Exact Tricritical Exponents for Polymers at the Θ Point in Two Dimensions

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We propose the exact values of the tricritical exponents of a collapsing polymer in two dimensions: $\nu=\frac{4}{7}$, $\gamma=\frac{8}{7}$, and $\phi=\frac{3}{7}$. They are obtained in a model of self-avoiding walk on a hexagonal lattice, with random forbidden hexagons, whose percolation threshold gives the exact tricritical point. The infinitely many exact *tricritical* exponents then derived from Coulomb gas methods are *critical* exponents of the $O(n=1)$ *Ising* model below T_c. The numerical check is very good.

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The possibility for a polymer chain in a solvent to undergo a collapse transition by having random flight dimensions at a certain temperature Θ was discovered by Flory in 1949.[1] It was shown by de Gennes,[2,3] three decades later, that this Θ transition corresponds to a tricritical point[4] (TP), while long polymers in a good solvent form a critical system.[3] Three dimensions (3D) is the upper tricritical dimension,[4] above which tricritical exponents take their mean-field values. Hence, in 3D, logarithmic deviations from the Gaussian behavior are expected for chains at the Θ point,[3,5,6] which can be observed experimentally.[7] The situation is quite different in *two dimensions* (2D) where new nontrivial tricritical exponents are expected, and are of experimental interest.[8] Expansions in $\epsilon'=3-d$ of these exponents have been developed[9-12] leading to some controversies,[11] now resolved.[12] However, one must note that these $\epsilon'=3-d$ expansions are highly asymptotic[10] and cannot yield directly precise values in 2D. 2D *tricritical* exponents for polymers are not known exactly so far, except on fractals,[13] whereas infinitely many exact values of the *critical* exponents for dilute self-avoiding walks (SAW) or compact ones in 2D have been derived,[14-18] starting from original works in 1982.[14] A lot of numerical studies have been devoted[19-23] to the collapse of polymers for $d=2$.

The most studied quantity is the exponent ν which governs the chain size at the Θ point. It must be larger than the Brownian value $\nu=\frac{1}{2}$, which corresponds also to a compact chain in 2D. Numerical results are quite dispersed. Monte Carlo calculations gave[20] $\nu\simeq 0.505$, series enumerations[21] $\nu=0.51\pm0.01$ or[22] $\nu=0.53\pm0.03$, and transfer matrices[23] $\nu=0.55\pm0.01$. A value was also experimentally determined,[8] $\nu=0.56\pm0.01$. The crossover exponent ϕ reads $\phi=\nu/\nu'$ where ν' characterizes the divergence of the thermal correlation length as the temperature becomes close to Θ. Monte Carlo calculations[20] and enumerations[21,22] suggest similar values $\phi=0.64\pm0.05$, while the transfer-matrix method[23] gives $\phi=0.48\pm0.07$. Finally, the exponent γ which governs the number of configurations at Θ has been only recently studied, with the estimate[23] $\gamma=1\pm0.05$. Numerical studies are especially difficult.[23] The TP is not exactly known, and difficult to locate. It is indeed unstable, separating stable excluded-volume and condensed-polymer phases. Also dense polymers lead to strong oscillations,[21,22] parity effects,[23] and sensitivity to boundary conditions[18] which affect the nearby Θ point.

We provide here a new tricritical model of SAW on the honeycomb lattice with vacancies. It allows the exact determination of the TP and of the tricritical exponents $\nu=\frac{4}{7}$, $\gamma=\frac{8}{7}$, and $\phi=\frac{3}{7}$, from Coulomb-gas methods in 2D.[24,25] An infinite series of higher exponents is also given. Surprisingly, these tricritical exponents are those of the $O(n=1)$ *Ising model,* in its *low-temperature phase* which is also critical.[14,25] They are also exponents of the $q=1$ *Potts model* at its *critical* point.[26] Note that vacancies have been introduced[27,28] in a different context. As will appear below, our model is inspired from the analogy found by Coniglio *et al.*[29] between a polymer chain at the Θ point and the hull[26,30] of a percolation cluster, and is thus also related to kinetic[31,32] or "dressed"[33] walks.

We consider a SAW on a dilute honeycomb lattice, the faces of which are absent with probability p. Edges of absent hexagons are forbidden for the SAW (Fig. 1). The model is annealed and every quantity is calculated by summation over the compatible configurations $\mathcal{C}$ of

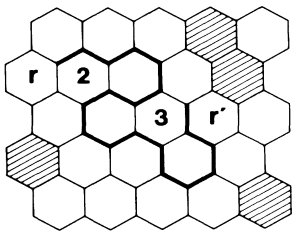

FIG. 1. A SAW of length $l=18$ in the presence of vacancies (hatched hexagons). The number of hexagons touching the SAW is $H=16$, and there are $N_2=1$ ($N_3=1$) faces of type 2 (type 3), with two (three) sequences of links on it.

the SAW and $\mathcal{C}'$ of the vacancies. Summing first on $\mathcal{C}'$ gives to any $\mathcal{C}$ a weight $(1-p)^H$, where H is the number of hexagons sharing edges with the chain. For a stretched chain, H is equal to $l+1$ (l is the number of links) since the first link is the edge of two faces, and each subsequent one adds a new face dressing the chain. When the polymer folds onto itself H is diminished each time several nonsuccessive pieces of the chain touch the same hexagon. If there are two such connected pieces on a face (faces of type 2, Fig. 1) H is lowered by 1, and by 2 if there are three such pieces (faces of type 3). The weight can be rewritten $(1-p)^{l+1-N_2-2N_3}$, where N_2 and N_3 are the numbers of type-2 and -3 faces. It clearly favorizes collapsed configurations. In fact, since it is determined by local properties only, it is equivalent to a certain type[26] of *short-range attractions,* depending on nearest-neighbor and next-nearest-neighbor edges on the lattice. Our model is thus expected to be in the same universality class as the usual Θ-point[19-23] ones.

Probability p governs the attraction energy between monomers and provides the usual "thermal" scaling field in tricritical phenomena.[4] The site percolation threshold (on the dual triangular lattice) is $p_c=\frac{1}{2}$. If $p<\frac{1}{2}$ the vacancies do not percolate. They disappear under successive renormalizations, reaching the $p=0$ fixed point. Hence the large-scale behavior of the chain has the usual (dilute) exponents.[14-17] In contrast to this, for $p>\frac{1}{2}$ the vacancies percolate and renormalization flows toward the $p=1$ fixed point. We then expect the chain to be compact with dense exponents.[18] Thus $p<\frac{1}{2}$ ($p>\frac{1}{2}$) corresponds to the high- (low-) temperature behavior of the chain, and $p_c=\frac{1}{2}$ is the TP.

Connected sets of missing faces $\mathcal{C}'$ can be represented by their perimeters (Fig. 1) which form nonintersecting self-avoiding loops. Now, at $p_c=\frac{1}{2}$, present and missing faces are equally probable. Hence the perimeters form a gas of arbitrary loops, which all have the same (relative) weight 1. This is just[26] the O(n) loop model of Nienhuis[14,25] on the hexagonal lattice, with partition function

$$Z_n=\sum_{\text{graphs}} K^B n^P, \tag{1}$$

the sum being taken over graphs formed by P perimeter loops and made of a total number B of bonds, here in the case $n=1$, $K=1$ (Ising model). $K=1$ is in the *low-temperature phase* of the O($n=1$) model [the critical point of (1) for $n=1$ is[14] $K_c=1/\sqrt{3}$], which is known[25] to be critical, with a universality class independent of $K>K_c$. Our model was primarily devised for an open SAW, but we can consider a closed one, the properties of which are, at the Θ point, those of any loop in the O(n) model (1) for $n=1$, $K=1$. Indeed, although this SAW loop and the polygons surrounding clusters of vacancies do not have the same origin, they are indistinguishable. We thus recover the nice conclusion by Coniglio *et al.*[29] that a ring polymer at Θ has the properties of a cluster perimeter (hull) at the percolation threshold.

The first of the tricritical exponents, ν, defined by $R^2\sim l^{2\nu}$, where R^2 is the size of a chain (or ring) of length l, follows[29] as $\nu=1/D_H$, where D_H is the hull fractal dimension. Its value $D_H=\frac{7}{4}$ has been recently obtained [26] with use of the above equivalence to the $n=1$ Ising model and Coulomb-gas methods,[24,25] confirming several conjectures.[26,30-33] Hence

$$\nu=\tfrac{4}{7}\simeq 0.5714. \tag{2}$$

Second, the crossover exponent ϕ is obtained by our noting that the collapse transition is driven by the percolation of vacancies. The thermal scaling field is $p-p_c$, with a percolation correlation length diverging like $|p-p_c|^{-\nu'}$ where[25] $\nu'=\frac{4}{3}$. Thus

$$\phi=\nu/\nu'=\tfrac{3}{7}\simeq 0.4286. \tag{3}$$

Finally the exponent γ is defined by

$$Z_l=\sum_{\mathcal{C}}(1-p_c)^H\sim\mu^l l^{\gamma-1},\quad l\gg 1, \tag{4}$$

where Z_l is the partition function of an open chain of length l and μ generalizes the usual SAW connectively constant. To obtain γ we introduce a correlation function

$$G(\mathbf{r},\mathbf{r}')=\sum_l Z_l(\mathbf{r},\mathbf{r}')K^l, \tag{5}$$

where $Z_l(\mathbf{r},\mathbf{r}')$ is a partition function similar to (4), where the configurations $\mathcal{C}$ relate $\mathbf{r}$ to $\mathbf{r}'$. G given by (5) is the standard diagrammatic expansion of the nonconnected spin-spin correlation function in the (hexagonal) Ising model. Since at the Θ point $K=1$ (low-temperature phase), there is a spontaneous magnetization, and $G\sim|\mathbf{r}-\mathbf{r}'|^{-\eta}$ goes to a constant at large distance; hence $\eta=0$. With the usual scaling relation[4] we obtain[13]

$$\gamma=(2-\eta)\nu=\tfrac{8}{7}=1.1428. \tag{6}$$

Note also that $\mu=K^{-1}=1$. While ν is also the exponent of the indefinitely growing SAW (IGSAW) as noticed in Refs. 29, 31, and 32, this is not true for γ (=1 for IGSAW) since Z_l involves "self-trapped" configurations. Note that determining γ is not possible by the consideration of only percolation hulls as in Ref. 29.

These results can be checked numerically. We calculate (5) on strips of width w with periodic boundary conditions with the transfer matrix.[2,3] The correlation length obeys the finite-size scaling form close to Θ,

$$\xi_w\simeq wF(w^{1/\nu}(K-\mu^{-1}),w^{1/\nu'}(p-p_c)).$$

Phenomenological renormalization equations

$$\xi_w/w=\xi_{w-1}/(w-1)=\xi_{w-2}/(w-2)$$

give estimates of μ and p_c, while[34] the derivatives give ν,ν'. Our results (Table I) converge rapidly to the expected values. At $K=\mu^{-1}$ and $p=p_c$, ξ_w is exactly infinite on periodic strips of any width. Indeed, the

TABLE I. Estimates of ν, ν' obtained by phenomenological renormalization. These converge rapidly to the expected values.

w	ν	ν'
3	0.55359	...
4	0.56631	1.6246
5	0.56838	1.4174
6	0.57022	1.3511
7	0.57073	1.3464
8	0.57106	1.3405
Expected	$\frac{4}{7}=0.57143$	$\frac{4}{3}=1.3333$

transfer matrix acts on a polymer with extremities at infinity, which is thus never self-trapped. The arguments of Coniglio *et al.*[29] give then the correct result here, $G(\mathbf{r},\mathbf{r}')=1$, and thus $\xi_w=\infty$. Conformal invariance[35] gives $\xi_w=w/\pi\eta$, and hence $\eta=0$. But the scaling relation (6) holds only for SAW and *not* for the kinetic IG-SAW.

ν and γ are particular cases of an infinite series of exponents. Consider indeed the correlation function $G_L(\mathbf{r}-\mathbf{r}')$ of the O(n) model defined as[15,25]

$$G_L(\mathbf{r}-\mathbf{r}')=\sum_{\mathcal{C}_L(\mathbf{r},\mathbf{r}')} K^B n^P, \tag{7}$$

where the graphs $\mathcal{C}_L(\mathbf{r},\mathbf{r}')$ on the honeycomb lattice are made of L lines joining the neighborhood of $\mathbf{r}$ to that of $\mathbf{r}'$, P external perimeter loops, and a total number B of bonds (Fig. 2). As above, for $n=1$ and $K=1$, G_L is the partition function of L SAW's at Θ, tied by their extremities at $\mathbf{r}$ and $\mathbf{r}'$. From previous works[15,25] on the O(n) model, we know that at criticality G_L decays like $G_L(\mathbf{r}-\mathbf{r}')\sim|\mathbf{r}-\mathbf{r}'|^{-2x_L}$, where the critical exponent x_L can be obtained exactly by the Coulomb-gas method,[15,25] $x_L=gL^2/8-(g-1)^2/2g$, where g parametrizes[25] $n=-2\cos\pi g$, and $g\in[1,2]$ at $K=K_c$, and $g\in[0,1]$ for $K>K_c$. Here $n=1$, $g=\frac{2}{3}$, and

$$x_L=(L^2-1)/12. \tag{8}$$

η, γ, and ν are given by[15,16] $\eta=2x_1$, $\gamma=(2-2x_1)\nu$, and $\nu^{-1}=2-x_2$. We thus recover $\eta=0$ and the values (2) and (6). For $L\geq 3$, x_L gives the tricritical scaling dimensions of higher L-leg polymer vertices.[15,16] G_L (7) can be generalized to the *ordinary surface transition*[36,37] of the O(n) model, by our letting the points $\mathbf{r}$ and $\mathbf{r}'$ in (7) go to a boundary line. Then a new scaling dimension x_L^s appears,[17,18] $x_L^s=\frac{1}{4}gL^2+\frac{1}{2}L(g-1)$. Hence for $g=\frac{2}{3}$, we find the exact tricritical polymer surface exponents

$$x_L^s=L(L-1)/6. \tag{9}$$

Other exponents are now derived from (8) and (9).

Let $P(r)$ be the probability that two points $\mathbf{r}_1$ and $\mathbf{r}_2$ on a SAW at Θ are at a distance $r=|\mathbf{r}_1-\mathbf{r}_2|$. For

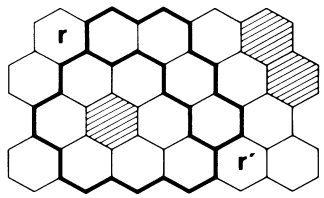

FIG. 2. A configuration contributing to $G_3(\mathbf{r}-\mathbf{r}')$, made of $L=3$ lines connecting $\mathbf{r}$ to $\mathbf{r}'$, $P=2$ perimeter loops encircling vacancies, and $B=46$ bonds (lengths of the three lines plus perimeters).

$r\to 0$, $P(r)\sim r^\theta$, where θ is a universal contact exponent,[16,38] with θ_0 $[=(\gamma-1)/\nu]$ for the contact of the two ends, θ_1 for that of one end inside the chain, and θ_2 for that of two interior points. One proves[16,18] $\theta_0=x_2-2x_1$, $\theta_1=x_3-x_2-x_1$, and $\theta_2=x_4-2x_2$. Using (8) we find at Θ the exact values $\theta_0=\frac{1}{4}$, $\theta_1=\frac{5}{12}$, and $\theta_2=\frac{3}{4}$. For dense SAW's[18] $\theta_0^D=\frac{3}{8}$, $\theta_1^D=\frac{1}{2}$, and $\theta_2^D=\frac{3}{4}$. Hence, contrary to a naive intuition, SAW's at Θ are less repulsive at short distance than compact ones.

Imagine a branched polymer[16] $\mathcal{G}$ in 2D made of $\mathcal{N}$ identical chains of lengths l tied together at n_L ($L\geq 1$) L-leg vertices, with an arbitrary but fixed topology. The number of configurations of $\mathcal{G}$ scales like[16]

$$Z_{\mathcal{G}}\sim\mu^{\mathcal{N}l}l^{\gamma_{\mathcal{G}}-1} \quad (l\gg 1), \tag{10}$$

where $\gamma_{\mathcal{G}}$ is a universal exponent, which generalizes γ in (4). From renormalization theory one finds[16]

$$\gamma_{\mathcal{G}}=\sum_{L\geq 1} n_L[(2-x_L)\nu-\tfrac{1}{2}L]+1-2\nu.$$

Hence, the 2D exact value is at Θ

$$\gamma_{\mathcal{G}}=\sum_{L\geq 1} n_L\tfrac{1}{42}(2-L)(2L+25)-\tfrac{1}{7}. \tag{11}$$

For instance, for an L-arm star at Θ, $n_1=L$, $n_L=1$, and $\gamma=(-L^2+3L+22)/21$. A similar formula exists for branched polymers grafted onto a surface. In particular, the usual exponents[36,37] γ_1 (γ_{11}) for a linear chain grafted by one (two) extremity on the surface are $\gamma_1=(2-x_1-x_1^s)\nu=\frac{8}{7}$ and $\gamma_{11}=(1-2x_1^s)\nu=\frac{4}{7}$, satisfying Barber's scaling law[36] $\gamma+\nu=2\gamma_1-\gamma_{11}$ generalized to a TP.

It is now known[15,17,18,39] that scaling dimensions like x_L (8) and x_L^s (9) belong to the so-called Kac table of the associated conformal theory, parametrized as

$$h_{p,q}=\{[(m+1)p-mq]^2-1\}/4m(m+1),$$

with a central charge[39] $c=1-6/m(m+1)$, where p, q, and m are integers. Here we have $c=0$, $m=2$, and Eqs. (8) and (9) read $x_L=2h_{L,L}$ and $x_L^s=h_{1,L+1}$. A central charge $c=0$ was expected, as in the dilute case.[15]

In conclusion, for L even, the x_L (8) have also a physical meaning[26] for percolation hulls in 2D. In Ref. 29 a notation Θ' has been used to distinguish a smart kinetic

walk[31] or an IGSAW[32] from a SAW at Θ with attractive two-body interactions. We believe that this is not necessary, from the equivalence discussed above. Note finally that here in 2D a *tricritical* O($n=0$) model maps onto a *critical* low-T Ising model. It would be most interesting to extend this to any n.

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