from all zeros are included and cannot be separated from each other. Furthermore, the partition function zeros close in toward the real axis regardless of the order of transition as long as such a transition exists, in contrast to real-valued quantities, which show singularity only when an appropriate derivative is taken.

We compute the zeros of the partition function in the complex plane of $y \equiv \exp(\beta\epsilon_1)$ by solving the polynomial equation with MATHEMATICA,

$$Z(y) = \sum_K \Omega_N(K) y^K = A(y) \prod_i (y - y_i) = 0, \quad (5)$$

where $A(y)$ is a function that is analytic in the whole complex plane. Figure 1 shows that the partition function zeros (y_i) distributed in the complex y plane for various R values have an approximate R-fold symmetry in the angular direction, due to the effect of NNN interaction. Note that the strength of NNN interaction is $\epsilon_2 = R\epsilon_1$, whereas the zeros are plotted in the plane of $y \equiv \exp(\beta\epsilon_1)$. In the absence of NN interaction, the zeros will have an exact R-fold symmetry when plotted in the y plane. In fact, the symmetry is broken due to the presence of NN interaction, and the apparent R-fold symmetry is only approximate. For large R values, the locus of the zeros can be approximated as a unit circle, as shown in Fig. 2 for $R = 50$.

On the other hand, the zeros for $R < 1$, plotted in the complex plane of $y' \equiv \exp(\beta\epsilon_2)$ in Fig. 3, do not show the pattern of $1/R$-fold symmetry, indicating that the distribution pattern of the zeros is mainly determined by NNN interaction.

IV. CRITICAL BEHAVIOR

The radius of gyration, R_N, of a polymer chain with N monomers is generally described near the critical temperature T_c by the scaling theory [2,15],

$$\langle R_N^2 \rangle \sim N^{2\nu} f(\tau N^\phi), \quad (6)$$
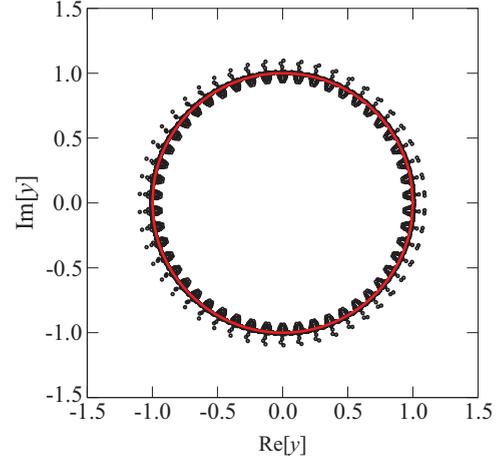
FIG. 2. (Color online) Partition function zeros in the complex $y = e^{\beta\epsilon_1}$ plane of the square-lattice homopolymer with $N = 38$ for $R = 50$. The solid line is a unit circle.

where the reduced temperature is defined as $\tau \equiv |T - T_c| / T_c$ and the scaling function $f(x)$ behaves as follows:

$$f(x) = \begin{cases} x^{(6/(d+2)-2\nu)/\phi} & \text{if} \quad x \to \infty, \\ \text{const.} & \text{if} \quad x \to 0, \\ x^{(2/d-2\nu)/\phi} & \text{if} \quad x \to -\infty, \end{cases} \quad (7)$$

where d is the space dimension and the exponent ν represents the geometrical properties of a polymer. The crossover exponent ϕ describes how rapidly the system undergoes the transition as T approaches T_c, which can be obtained by how rapidly the first zeros, y_1s, approach the positive real axis as N increases [33,36],

$$\text{Im}[y_1(N)] \sim N^{-\phi}. \quad (8)$$

In finite-size systems with even N, the crossover exponent is approximated as

$$\phi(N) = -\frac{\ln\{\text{Im}[y_1(N+2)]/\text{Im}[y_1(N)]\}}{\ln\{(N+2)/N\}}, \quad (9)$$

which reduces to the exact value of ϕ in $N \to \infty$ limit, estimated by using the Bulirsch-Stoer (BST) extrapolation

TABLE I. The estimated values of the critical point y_c and the crossover exponent ϕ for various R values.

R	ϕ	y_c
0	0.430(29)	2.15(24)
$\frac{1}{4}$	0.435(61)	1.708(50)
$\frac{1}{2}$	0.43(12)	1.507(14)
1	0.439(45)	1.320(24)
2	0.446(70)	1.185(30)
3	0.45(13)	1.130(43)
4	0.430(56)	1.100(35)
5	0.441(18)	1.081(26)
10	0.451(15)	1.0419(41)
20	0.451(35)	1.0213(34)
30	0.451(38)	1.0143(25)
40	0.451(39)	1.0107(18)
50	0.451(39)	1.0086(14)
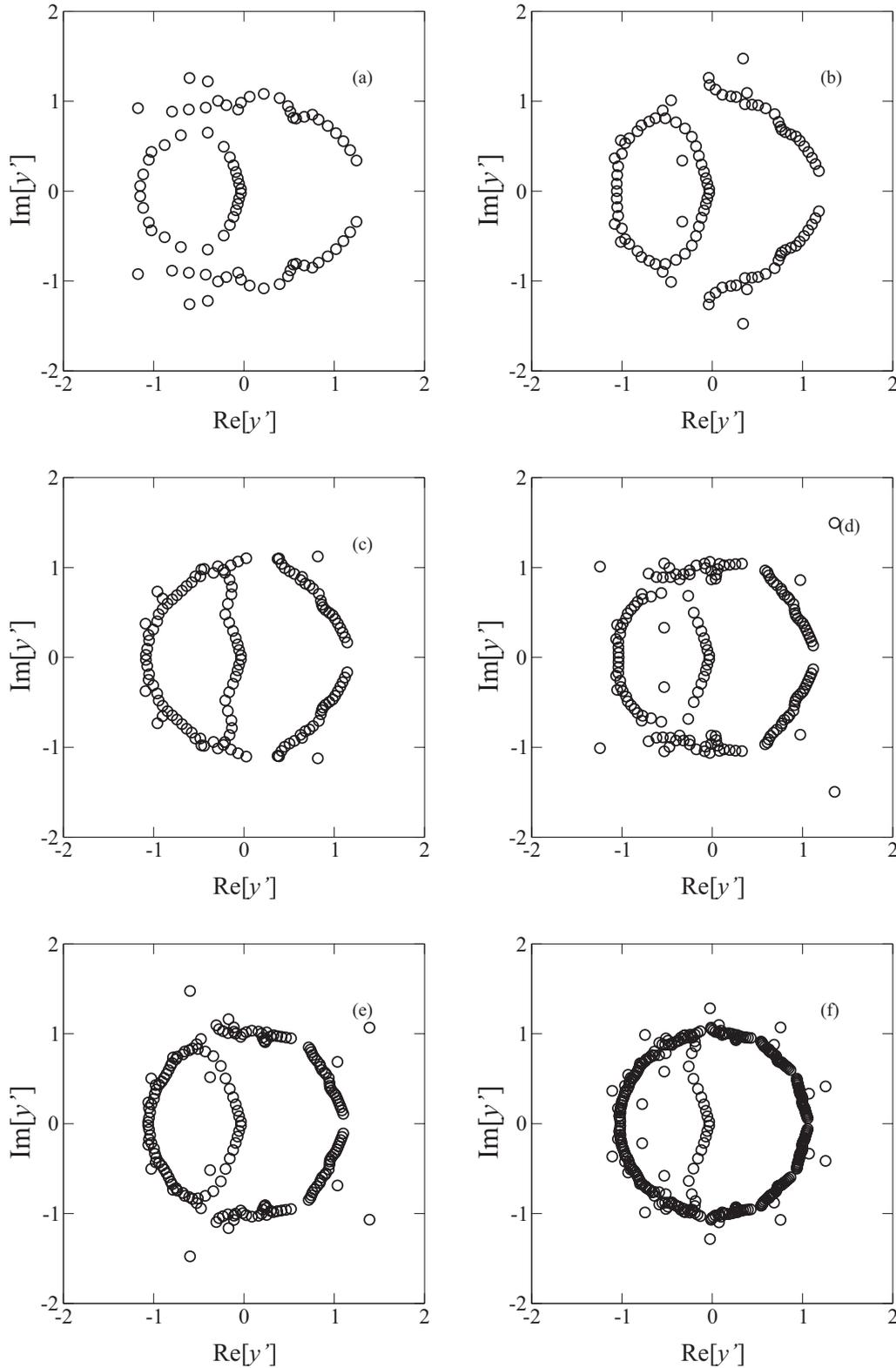
FIG. 3. Partition function zeros in the complex $y' = e^{\beta \epsilon_2}$ plane of the square-lattice homopolymer with $N = 38$ for (a) $R = 1$, (b) 1/2, (c) 1/3, (d) 1/4, (e) 1/5, and (f) 1/10.

[47]. The extrapolation of ϕ to infinite N is presented in Table I and Fig. 4 as a function of R, all of which are seen to agree with the conjectured exact value 3/7 [18,34] within the errors. The ϕ value for $R = 0$ was estimated to be

0.422 using data for chain lengths up to $N = 36$. The current estimate $\phi = 0.430$ for $R = 0$ obtained using the data that includes a longer chain with $n = 38$, is closer to 3/7. It is also in a reasonable agreement with previous estimates obtained
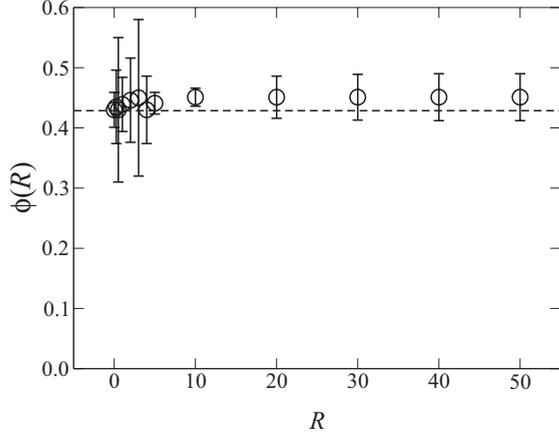
FIG. 4. The values of $\phi(R)$ with error bars are shown as a function of R. The dotted line indicates the conjectured exact value 3/7.

by other methods, as listed in Table I of Ref. [33] (See also Ref. [48]).

The result suggests that the polymer with NN and NNN interactions on a square lattice all belong to the same universality class.

The critical temperature, y_c, the point on the x axis at which the real parts of the first zeros approach in the limit of $N \to \infty$, can be also obtained by applying the BST extrapolation to the finite-size scaling,

$$\text{Re}[y_1(N)] - y_c \sim N^{-\phi}. \tag{10}$$

Table I and Fig. 5 show the estimated values of y_c for various R values, for $0 \leqslant R \leqslant 50$. In Fig. 5, we re-express $y_c(R)$ in terms of (a) coupling constants $(\beta\epsilon_1 - \beta\epsilon_2)$ and (b) temperature versus R. In both diagrams, the data points are well-fitted by a linear equation form, $y = ax + b$, with (a) $a = -0.5635(38)$ and $b = 0.4340(12)$, and (b) $a = 2.312(34)$ and $b = 1.262(70)$, i.e.,

$$\text{(a)} \quad \beta\epsilon_2 = -0.5635\beta\epsilon_1 + 0.434, \tag{11}$$
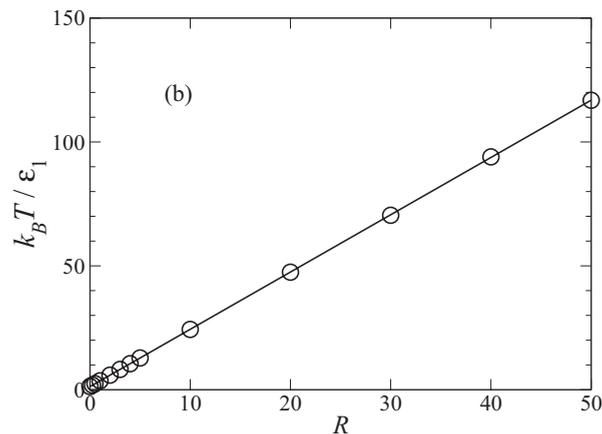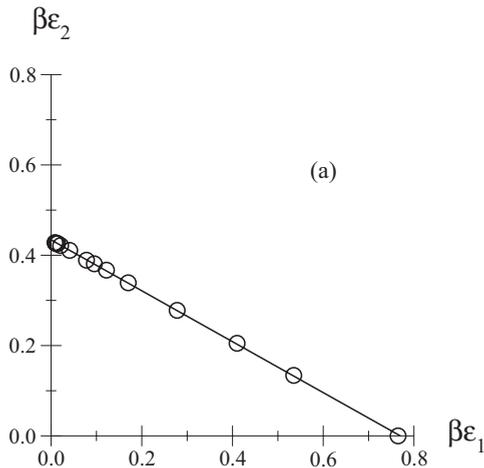
and

$$\text{(b)} \quad k_B T/\epsilon_1 = 2.312R + 1.262, \tag{12}$$

but the deep reason behind this apparent linearity is not clear to the authors. The value of b in (a), the y-axis intercept point, indicates the critical temperature $\beta_c\epsilon_2$ in the limit $R \to \infty$, i.e., in the case without NN interaction. Equation (12) with $R = 0$ directly indicates the transition temperature of the case with NN interaction only, $k_B T/\epsilon_1 = 1.262$, which is in reasonable agreement with the value 1.30(17) obtained from the finite-size scaling up to chain length 36 [33].

V. DISCUSSIONS

We studied the collapse transition of a square-lattice polymer with both NN and NNN interactions for various values of ratio $R = \epsilon_2/\epsilon_1$, by calculating the exact partition function zeros up to chain length $N = 38$, the longest one to be enumerated exactly up to present. It was revealed that the partition function zeros show the repeated pattern of substructures with an approximate R-fold symmetry. For R as large as 50, the locus of the partition function zeros is approximately a unit circle, which means that the critical temperature y_c in the limit $R \to \infty$ approaches one, i.e., $T_c \to \infty$ for $R \to \infty$ in accordance with Eq. (12). The crossover exponent and the transition temperature were estimated by finite-size scaling of the zeros. The crossover exponents were shown to be independent of R with error bars and coincided with the θ-point value 3/7, suggesting that the polymer on a square lattice with NN and NNN interactions all belong to the same θ-point universality class. Such a universal behavior of the square-lattice polymer is in contrast with some of the other systems, such as Ising model, where the critical exponent is known to depend on the ratio of NNN interaction to NN one, leading to nonuniversal behaviors [49]. We could also obtain the phase diagram of a square-lattice polymer with NN and NNN interactions, by examining the transition temperature for various R values.

FIG. 5. The phase diagrams of the square-lattice homopolymer in (a) the $\beta\epsilon_1 - \beta\epsilon_2$ plane (for $\epsilon_1 > 0$ and $\epsilon_2 > 0$) and (b) the temperature $(k_B T/\epsilon_1)$ versus the coupling ratio $(R = \epsilon_2/\epsilon_1)$ plane. The solid lines are (a) $\beta\epsilon_2 = -0.5635\beta\epsilon_1 + 0.434$ and (b) $k_B T/\epsilon_1 = 2.312R + 1.262$.

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