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# Exact $\theta$ point and exponents for polymer chains on an oriented two-dimensional lattice

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The collapse transition of a polymer chain on a two-dimensional lattice with directed bonds, the Manhattan lattice, is shown to occur at temperature $T_\theta = 2\varepsilon/\ln 2$, where $\varepsilon$ is the attractive energy between nearest-neighbor pairs of monomers. The exact tricritical exponents are $\nu_t = \frac{4}{7}$ and $\gamma_t = \frac{6}{7}$. The latter result differs from two recently proposed values of $\gamma_t$.

At high temperatures, a polymer chain in a good solvent behaves essentially as if it were a self-avoiding walk (SAW): Its mean radius of gyration grows as $\langle R \rangle \sim N^\nu$, where $\nu$ has the same value as for the SAW and $N$ is the molecular weight.[1] As the temperature $T$ is reduced, however, the short-range van der Waals attraction between monomers becomes increasingly important. At a certain temperature $T_\theta$, the chain collapses. The exponent $\nu$ is $1/d$ in $d$ dimensions for all $T < T_\theta$. Finally, the $\theta$ point $T = T_\theta$ is a tricritical point.[1]

Considerable progress has been made recently in understanding the nature of the collapse transition in two dimensions (2D). Coniglio *et al.*[2] have shown that a polymer ring on the hexagonal lattice at its collapse transition can be mapped onto the hull of a percolation cluster at threshold. Since it has been proven[3] that the radius of gyration exponent $\nu$ is $\frac{4}{7}$ for the perimeter of a percolation cluster at threshold in 2D, Coniglio *et al.* argued that the value of the size exponent at the tricritical point $\nu_t$ must also be $\frac{4}{7}$. This argument is not rigorous, however, since a subset of next-nearest-neighbor interactions appears in the polymer chain's Hamiltonian. Similarly, Duplantier and Saleur[4] have shown that $\nu_t = \frac{4}{7}$ for a tricritical SAW on the honeycomb lattice with vacancies. This SAW also has a subclass of next-nearest-neighbor interactions, so the collapse transition in this model is more properly referred to as a $\theta'$ point rather than a $\theta$ point. It is currently a matter of intense debate whether these additional interactions are relevant or not.[5-7]

In this Rapid Communication, I establish a rigorous correspondence between the statistics of a polymer ring on the Manhattan lattice at the $\theta$ point and the hull of a percolation cluster at threshold in bond percolation on the square lattice. This mapping has three important consequences. First, it is shown that $\nu_t = \frac{4}{7}$ for SAW's on the Manhattan lattice with nearest-neighbor interactions only. Second, I demonstrate that the $\theta$ temperature is *exactly* $T_\theta = 2\varepsilon/\ln 2$, where $\varepsilon$ is the attractive energy between nearest-neighbor pairs of monomers. Previously, the collapse transition temperature was known exactly only for the rather nonstandard problem of Ref. 4 which included next-nearest-neighbor interactions. This result should be quite useful in Monte Carlo studies of the tricritical point, since critical exponents can be computed much more precisely when the transition temperature is known. The third and final consequence is that the exponent $\gamma_t$ is exactly $\frac{6}{7}$ for tricritical SAW's on the Manhattan lattice. Since Duplantier and Saleur[4] have shown that $\gamma_t = \frac{8}{7}$ for their tricritical SAW, we conclude that the $\theta'$ point is in a different universality class than the $\theta$ point for polymer chains on the Manhattan lattice. The conjecture[6,8] that the $\theta$ point is a $C = \frac{1}{2}$ superconformal theory leads to $\gamma_t = \frac{15}{14}$, which differs from both our result and that of Duplantier and Saleur.

I expect polymer chains on the Manhattan lattice to be in the same universality class as chains on undirected lattices. The only effect of the lattice orientation should be to introduce short-range correlations which do not alter the asymptotic behavior. Good evidence that this is true for $T = \infty$ has been obtained by exact enumeration[9] and real-space renormalization-group[10] studies of polymer chains on the Manhattan lattice. It has also been demonstrated that the Manhattan orientation is irrelevant at $T = 0$.[11] Therefore, the exponents for the $\theta$ point on an undirected 2D lattice are expected to be the same as those obtained here.

Consider the equilibrium statistical mechanics of a self-avoiding loop of length $N$ on the Manhattan lattice (Fig. 1). For simplicity, we take the loop to be anchored at a point. Each nearest-neighbor pair of monomers which is not bonded will be assigned an energy $-\varepsilon$. Thus, if $n(C)$ is the number of such monomer pairs in a loop configuration $C$, the loop's energy is $-\varepsilon n(C)$. The loop partition function is

$$Z_N^{\text{loop}}(T) = \sum_{C'} \exp[\beta \varepsilon n(C')] , \tag{1}$$

where $\beta \equiv T^{-1}$ is the inverse temperature and the sum runs over all allowed loop configurations. The Boltzmann weight of a particular configuration $C$ is

$$w(C,N,T) = \exp[\beta \varepsilon n(C)]/Z_n^{\text{loop}} . \tag{2}$$

Our first step will be to show that for $T = T_0 \equiv 2\varepsilon/\ln 2$, the problem is equivalent to the kinetic growth walk[12] (KGW) on the Manhattan lattice. The KGW is a growing SAW in which all self-avoiding moves are weighted equally at each step. On undirected lattices, the walk terminates if a closed loop is formed or if no self-avoiding moves are available. The second type of termination does not occur on the Manhattan lattice, since if the walk

 

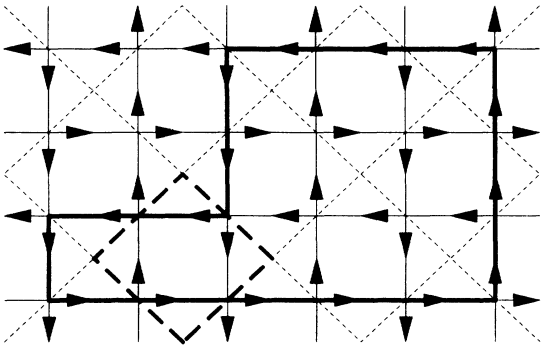

FIG. 1. The Manhattan lattice (solid directed lines) and the underlying square lattice (undirected dashed lines). A SAW on the Manhattan lattice is shown in bold lines. The plaquette in the underlying lattice which this walk visits twice is delineated by bold dashed lines. There are two nearest-neighbor pairs in this SAW.

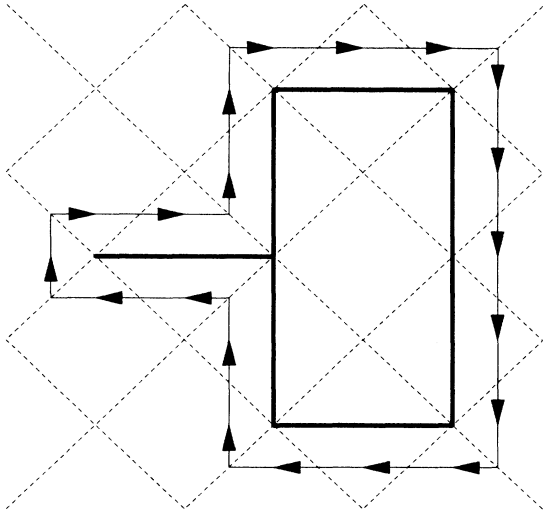

FIG. 2. A KGW on the Manhattan lattice (directed solid lines) walks around the perimeter of a bond percolation cluster on the square lattice (bold lines). The underlying lattice is shown with dashed lines. For clarity, the Manhattan lattice itself has not been shown.

enters a cul de sac, an exit always exists.[13] This has the interesting consequence that the KGW and the indefinitely growing SAW (IGSAW)[14,15] coincide on the Manhattan lattice.

To see the equivalence between the polymer loop and the KGW, consider the ensemble of all KGW's which begin at a given point and which form closed loops after $N$ steps. For an arbitrary loop configuration $C$, the number of twice-visited plaquettes in the underlying square lattice is $\frac{1}{2}n(C)$ (see Fig. 1). The probability that a loop of length $N$ is formed is therefore

$$P(N)=\sum_{C'}2^{-N}\exp\left[\frac{\ln 2}{2}n(C')\right], \tag{3}$$

where the sum runs over all possible self-avoiding configurations of the loop. The probability of a particular loop configuration $C$ (given that the walk closes in $N$ steps) is

$$p(C,N)=P^{-1}(N)2^{-N}\exp\left[\frac{\ln 2}{2}n(C)\right]. \tag{4}$$

Comparing Eqs. (1) and (3), we see that

$$Z_N^{\text{loop}}(T_0)=2^N P(N),$$

while from Eqs. (2) and (4) we obtain

$$w(C,N,T_0)=p(C,N).$$

The second and final step in establishing our correspondence between the tricritical polymer loop and the percolation hull will be to show that the KGW on the Manhattan lattice traces out the perimeter of a bond percolation cluster on the square lattice at the percolation threshold $p=p_c=\frac{1}{2}$.[16] To see this, each time the walker in the KGW traverses a new plaquette in the underlying lattice, we place a bond along the main diagonal of the plaquette parallel to the walker's step, provided the diagonal is to the *right* of the walk (Fig. 2). In this way, each time the KGW enters a new plaquette a bond is placed on the plaquette diagonal with probability $\frac{1}{2}$. No new bond is added if the walker returns to a plaquette. The bonds on the main diagonals of the plaquettes are then the perimeter bonds of a percolation cluster on the square lattice at $p=p_c=\frac{1}{2}$, and the KGW walks around this perimeter, as claimed.

Recently, Saleur and Duplantier[3] proved that the fractal dimension of percolation cluster hulls at threshold is exactly $D=\frac{7}{4}$ for bond percolation on the square lattice.[17] This result is consistent with a wide range of analytical and Monte Carlo work.[18] Our mapping between this problem and a polymer loop on the Manhattan lattice at $T=T_0$ then shows that $\nu=D^{-1}=\frac{4}{7}$ for loops at this temperature. Now in 2D, the exponent $\nu$ is $\frac{1}{2}$ for polymer loops at temperatures $T<T_\theta$, while $\nu$ takes on the equilibrium SAW value[19] $\frac{3}{4}$ for $T>T_\theta$. Since $\nu=\frac{4}{7}$ at $T=T_0$, we conclude that $T_\theta=T_0$. The exact $\theta$ temperature is therefore $T_\theta=2\varepsilon/\ln 2$. In addition, the value of $\nu$ at the tricritical point is $\nu_t=\frac{4}{7}$.

We next demonstrate that the tricritical exponent $\gamma_t$ is exactly $\frac{6}{7}$. First, recall that $\gamma_t$ is defined by

$$Z_N^{\text{open}}(T_\theta)\sim\mu^N N^{\gamma_t-1},\quad \text{for } N\gg 1,$$

where $Z_N^{\text{open}}(T_\theta)$ is the partition function of an open chain of length $N$ at the $\theta$ point and the constant $\mu$ is the analog of the usual SAW connectivity constant. Since the free energy per monomer is the same for loops and open chains in the $N\to\infty$ limit,

$$\lim_{N\to\infty}\ln Z_N^{\text{loop}}(T_\theta)/N=\lim_{N\to\infty}\ln Z_N^{\text{open}}(T_\theta)/N=\ln\mu.$$

As shown above, $Z_N^{\text{loop}}(T_\theta)=2^N P(N)$, and $P(N)$ is the probability that a bond percolation cluster on the square lattice at threshold has a perimeter of length $N$. From

Ref. 20 we then have $P(N) \sim N^{-\tau'+1}$ for $N \gg 1$, where $\tau' = \frac{15}{7}$. We conclude that $\mu = 2$.

Having obtained the leading-order asymptotic behavior of $Z_N^{\text{open}}(T_\theta)$, we turn to the first correction to this scaling behavior. We will compare $Z_N^{\text{open}}(T_\theta)$ with $P^{\text{open}}(N)$, the probability that the KGW on the Manhattan lattice performs an $N$-step walk without closing. To this end, let $\kappa(C)$ be the number of twice-traversed plaquettes in the underlying lattice in the chain conformation $C$. Then

$$P^{\text{open}}(N) = 2^{-N} \sum_C 2^{\kappa(C)},$$

while

$$Z_N^{\text{open}}(T_\theta) = \sum_C 2^{n(C)/2}.$$

Both of these sums run over all open self-avoiding configurations of length $N$. For closed loops we have the equality $2\kappa(C) = n(C)$. For open chains this is replaced by the inequality $2\kappa(C) \leq n(C) \leq 2\kappa(C)+2$, since each chain end can have a nearest-neighbor bond with energy $-\varepsilon$ which does not lie in a twice-traversed plaquette of the underlying lattice. Therefore

$$P^{\text{open}}(N) \leq 2^{-N} Z_N^{\text{open}}(T_\theta) \leq 2P^{\text{open}}(N). \quad (5)$$

Monte Carlo work[13] strongly suggests that the KGW on the Manhattan lattice must ultimately form a closed loop, so

$$P^{\text{open}}(N) = \sum_{M=N+1}^{\infty} P(M) \sim N^{-\tau'+2}$$

for $N \gg 1$. Applying this to Eq. (5) and using the result $\mu = 2$, we have $\gamma_t = 3 - \tau' = \frac{6}{7}$.

Our exact result $\gamma_t = \frac{6}{7}$ differs from the transfer-matrix value[21] $\gamma_t = 1.00 \pm 0.05$ and the Monte Carlo result[6,22] $\gamma_t = 1.075 \pm 0.04$. This discrepancy may be due to the extreme difficulty in computing $\gamma_t$ numerically. Alternatively, it may result from the fact that we have studied the tricritical point on the Manhattan lattice instead of the square lattice, as was done in Refs. 21 and 22. If the latter explanation is correct, the 2D tricritical point must be anomalously sensitive to details of the lattice structure.

The results obtained here also have implications for the theory of self-avoiding trails (SAT's). SAT's are paths on regular lattices in which sites may be revisited but bonds may not, and have been studied to determine whether the large-scale behavior of a polymer chain is affected by the presence of loops.[23-26] Recently, it has been suggested that the collapse transition in self-attracting SAT's may be in a different universality class than the $\theta$ point.[24,25] In a forthcoming publication[27] I will show that the self-attracting SAT on the square lattice in which consecutive bonds are restricted to be at right angles can be mapped onto the self-attracting SAW on the Manhattan lattice. This bond-to-site mapping[28] between the two problems is valid for all temperatures $T$, and so yields the exact tricritical point and exponents for the SAT. I find that the SAT and SAW have the same values of $\nu_t$ and $\gamma_t$, as suggested by new high-precision simulations.[26] Mapping techniques of the kind employed here also lead to a conjectured value for the exact $\theta$ temperature for the unrestricted SAT on the square lattice.[27] This conjecture is in good agreement with numerical work.[25-27]

Finally, note that the problem of self-attracting polymer chains on the Manhattan lattice has now been solved exactly at $T = 0$,[29] $T = T_\theta$, and $T = \infty$.[19] This raises the tantalizing possibility that the problem may be solvable for all temperatures $T$.

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