Exact contact critical exponents of a self-avoiding polymer chain in two dimensions

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Using previous results obtained from conformal invariance, we propose exact values in two dimensions for the contact exponents θ_1 of one end point inside a self-avoiding polymer chain, and θ_2 of two interior points inside the chain: $\theta_1 = \frac{5}{6}$ and $\theta_2 = \frac{19}{12}$. These values, as well as the "limiting-ring-closure probability index" $\Upsilon_1 \equiv \nu(2+\theta_1) = \frac{17}{8}$, are in excellent agreement with numerical data. They are particular cases of an infinite set of exact critical exponents for multiple contacts, which we give here.

The end-to-end distance distribution function of a self-avoiding walk (SAW) chain, i.e., a polymer chain in a good solvent, has been the subject of numerous studies from the early days of polymer and critical-phenomena physics.[1,2] The correlations between two points forming a segment inside a chain have also been considered[3-10] (for references, see in particular Ref. 7). Of special interest[6] are the universal distributions of the probability in d dimensions

$$P_a(\mathbf{r}) = S^{-\nu d} F_a(r/S^\nu) \ , \quad a = 0,1,2 \ , \tag{1}$$

of having the extremities of a large chain segment of S links inside a large polymer chain at a relative distance $\mathbf{r}$ (Fig. 1). The case $a=0$ corresponds to the two extremities of a chain, $a=1$ to one segment at the extremity of an infinite chain, and $a=2$ to a segment inside a very large chain. ν is the well-known critical exponent governing the swelling of a polymer. The short-distance behavior of the functions F_a is characterized by the critical exponents θ_a: $F_a(x) \sim x^{\theta_a}$ for $x \to 0$. One has[11] $\theta_0 = (\gamma - 1)/\nu$, while θ_1, θ_2 are only known[6] to order $O(\varepsilon^2)$, $\varepsilon = 4-d$. The numerical results for θ_1, θ_2 in two and three dimensions have been reviewed.[7] The exponent θ_1 is related by hyperscaling to the probability P_1 for a polymer to form a "tadpole" ring of size S: $P_1 \sim S^{-\Upsilon_1}$, since the "limiting-ring-closure probability"[3,4] exponent $\Upsilon_1 = (d+\theta_1)\nu$. It was studied in detail fifteen years ago by Trueman and Whittington[3] and Guttmann and Sykes[4] (for earlier studies, see Refs. 3 and 4). In this Brief Report, we propose exact values in two dimensions (2D) of the critical exponents θ_1 and θ_2, using recent results of conformal invariance theory.[12-14] We find $\theta_1 = \frac{5}{6}$, $\theta_2 = \frac{19}{12}$. Thus we also obtain, using[15,16] $\nu = \frac{3}{4}$ in 2D, $\Upsilon_1 = \frac{17}{8}$. These results are only two particular cases of an *infinite set,* given here, of *exact* 2D *critical exponents* corresponding to the *multiple contacts* inside a SAW chain. These multiple-contact exponents are entirely new, since their existence has not been recognized before (except for θ_1, θ_2). Here we define them and give their exact values in 2D and also $d = 4-\varepsilon$, to $O(\varepsilon)$. For proving these results, we shall rely on a very recent work of ours,[14] where we derived an infinite set of 2D exact critical "enhancement" exponents γ, associated with polymer networks of arbitrary and fixed topology.

Let us consider a SAW chain and a general set of correlation points along the chain [Fig. 2(a)]. We assume the different parts of the polymer separated by successive correlation points to have (approximately) the *same large size S.* We group the correlation points into I subgroups $i = 1, \ldots, I$, the subgroup i having m_i points. Then we look at correlations *inside* each subgroup i: The m_i points have $m_i - 1$ *relative* positions $\mathbf{r}_1^i, \ldots, \mathbf{r}_{m_i-1}^i$. Thus we define a restricted probability weight

$$P_{\mathcal{G}}(\mathbf{r}_1^1, \ldots, \mathbf{r}_{m_1-1}^1, \ldots, \mathbf{r}_1^I, \ldots, \mathbf{r}_{m_I-1}^I) \tag{2}$$

of having these relative configurations $\mathbf{r}_\alpha^i$, $\alpha = 1, \ldots, m_i - 1$ in subgroup i. (Note that the relative positions of subgroups i are not considered and are integrated over.)

When the distances $\mathbf{r}_\alpha^i$ vanish, the configurations of the

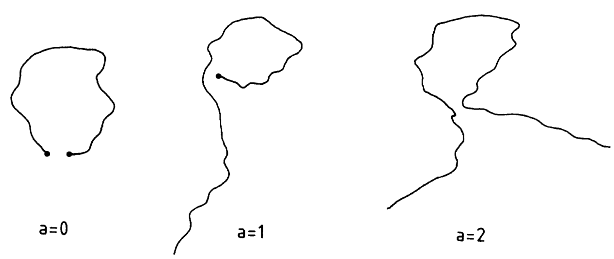

FIG. 1. Short-range two-point correlations inside a SAW chain.

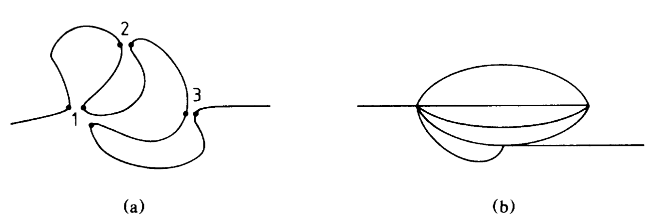

FIG. 2. (a) Correlation points on a SAW chain, with $I=3$ subgroups $i = 1,2,3$, $m_1 = 3$, $m_2 = m_3 = 2$. (b) Reduced graph associated with short-range correlations: $n_4 = 2$, $n_6 = 1$, $\mathcal{L} = 4$.

SAW coalesce to a reduced graph $\mathcal{G}$ [Fig. 2(b)], obtained by contracting the m_i points of each subgroup i to a simple vertex. $\mathcal{G}$ is then exactly the graph of a polymer network, or branched polymer, with fixed topology, which we studied in Ref. 14. This branched polymer is a physical system different from the SAW chain, i.e., its branching points can be imagined to be of a chemical nature, but we shall see that the statistical properties of this branched polymer are related to those of the contacts inside the SAW chain. It is described by the set of numbers $\{n_L\}$ of L-leg vertices, $L \geq 1$ [Fig. 2(b)]. ($L=1$ corresponds to the extremities of the chain.) Naturally, the set $\{n_L\}$ can be deduced from the set $\{m_i\}$. We only need the simple topological result

$$\sum_{i=1}^{I}(m_i-1)=\sum_{L(\geq 1)}\tfrac{1}{2}(L-2)n_L+1\equiv\mathcal{L} \;, \qquad (3)$$

where $\mathcal{L}$ is the number of independent loops inside the reduced graph $\mathcal{G}$ (Fig. 2). Thus, according to (3), the total number of independent relative variables $\mathbf{r}_\alpha^i$ in the I subgroups appearing in $P_\mathcal{G}(2)$ is exactly equal to $\mathcal{L}$. The latter is also given in terms of $\{n_L\}$ by the second sum in (3).

Here, graph $\mathcal{G}$ is Eulerian: It exists by construction as a walk which reaches once and only once all the edges of $\mathcal{G}$; it is the polymer itself. According to Euler's famous solution[17] of Königsberg's seven bridges, this is equivalent to having the total number of odd vertices inside the graph equal to 0 or 2: $\sum_{\text{odd } L\geq 1} n_L=0$ or 2, a rule satisfied, e.g., by the graphs of Figs. 1 and 2. Graphs not satisfying this condition correspond to correlations between several chains. Actually, Euler's rule will not play any crucial role here, and our results can be extended to correlations between different chains.

The end-to-end mean squared distance R^2 of a *single* self-avoiding chain of number of links S scales like

$$R^2 \propto S^{2\nu} \qquad (4)$$

for S large. This swollen radius R *gives the physical scale of the correlations* and we may use for $P_\mathcal{G}$, according to scaling principles

$$P_\mathcal{G}\{\mathbf{r}_\alpha^i\}=R^{-d\mathcal{L}}F_\mathcal{G}\{\mathbf{r}_\alpha^i/R\} \;, \qquad (5)$$

where $F_\mathcal{G}$ is a universal function of the reduced dimensionless variables $\mathbf{r}_\alpha^i/R$. $F_\mathcal{G}$ generalizes functions $F_a(1)$. The dimensional factor $R^{-d\mathcal{L}}$ in (5) comes from the normalization condition

$$\int P_\mathcal{G}\{\mathbf{r}_\alpha^i\}\prod_{i=1}^{I}\prod_{\alpha=1}^{m_i-1}d^d r_\alpha^i=1$$

and from equality (3).

Now, when all the $\mathcal{L}$ variables $\mathbf{r}_\alpha^i/R=x\mathbf{u}_\alpha^i$ (the $\mathbf{u}_\alpha^i$ being *fixed* vectors), tend to zero with the *same scale* x, $F_\mathcal{G}$ will develop an asymptotic short-distance behavior (in concise notations)

$$F_\mathcal{G}(x\{\mathbf{u}\})\sim x^{\theta_\mathcal{G}},\;(x\to 0) \;, \qquad (6)$$

where $\theta_\mathcal{G}$ is a new critical exponent depending on $\mathcal{G}$. Accordingly, fixing the relative distances $\mathbf{r}_\alpha^i$ to arbitrary values, and letting R (i.e., S) go to infinity, $P_\mathcal{G}(5)$ scales like

$$P_\mathcal{G}\sim R^{-d\mathcal{L}-\theta_\mathcal{G}} \;, \qquad (7)$$

and we call this short-distance limit of $P_\mathcal{G}$ the *$\mathcal{G}$-contact probability*. It is the probability for a SAW to form the set $\mathcal{G}$ of contacts. Using (4) we find the scaling behavior of the $\mathcal{G}$-contact probability

$$P_\mathcal{G}\sim S^{-\Upsilon_\mathcal{G}} \;,\qquad \Upsilon_\mathcal{G}\equiv\nu(d\mathcal{L}+\theta_\mathcal{G}) \;. \qquad (8)$$

We call these *new exponents* Υ and θ the *contact exponents.* Υ is the contact *probability* exponent, while θ is the *spatial* contact exponent. We now give the exact value in 2D of $\Upsilon_\mathcal{G}$ (hence $\theta_\mathcal{G}$) and also in $d=4-\varepsilon$, to $O(\varepsilon)$. The contact probability $P_\mathcal{G}$ is equal to

$$P_\mathcal{G}=\mathcal{Z}_\mathcal{G}/\mathcal{Z} \;, \qquad (9)$$

where $\mathcal{Z}_\mathcal{G}$ is the restricted partition function of the polymer network $\mathcal{G}$, and $\mathcal{Z}$ the full partition function of the single self-avoiding chain. Recently, using results of conformal invariance theory,[12] of numerical simulations,[13] and renormalization theory,[18,19] we have found[14] the exact scaling behavior of $\mathcal{Z}_\mathcal{G}$ for any topology of $\mathcal{G}$:

$$\mathcal{Z}_\mathcal{G}\sim S^{\gamma_\mathcal{G}-1},\;(S\to\infty) \;, \qquad (10)$$

$$\gamma_\mathcal{G}-1=\sum_{L(\geq 1)}n_L\hat{\sigma}_L-\nu d\mathcal{L} \;, \qquad (11)$$

and where $\hat{\sigma}_L$ are new irreducible critical exponents, associated with L-leg vertices. The physical meaning of Eq. (11) is the following. Each L-leg vertex appearing n_L times in the self-avoiding graph contributes a *partial* critical exponent $\hat{\sigma}_L$ to the overall critical enhancement exponent $\gamma_\mathcal{G}-1$. This $\hat{\sigma}_L$ differs from zero only for $d<4$ (i.e., below the upper critical dimension) and would be identically zero for Brownian chains. Therefore, for the latter with $\nu=\frac{1}{2}$, one has $\gamma_\mathcal{G}^B-1=-\frac{1}{2}d\mathcal{L}$, a result which can be obtained by straightforward dimensional analysis. Correspondingly, the term $-\nu d\mathcal{L}$ in (11) has the same dimensional origin, but with a general exponent ν, the size $R(4)$, instead of S, giving indeed the physical scale for a self-avoiding polymer. We have given[14] the fundamental exact values in two dimensions

$$\hat{\sigma}_L=(2-L)(9L+2)/64 \;. \qquad (12)$$

These $\hat{\sigma}_L$ are found in two dimensions from conformal invariance. We have shown[20] that they read in d dimensions $\hat{\sigma}_L=-\nu x_L+(\nu d-1)L/2$, where $2x_L$ is the decay exponent for the correlation function of a bundle of L polymers attached together at both ends ("watermelon" configuration).[13] In two dimensions, the values of x_L belong to the conformal table of central change $C=0$, and are given by Kac's[21] formula $x_{L=2p-1}=2h_{p+1/2,3/2}$, $x_{L=2p}=2h_{p+2,3}$, both giving $x_L=(9L^2-4)/48$ for $L\geq 1$. These values were identified numerically on strips.[13] Using $\nu=\frac{3}{4}$ in 2D gives (12). In $d=4-\varepsilon$ dimensions, $\hat{\sigma}_L$ is found[14,20] to be

$$\hat{\sigma}_L=(2-L)L\varepsilon/16+O(\varepsilon^2) \;. \qquad (13)$$

Therefore we obtain from (9)

$$P_{\mathcal{G}} = S^{\gamma_{\mathcal{G}} - \gamma} , \tag{14}$$

where γ is the usual enhancement exponent of a self-avoiding chain, which corresponds to a simple graph with $n_1 = 2$, $n_{L \neq 1} = 0$, $\mathcal{L} = 0$. We therefore find from (8), (14), and (11)

$$\Upsilon_{\mathcal{G}} \equiv \gamma - \gamma_{\mathcal{G}} = 2\hat{\sigma}_1 - \sum_{L(\geq 1)} n_L \hat{\sigma}_L + \nu d \mathcal{L} . \tag{15}$$

According to (8), we get the result for the short-distance exponent $\theta_{\mathcal{G}}$,

$$\nu \theta_{\mathcal{G}} = 2\hat{\sigma}_1 - \sum_{L(\geq 1)} n_L \hat{\sigma}_L . \tag{16}$$

Formulas (15) and (16), together with (12) and (13), are our main results, giving the exact values of $\Upsilon_{\mathcal{G}}$ and $\theta_{\mathcal{G}}$ in 2D, or in $d = 4 - \varepsilon$ to $O(\varepsilon)$, for any contact graph $\mathcal{G}$.

Let us specialize to $D = 2$, for which[15,16] $\nu = \frac{3}{4}$ (and $\gamma = \frac{43}{32}$). We have, using (3),

$$\Upsilon_{\mathcal{G}} = \tfrac{59}{32} + \tfrac{1}{64} \sum_{L(\geq 1)} n_L (L-2)(9L+50) , \tag{17}$$

and

$$\theta_{\mathcal{G}} = \tfrac{11}{24} + \tfrac{1}{48} \sum_{L(\geq 1)} n_L (L-2)(9L+2) . \tag{18}$$

Let us consider now the three geometrical cases of Fig. 1. Cases a,b,c correspond, respectively, to reduced graphs $\mathcal{G}_0[n_2 = 1, \mathcal{L} = 1]$, $\mathcal{G}_1[n_1 = 1, n_3 = 1, \mathcal{L} = 1]$, and $\mathcal{G}_2[n_1 = 2, n_4 = 1, \mathcal{L} = 1]$. Therefore, (17) and (18) give

$$\begin{aligned} &\Upsilon_0 = \tfrac{59}{32} \, (\equiv 2\nu + \gamma - 1), \quad \theta_0 = \tfrac{11}{24} \left(\equiv \frac{\gamma - 1}{\nu} \right) , \\ &\Upsilon_1 = \tfrac{17}{8}, \quad \theta_1 = \tfrac{5}{6} , \\ &\Upsilon_2 = \tfrac{43}{16}, \quad \theta_2 = \tfrac{19}{12} . \end{aligned} \tag{19}$$

For the tadpole graph $\mathcal{G}_1$, our exact result $\Upsilon_1 = 2.125$ compares extremely well with $\Upsilon_1 = 2.13 \pm 0.01$, obtained long ago by Trueman and Whittington[3] (TW) by the Monte Carlo method, and $\Upsilon_1 = 2.10 \pm 0.10$ and $\Upsilon_1 = 2.15^{+0.30}_{-0.15}$ obtained by Guttmann and Sykes[4] (GS) by series expansions. Accordingly, the exact value $\theta_1 = \frac{5}{6} = 0.8333\ldots$ agrees extremely well with the values $\theta_1 = 0.84 \pm 0.01$ (TW)[3] and $\theta_1 = 0.84 \pm 0.13$ (GS)[4] given in a review.[7] A numerical value of θ_2 has been obtained by Redner:[7] $\theta_2 = 1.93 \pm 0.27$. This is slightly too high, with respect to our conjectured exact value $\theta_2 = \frac{19}{12} = 1.583\,33\ldots$, but the agreement is still good.

Let us also note a striking fact. The Brownian values of the above critical exponents are $\gamma_{\mathcal{G}}^{B} - 1 = -(d/2)\mathcal{L}$, $\Upsilon_{\mathcal{G}}^{B} = (d/2)\mathcal{L}$, $\theta_{\mathcal{G}}^{B} = 0$, in agreement with (8), and (13) and (15) for $\varepsilon = 0$. Therefore, due to (17) and (3) one has

$$\Upsilon_{\mathcal{G}} - \Upsilon_{\mathcal{G}}^{B} = \tfrac{9}{64} \left[6 + \sum_{L(\geq 1)} n_L (L^2 - 4) \right] , \quad d = 2 .$$

If one uses the $O(\varepsilon)$ expansion of $\Upsilon_{\mathcal{G}}$ given by (15) and (13) and[2] $2\nu = 1 + \varepsilon/8 + O(\varepsilon^2)$, one finds for $\varepsilon = 2$, the approximation

$$\Upsilon_{\mathcal{G}} - \Upsilon_{\mathcal{G}}^{B} = \tfrac{1}{8} \left[6 + \sum_{L(\geq 1)} n_L (L^2 - 4) \right] + \cdots ,$$

i.e., a frontal coefficient $\frac{1}{8}$ replaces the exact $\frac{9}{64}$! This extraordinary coincidence of $O(\varepsilon)$ asymptotic expansion for $\varepsilon = 2$ and 2D exact values, explains the numerical observations which puzzled various authors.[7,22]

Let us finally illustrate our general result in three geometrical cases, which generalize that of Fig. 1. We consider the probabilities of making a multiple contact point of order $\mathcal{L}$ with $\mathcal{L}$ loops (Fig. 3), and with initial [Fig. 3(a)], initial-internal [Fig. 3(b)], and internal [Fig. 3(c)] closures. The graphs are, respectively, $\mathcal{G}_{0,\mathcal{L}}[n_{2\mathcal{L}} = 1]$, $\mathcal{G}_{1,\mathcal{L}}[n_1 = 1, n_{2\mathcal{L}+1} = 1]$, and $\mathcal{G}_{2,\mathcal{L}}[n_1 = 2, n_{2\mathcal{L}+2} = 1]$. Therefore, Eqs. (17) and (18) give, respectively,

$$\begin{aligned} &\Upsilon_{0,\mathcal{L}} = \tfrac{9}{16}\mathcal{L}^2 + \mathcal{L} + \tfrac{9}{32}, \quad \theta_{0,\mathcal{L}} = \tfrac{3}{4}\mathcal{L}^2 - \tfrac{2}{3}\mathcal{L} + \tfrac{3}{8} , \\ &\Upsilon_{1,\mathcal{L}} = \frac{\mathcal{L}}{16}(9\mathcal{L} + 25), \quad \theta_{1,\mathcal{L}} = \mathcal{L}(9\mathcal{L} + 1)/12 , \\ &\Upsilon_{2,\mathcal{L}} = \frac{\mathcal{L}}{16}(9\mathcal{L} + 34), \quad \theta_{2,\mathcal{L}} = \mathcal{L}(9\mathcal{L} + 10)/12 . \end{aligned}$$

For $\mathcal{L} = 1$, we recover (19).

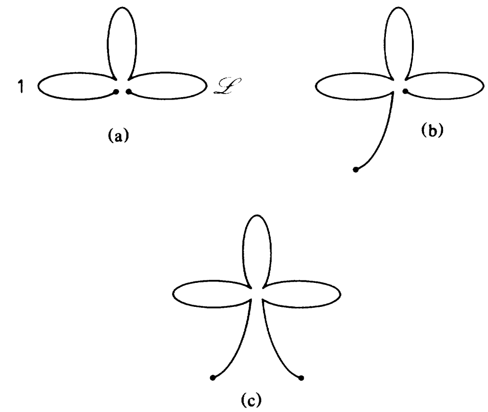

FIG. 3. Multiple contacts forming $\mathcal{L}$ loops, generalizing the case $\mathcal{L} = 1$ of Fig. 1.

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