

Exact Partition Function Zeros of Two-Dimensional Lattice Polymers

Julian LEE*

*Department of Bioinformatics and Life Science, Soongsil University, Seoul 156-743
Bioinformatics and Molecular Design Technology Innovation Center, Soongsil University, Seoul 156-743 and
Computer Aided Molecular Design Research Center, Soongsil University, Seoul 156-743*

(Received 8 October 2003)

We study the zeros of the exact partition function of lattice polymers on two-dimensional square lattices up to the chain length 28. We observe that the leading zeros tend to approach the real axis as the chain length increases. The results suggest that the locus of zeros may intersect the real axis in the limit of infinite chain length, which is the necessary condition for the existence of the collapse transition.

PACS numbers: 42.30.Sy, 89.75.Kd, 87.14.Ee, 87.15.Cc

Keywords: Lattice polymer, Lattice protein, Partition function zeros, Collapse transition

It is generally believed that a polymer in a poor solvent undergoes the collapse transition to compact conformations at low temperature, due to the hydrophobic interaction between monomers. Theoretical studies [1–19] of the collapse transition using various models have been performed, as well as experimental investigations [20–30]. However, due to the finite chain length of a polymer, there is no definite conclusion on whether a phase transition really exists in the thermodynamic limit in a rigorous sense, not to mention more subtle issues such as the order of the phase transition if one exists. The collapse of homopolymers is of interest not only in its own right, but also because it is a precursor to understanding heteropolymer collapse, which is of interest in protein folding [31].

One of the important tools for the theoretical study of the polymer has been the use of exhaustive simulations of self-avoiding chains on lattices [32–36]. This system is a special case of the HP model of lattice heteropolymer, which has been studied as a simple model of the protein [37–45]. Although there have been some studies on the collapse transition of HP model lattice polymers, much of the work has been concentrated on Monte Carlo simulations [42,44,45], and studies using exact enumeration have been restricted to relatively short chain lengths [32, 34,38]. Moreover, to the best of our knowledge, investigation of the properties of the partition function zeros has never been attempted.

The zeros of the partition function in the complex temperature plane, called Fisher zeros [46,47], are interesting because they give crucial information on phase transitions of the system. Fisher zeros have been the subject of research for various physical systems [48–59]. Theo-

ries on general properties of partition function zeros have also been developed [60–63].

In this work, we investigate the exact partition function of homopolymers on two-dimensional square lattices by exhaustively enumerating the conformations of self-avoiding chains up to the chain length 28, which is much larger than those reported in the literature. By solving the polynomial equations resulting from the exact partition function, we obtain the positions of the Fisher zeros. We observe that the locus of zeros tends to close in the positive real axis as the chain length increases. In particular, the leading zeros seem to converge to the real axis, suggesting the collapse transition in the thermodynamic limit.

In our model, the conformations of a polymer chain with N monomers are modelled as two-dimensional self-avoiding chains of length N on the square lattice. The bond length is unity, so the position of monomer i is given by $\mathbf{r}_i = (k, l)$, where integers k and l are the Cartesian coordinates relative to an arbitrary origin. Chain connectivity requires $|\mathbf{r}_i - \mathbf{r}_{i+1}| = 1$. Because of excluded volume, there can be no more than one monomer on each lattice site, $\mathbf{r}_i \neq \mathbf{r}_j$ for $i \neq j$. Conformations are classified by the number t of inter-chain contacts, *i.e.*, the number of pairs of monomers (i, j) , $|i - j| > 1$, which are not adjacent in the chain sequence but are nearest spatial neighbors on the lattice, satisfying $|\mathbf{r}_i - \mathbf{r}_j| = 1$. The number of conformations with N monomers and t contacts is denoted by $\Omega^{(t)}(N)$ ¹. A conformation and its rigid rotations, mirror images, and translations are considered indistinguishable and counted only once in

¹ It should be noted that there is a difference in our notation from that of Ref. 32. $\Omega^{(t)}(N)$ in our work corresponds to $\Omega^{(t)}(N - 1)$ in that reference.

*E-mail: jul@ssu.ac.kr; Fax: +82-2-812-5762

$\Omega^{(t)}(N)$. However, it is assumed that there is an intrinsic direction in the chain, so the conformations related by the exchange of labels $i \leftrightarrow N - i + 1$ for all $(i = 1, \dots, N)$ are considered distinct. We note that since the rigid rotations and reflections in two dimensions form an eight-fold symmetry, the total number of conformations generated by rotations and reflections from a given two-dimensional conformation is eight. An exception is the straight chain, which is, in fact, a one-dimensional conformation, and is invariant with respect to reflection perpendicular to the chain. Consequently, the total number of conformations generated by rotations and reflections is four in this case. Therefore, the number of conformations with rigid rotations and reflections considered distinct, denoted by $Q^{(t)}(N)$, can easily be obtained by

$$\begin{aligned} Q^{(0)}(N) &= 8\Omega^{(0)}(N) - 4 \\ Q^{(t)}(N) &= 8\Omega^{(t)}(N) \quad (t > 0). \end{aligned} \quad (1)$$

The quantities $\Omega^{(t)}(N)$ for $4 \leq N \leq 16$ are given in Ref. 32, and $Q^{(t)}(N)$ for $17 \leq N \leq 20$ are given in Ref. 34. We enumerate non-redundant conformations generated by self-avoiding random walks, and the results for $N \leq 20$ do indeed agree with those reported in the references. The values of $\Omega^{(t)}(N)$ for $21 \leq N \leq 28$ are the new results we obtained (Table 1).

The model Hamiltonian is simply

$$H = -J \sum_{i < j} \Delta(\mathbf{r}_i, \mathbf{r}_j) \quad (2)$$

where $J > 0$ is a constant parameter which can be absorbed into the inverse temperature when evaluating the partition function, and $\Delta(\mathbf{r}_i, \mathbf{r}_j) = 1$ if \mathbf{r}_i and \mathbf{r}_j are nearest-neighbor sites with i and j not adjacent along the chain, and zero otherwise. This model is a special case of the HP model, where two types of monomers H (hydrophobic) and P (polar) exist and different weights are given depending on the types of monomers involved in pairwise interaction. Since we use the same negative weight $-J$ for all the monomers, our model is a homopolymer with only H type monomers present, which attract each other with hydrophobic interaction.

Since the energy of a conformation depends only on the total number of contacting pairs of monomers, the partition function can easily be calculated from $\Omega^{(t)}(N)$ when we do not distinguish the conformations related by rotations and reflections:

$$Z = \sum_{t=0}^{t_{\max}} \Omega^{(t)}(N) z^t \quad (3)$$

where $z \equiv e^{\beta J}$. For a given chain length N , the maximum number of possible contacts is given by [32]

$$\begin{aligned} t_{\max} &= N - 2m \quad \text{for } m^2 < N \leq m(m + 1) \\ t_{\max} &= N - 2m - 1 \quad \text{for } m(m + 1) < N \leq (m + 1)^2 \end{aligned} \quad (4)$$

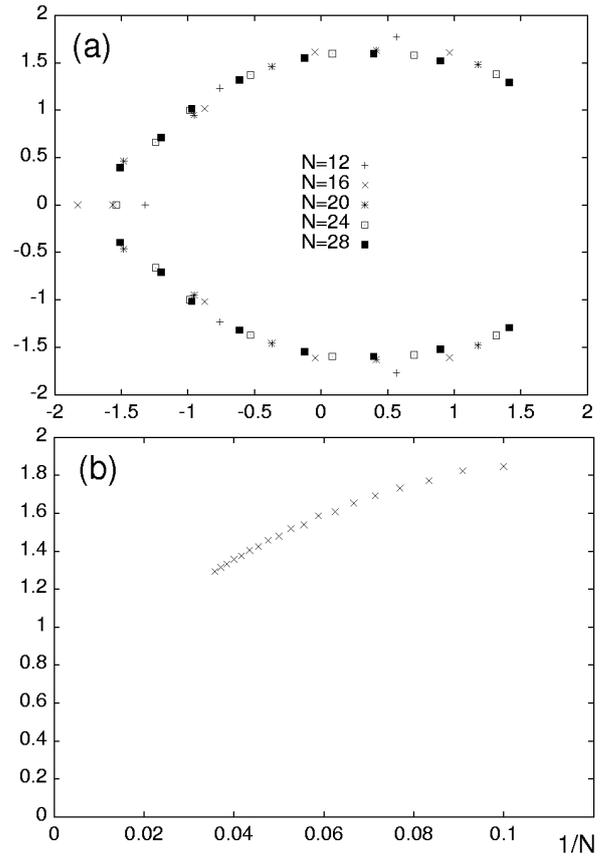


Fig. 1. (a) The positions of the zeros of the partition function in the complex plane of $z = e^{\beta J}$, for several values of chain length N . For each N , there are one or two additional zeros lying on the negative real axis with $\Re(z) < -2.0$, which are not shown here for the overall clarity of the figure. We observe that the locus tends to close in the positive real axis as the system size grows. (b) The imaginary part of the leading zeros plotted as a function of the inverse chain length. The extrapolation of the data to $1/N = 0$ is consistent with the vanishing value of the imaginary part of the leading zero.

where m is a positive integer. Therefore, the partition function Z is a polynomial of order t_{\max} in z , and consequently there are t_{\max} zeros in the complex z plane.

At a finite system size, the partition function is analytic for real values of temperature, so there is no zero lying on the positive real axis. However, if the system exhibits a phase transition, we expect that the locus of zeros will intersect the positive real axis at the transition point $z_c \equiv e^{J\beta_c}$, in the limit of infinite chain length, where β_c is the inverse of the transition temperature.

Using the values of $\Omega^{(t)}(N)$, we calculated the zeros of the partition function Z for the chain length $4 \leq N \leq 28$ by solving polynomial equations. The loci of zeros for several values of the chain length are depicted in Figure 1(a). We observe that as the chain length grows, the locus of zeros tends to approach the positive real axis as expected. The real parts of the zeros are all negative for $N \leq 9$, and we define the leading zero as the one

Table 1. Number of conformations $\Omega^{(t)}(N)$ on square lattices as a function of the chain length N and the number of contacts t . Those for $4 \leq N \leq 20$ are given in Refs. 32, 34.

| t | $N = 21$ | $N = 22$ | $N = 23$ | $N = 24$ | $N = 25$ | $N = 26$ | $N = 27$ | $N = 28$ |
|-------|-----------|-----------|-----------|------------|------------|-------------|-------------|--------------|
| 0 | 8421787 | 19752218 | 46419252 | 108774694 | 255351250 | 597911624 | 1402287935 | 3281303693 |
| 1 | 18600478 | 45756483 | 112444948 | 275204606 | 673031750 | 1640168584 | 3994716336 | 9699476314 |
| 2 | 23517452 | 60431603 | 154608247 | 393755587 | 999333185 | 2526164978 | 6367872760 | 15995302728 |
| 3 | 21628048 | 57959791 | 154158232 | 407885572 | 1072782954 | 2808636641 | 7317574830 | 18987719929 |
| 4 | 16574559 | 46117659 | 127031251 | 347920091 | 945260569 | 2555187024 | 6861628501 | 18343927787 |
| 5 | 10948158 | 31659735 | 90321508 | 255975474 | 717661856 | 2001375177 | 5533056628 | 15223373459 |
| 6 | 6456064 | 19421102 | 57228910 | 167929055 | 485676817 | 1396686571 | 3971125472 | 11237454069 |
| 7 | 3381622 | 10656029 | 32726474 | 99584556 | 296862008 | 881852813 | 2580279898 | 7512575526 |
| 8 | 1637105 | 5396353 | 17011724 | 54002538 | 166850648 | 511995996 | 1540198043 | 4618983588 |
| 9 | 684708 | 2446760 | 8171310 | 27015060 | 85910838 | 274214999 | 851735068 | 2632323506 |
| 10 | 259353 | 993476 | 3514924 | 12394518 | 41204322 | 136549589 | 436636946 | 1398796860 |
| 11 | 91586 | 378317 | 1331552 | 5146120 | 17970134 | 62915928 | 208783232 | 693567093 |
| 12 | 11226 | 119644 | 487154 | 1923545 | 7022209 | 26682016 | 92279718 | 321343949 |
| 13 | | 11584 | 109998 | 679418 | 2528252 | 10126804 | 37030110 | 138013816 |
| 14 | | | 4577 | 131896 | 761832 | 3598561 | 13482884 | 53972071 |
| 15 | | | | 3997 | 89960 | 1001309 | 4430448 | 19198892 |
| 16 | | | | | 1081 | 100750 | 926875 | 6144833 |
| 17 | | | | | | | 52594 | 1163103 |
| 18 | | | | | | | | 45238 |
| Total | 112212146 | 301100754 | 805570061 | 2158326727 | 5768299665 | 15435169364 | 41214098278 | 110164686454 |

closest to the positive real axis for $N \geq 10$. Since the distribution of zeros is symmetric with respect to the real axis, due to the fact that the coefficients of the polynomial are all real, it is sufficient to consider only the zeros with positive values of the imaginary parts, without loss of generality. The imaginary parts of the leading zeros are plotted against the inverse of the chain length in Figure 1(b). The infinite chain length corresponds to $1/N = 0$. The numerical extrapolation [64] results in the value 0.3 ± 0.4 for $1/N = 0$, consistent with the value zero within the uncertainty. The results suggest that the locus of zeros intersects the positive real axis in the thermodynamic limit, and there is a phase transition. However, the results are not conclusive, due to a rather large uncertainty. Further studies for longer chain lengths seem necessary for a definite conclusion on whether a true phase transition exists.

When we consider all the conformations generated by rigid rotations and reflections, $\Omega^{(t)}(N)$ in Eq. (3) should be replaced by $Q^{(t)}(N)$. Denoting the resulting partition function as Z' , we see from Eq. (1) that the partition function Z' is obtained from Z by replacing $\Omega^{(0)}(N)$ by $\Omega^{(0)}(N) - 0.5$, up to an overall constant factor which is irrelevant. Since $\Omega^{(t)}(N)$ s are numbers much larger than unity, we expect that the positions of zeros of Z' are almost the same as those of Z , which is corroborated by explicit calculations. In fact, the plots of the zero positions are exactly the same as Figure 1, within the resolution of the figure.

In this work, we obtained the exact partition function of two-dimensional lattice polymers of various chain lengths by using exhaustive enumerations. This provided us with the positions of zeros. Although it is rather premature to draw a definite conclusion from the results, one can observe that the locus of zeros closes in toward the positive real axis as the chain length grows, which suggests the existence of a phase transition. It would be interesting to extend the calculation to much longer chains, so that a more definite conclusion can be drawn on the issue of the phase transition. Extensive parallel computations would be necessary for such an endeavor. It would also be interesting to investigate the partition function zeros of heteropolymers. We expect that in the case of a protein, heteropolymers specially designed so that there is a unique ground state which has much lower energy than the average energy of the other conformations, there should be another locus intersecting the positive real axis in the limit of infinite chain length, corresponding to the folding transition to the ground state. Of course, defining the thermodynamic limit for a heteropolymer is a non-trivial task, in contrast to the homopolymer we studied. All these points are left for future investigations.

ACKNOWLEDGMENTS

The author thanks Seung-Yeon Kim for useful discussions. This work was supported by the Soongsil University Research Fund.

REFERENCES

- [1] I. M. Lifshitz, Zh. Eksp. Theor. Fiz. **55**, 2408 (1968), [Sov. Phys. - JETP, **28**, 545, 1969].
- [2] C. Domb, Polymer **15**, 259 (1974).
- [3] P. -G. de Gennes, J. Physique Lett. **36**, L55 (1975)
- [4] M. J. Stephen, Phys. Lett. A. **53**, 363 (1975).
- [5] I. M. Lifshitz, A. Y. Grosberg and A. R. Khokhlov, Zh. Eksp. Theor. Fiz. **71**, 1634 (1976), [Sov. Phys. - JETP, **44**, 1976].
- [6] M. A. Moore, J. Phys. A **10**, 305 (1977).
- [7] I. M. Lifshitz, A. Y. Grosberg and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
- [8] I. C. Sanchez, Macromolecules **12**, 980 (1979).
- [9] A. R. Khokhlov, Physica A. **105**, 357 (1981).
- [10] C. Williams, F. Brochard and H. L. Frisch, Annu. Rev. Phys. Chem. **32**, 433 (1981).
- [11] B. Duplantier, J. Physique **43**, 991 (1982).
- [12] A. L. Kholodenko and K. F. Freed, J. Phys. A **17**, 2703 (1984).
- [13] J. F. Douglas and K. F. Freed, Macromolecules **18**, 2445 (1985).
- [14] M. Hankel and F. Seno, Phys. Rev. E **53**, 3662 (1996).
- [15] T. Prellberg and A. L. Owczarek, Phys. Rev. E. **62**, 3780 (2000).
- [16] A. L. Owczarek and T. Prellberg, Europhys. Lett. **51**, 602 (2000).
- [17] T. Prellberg, J. Phys. A **34**, L599 (2001).
- [18] T. Prellberg and A. L. Owczarek, Physica A **297**, 275 (2001).
- [19] P. Rein ten Wolde and D. Chandler, Proc. Natl. Acad. Sci. USA **99**, 6539 (2002).
- [20] S. T. Sun, I. Nishio, G. Swislow and T. Tanaka, J. Chem. Phys. **73**, 5971 (1980).
- [21] B. Chu, I. H. Park, Q. -W. Wang and C. Wu, Macromolecules **20**, 2833 (1987).
- [22] G. Swislow, S. T. Sun, I. Nishio and T. Tanaka, Phys. Rev. Lett **44**, 1965 (1987).
- [23] I. H. Park, Q. -W. Wang and B. Chu, Macromolecules **20**, 1965 (1987).
- [24] B. Chu and Z. Wang, Macromolecules **21**, 2283 (1988).
- [25] B. Chu, R. Xu, Z. Wang and J. Zuo, J. Appl. Crystal. **21**, 707 (1988).
- [26] B. Chu, R. Xu and J. Zuo, Macromolecules **21**, 273 (1988).
- [27] B. Chu and Z. Wang, Macromolecules **22**, 380 (1989).
- [28] B. Chu, Q. Ying and A. Yu. Grosberg, Macromolecules **28**, 180 (1995).
- [29] S. Hagen, J. Hofrichter, A. Szabo and W. A. Eaton, Proc. Natl. Acad. Sci. USA **93**, 11615 (1996).
- [30] S-K Kim and H. R. Fetterman, J. Korean Phys. Soc. **42**, 305 (2003).
- [31] S.-Y. Kim, J. Lee and J. Lee, J. Korean Phys. Soc. **44**, ?? (2004).
- [32] H. S. Chan and K. A. Dill, Macromolecules **22**, 4559 (1989).
- [33] Y. Kim, J. Korean Phys. Soc. **24**, 106 (1991).
- [34] H. S. Chan and K. A. Dill, Annu. Rev. Biophys. Biophys. Chem. **20**, 447 (1992).
- [35] H. S. Chan and K. A. Dill, J. Chem. Phys. **99**, 2116 (1993).
- [36] Y. Kim, J. Korean Phys. Soc. **28**, 539 (1995).
- [37] K. A. Dill, Biochemistry **24**, 1501 (1985).
- [38] K. F. Lau and K. A. Dill, Macromolecules **22**, 3986 (1989).
- [39] C. J. Camacho and D. Thirumalai, Phys. Rev. Lett. **71**, 2505 (1993).
- [40] H. S. Chan and K. A. Dill, J. Chem. Phys. **100**, 9238 (1994).
- [41] H. Li, R. Helling and C. Tang, Science **273**, 666 (1996).
- [42] R. M'elin, H. Li, N. S. Wingreen and C. Tang, J. Chem. Phys. **110**, 1252 (1999).
- [43] T. Wang, J. Miller, N. S. Wingreen, C. Tang and K. A. Dill, J. Chem. Phys. **113**, 8329 (2000).
- [44] N. D. Socci and J. N. Onuchic, J. Chem. Phys. **101**, 1519 (1994).
- [45] N. D. Socci and J. N. Onuchic, J. Chem. Phys. **103**, 4732 (1995).
- [46] M. E. Fisher, *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, 1965), Vol. 7c, p. 1.
- [47] C. Itzykson, R. B. Pearson and J. B. Zuber, Nucl. Phys. B **220**, 415 (1983).
- [48] R. J. Creswick and S.-Y. Kim, Physical Review E **56**, 2418 (1997).
- [49] R. J. Creswick and S.-Y. Kim, in *Computer Simulations Studies in Condensed-Matter Physics*, edited by D. P. Landau, K. K. Mon and H.-B. Schüttler (Springer, Berlin, 1998), Vol. 10, p. 224.
- [50] S.-Y. Kim and R. J. Creswick, Phys. Rev. Lett. **81**, 2000 (1998).
- [51] S.-Y. Kim and R. J. Creswick, Phys. Rev. E **58**, 7006 (1998).
- [52] S.-Y. Kim and R. J. Creswick, in *Computer Simulations Studies in Condensed-Matter Physics*, edited by D. P. Landau, K. K. Mon and H.-B. Schüttler (Springer, Berlin, 1998), Vol. 11, p. 140.
- [53] S.-Y. Kim and R. J. Creswick, Phys. Rev. Lett. **82**, 3924 (1999).
- [54] R. J. Creswick and S.-Y. Kim, Comput. Phys. Commun. **121**, 26 (1999).
- [55] S. Lee, S. Kim, S. H. Park, H.-B. Pyo and K.-C. Lee, Phys. Rev. B **60**, 9256 (1999).
- [56] S.-Y. Kim and R. J. Creswick, Physica A **281**, 252 (2000).
- [57] S.-Y. Kim, R. J. Creswick, C.-N. Chen and C.-K. Hu, Physica A **281**, 262 (2000).
- [58] S.-Y. Kim and R. J. Creswick, Phys. Rev. E **63**, 066107 (2001).
- [59] S.-Y. Kim, Nucl. Phys. B **637**, 409 (2002).
- [60] K.-C. Lee, Phys. Rev. E **48**, 3495 (1993).
- [61] K.-C. Lee, Phys. Rev. Lett. **73**, 2801 (1994).
- [62] K.-C. Lee, Phys. Rev. E **53**, 6558 (1996).
- [63] J. Lee and K.-C. Lee, Phys. Rev. E **62**, 4558 (2000).
- [64] W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, New York, 1986), p. 83.