Polymer Network of Fixed Topology: Renormalization, Exact Critical Exponent γ in Two Dimensions, and $d=4-\epsilon$

Bertrand Duplantier
Service de Physique Théorique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette Cedex, France
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I consider a connected self-avoiding polymer network made of identical long chains, with fixed topology. Using renormalization theory and conformal invariance, I conjecture in 2D, and give in $d=4-\epsilon$, to order $O(\epsilon)$, the exact value of its critical exponent γ as a function of the topological invariants. In 2D, the exact result fits with recent numerical data for three- and four-leg stars by Lipson *et al.*

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Critical exponents ν and γ, characterizing linear polymer chains with excluded volume, i.e., self-avoiding walks, are well known.[1] The exact value $\nu=\frac{3}{4}$ in 2D has been conjectured by Cardy and Hamber[2] and theoretically confirmed by Nienhuis,[3] who also conjectured the exact value $\gamma=\frac{43}{32}$. For animals, similar exact exponents in 2D and 3D have been given by Parisi and Sourlas.[4] The configuration number of *polydispersed* branched polymers with specified topologies and a fixed total length has also been studied numerically by Gaunt *et al.*[5] The critical behavior of a different model, *monodispersed* branched polymers with fixed topology and branches of *equal* length, is much less known. (For uniform star polymers, see Miyake and Freed[6] and Lipson *et al.*[7]) In this Letter, I consider a general self-avoiding network made of identical long polymer chains linked together (Fig. 1). A connected network G can be characterized by simple topological numbers: the numbers $\{n_L, L\geqslant 1\}$ of vertices connecting L chains ($L=1$ corresponds to external legs). I give the exact value of the critical exponent governing the asymptotic number of configurations ω_G of such a network in $d=4-\epsilon$ dimensions, and in *two dimensions*, using results of conformal invariance. I conjecture in 2D the quite general result (on a lattice) $\omega_G \sim N^{\mathcal{N}l} l^{\gamma_G -1}$ $(l\to\infty)$, with

$$\gamma_G = -\tfrac{1}{2}+\tfrac{1}{64}\sum_{L\geqslant 1} n_L(2-L)(9L+50), \qquad (1)$$

where, on a lattice, μ is the effective connectivity constant for self-avoiding walks, $\mathcal{N}$ the total number of chains, and l the common large length of the chains. This result covers all possible topologies (on a lattice, for L larger than the lattice connectivity constant, the chains of an L vertex are tied together in a fixed neighborhood). (1) is obtained by combining a new extension of direct renormalization theory for polymers,[8,9] Nienhuis's results[3] for linear polymers, and a very recent seminumerical conjecture by Saleur,[10] which I adapt here, and which was itself obtained when studying conjectures by Dotsenko and Fateev[11] in conformal invariance theory. Result (1) gives, for instance, for L branch star polymers

$$\gamma=[68+9L(3-L)]/64, \qquad (1a)$$

and for a rectangular polymer network $N\times M$ (N and M bounds),

$$\gamma=-43NM/16+9(N+M)/32+13/8. \qquad (1b)$$

I also give the corresponding value of γ_G for $d=4-\epsilon$ to first order in ϵ. For doing this, I study the direct multiplicative renormalization of the partition function of the network. For a general network G containing n_L L-leg vertices ($L\geqslant 1$), the total numbers $\mathcal{N}$ of chains, and $\mathcal{L}$ of loops read

$$2\mathcal{N}=\sum_{L\geqslant 1} L n_L, \qquad (2)$$

$$\mathcal{L}=\sum_{L\geqslant 1}\tfrac{1}{2}(L-2)n_L+1. \qquad (3)$$

I then describe the $a=1,\ldots,\mathcal{N}$ interacting chains by generalizing Edwards's *continuum* model.[12] The con-

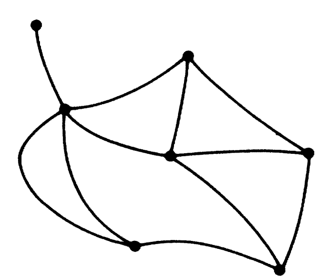

FIG. 1. A network made of $\mathcal{N}=11$ chains, $\mathcal{L}=5$ loops, and vertices of type 1–5 with $n_1=1$ (dangling chain), $n_3=4$, $n_4=1$, $n_5=1$.

tinuous probability weight is

$$P_{\mathcal{N}}\{\mathbf{r}\} = \exp\left[-\frac{1}{2}\sum_{a=1}^{\mathcal{N}}\int_0^S ds\left(\frac{d\mathbf{r}_a}{ds}\right)^2 - \frac{b}{2}\sum_{a,a'=1}^{\mathcal{N}}\int_0^S ds\int_0^S ds'\delta^d[\mathbf{r}_a(s)-\mathbf{r}_{a'}(s')]\right]. \tag{4}$$

Here $\mathbf{r}_a(s)$ is the configuration of chain a in $\mathcal{R}^d$, S is the Brownian area[8] such that the mean-squared end-to-end distance of a free Brownian chain is ${}^0R^2 \equiv dS$. Thus S is an *area*, with the dimension of a *squared length*. On a lattice, S thus represents the *number* of *links*, or monomer number of each chain. I use the *dimensionless* Zimm-Yamakawa parameter[8]

$$z = (2\pi)^{-d/2} b S^{2-d/2}, \tag{5}$$

and the excluded volume, or self-avoiding limit, corresponds to $z \to \infty$. Of course, (1) represents *free* interacting chains. Since the chains are actually bound together inside network G, I introduce the restricted partition function $Z(G)$,

$$Z(G) = \int d\{\mathbf{r}\} P_{\mathcal{N}}\{\mathbf{r}\}\delta^d(G)\left[\int d\{\mathbf{r}\}{}^0P_{\mathcal{N}}\{\mathbf{r}\}\prod_{a=1}^{\mathcal{N}}\delta^d[\mathbf{r}_a(0)]\right]^{-1} \tag{6}$$

calculated in *dimensional regularization*. $\delta^d(G)$ is symbolic: It is the product of all necessary δ^d distributions in *direct* space, connecting the chains in the network, plus one for fixing the origin. ${}^0P$ is the free weight of Brownian chains, obtained from (4) for $b=0$. The number Δ of $\delta^d(\mathbf{r})$ distributions in $\delta^d(G)$ is

$$\Delta = \sum_{L \geqslant 1}(L-1)n_L + 1, \tag{7}$$

i.e., the total number of conditions at the vertices, plus one. Hence, the canonical dimension of $Z(G)$ obtained from (5) to (7) (exhibiting all variables in Z) is

$$Z(G, b, S, d) = S^{(\mathcal{N}-\Delta)d/2} \mathcal{Z}(G, z, d), \tag{8}$$

where $\mathcal{Z}$ is a dimensionless quantity, which thus is a function of z, Eq. (5), only (and of d, G). Using now (2) and (3), I find for the canonical dimension $\mathcal{D}$ of Z in *area* units

$$\mathcal{D} \equiv (\mathcal{N}-\Delta)d/2 = -\mathcal{L}\, d/2. \tag{9}$$

For $z=0$, $\mathcal{Z}$ has a finite value. Therefore from (8), one sees that $\mathcal{D} = -\mathcal{L}\, d/2$ is the *Brownian* value of $\gamma_G - 1$ in absence of excluded volume, and is entirely determined by topological constraints defining the network. On the contrary, for large z (excluded volume limit) the dimensionless part $\mathcal{Z}(G, z, d)$ scales like

$$\mathcal{Z}(G) \sim z^{\sigma_G/(2-d/2)} \sim S^{\sigma_G}, \tag{10}$$

where σ_G is a new critical exponent, which I calculate below. Then, as a result of (8), (9), and (10), Z scales like

$$Z \sim S^{\gamma_G - 1} \quad (S \to \infty),$$
$$\gamma_G - 1 \equiv -\tfrac{1}{2} d\mathcal{L} + \sigma_G. \tag{11}$$

(Note that in dimensional regularization the "effective connectivity constant" is[8] 1.)

I now generalize to arbitrary polymer netowrks the direct renormalization method introduced in Ref. 8 for simple linear polymer chains. The renormalized length scale is given by the mean-squared end-to-end distance R^2 of a *single* polymer chain with excluded volume. In the excluded volume $S \to \infty$, i.e., $z \to \infty$, one has

$$R^2 \sim S^{2\nu}. \tag{12}$$

Now, we need for renormalizing any polymer network an infinite set of new partition functions. These are the partition functions $Z(\mathcal{S}_L)$ of *star polymers* $\mathcal{S}_L$ made of an arbitrary number $L \geqslant 1$ of equal branches (Fig. 2), corresponding to the constitutive vertices of the network. These functions $Z(\mathcal{S}_L)$ are defined as in (6). Since stars $\mathcal{S}$ have no constitutive loops, one has from (9), $\mathcal{D}_{\mathcal{S}} \equiv 0$; hence from (8), $Z(\mathcal{S}_L) \equiv \mathcal{Z}(\mathcal{S}_L)$ is *dimensionless*. Note that the star $\mathcal{S}_1$ is nothing but a linear chain. I then define (for topological convenience), for each L vertex, $L \geqslant 1$, a reduced dimensionless partition function, or renormalization factor

$$\hat{Z}_L \equiv Z(\mathcal{S}_L) Z^{-L/2}(\mathcal{S}_1). \tag{13}$$

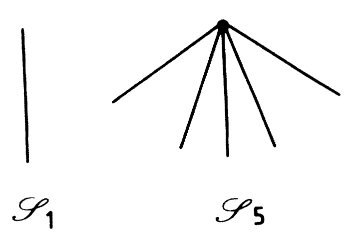

FIG. 2. Star polymers $\mathcal{S}_1$, $\mathcal{S}_5$.

For $L=1$, $\hat{Z}_1 \equiv Z^{1/2}(\mathcal{S}_1)$. Note that all these dimensionless quantities are functions only of z and d.

Now, for a general network G, described by (6), I state that the renormalization is the following: $Z(G)$ (8) can be rewritten as

$$Z(G,b,S,D) = \prod_{L\geq 1}(\hat{Z}_L)^{n_L}(R^2)^{-d/2\mathcal{L}}\mathcal{A}(G,z,d). \quad (14)$$

This equation is simple to understand: A (dimensionless) renormalization factor $\hat{Z}_L$ is associated with each constitutive L vertex, and the physical (renormalized) area R^2 is substituted to the (bare) Brownian area S. Then I state that in the excluded volume limit $z\rightarrow\infty$ of very long chains. $\mathcal{A}$ reaches a *finite fixed point value* (calculable in $\epsilon=4-d$ expansion). Details of a field-theoretic proof of (14) will be given elsewhere. Following Ref. 8, partition function $Z(G)$ can be mapped, by multiple Laplace transforms, onto the correlation function $\langle\prod_{L\geq 1}(\phi^L)^{n_L}\rangle$ of $(\phi^2)^2_d$ field theory, with $\mathcal{N}$ different n-component fields, in the limit $n\rightarrow 0$ and a $O(\mathcal{N}\times n)$ symmetry in the interaction term. Then the renormalization factors $\hat{Z}_L$ correspond essentially to those of the composite operators ϕ^L of L different fields at the same point. Now vertex factor $\hat{Z}_L$ (13) scales for $z\rightarrow\infty$ like

$$\hat{Z}_L(z,d) \sim z^{\hat{\sigma}_L/(2-d/2)} \sim S^{\hat{\sigma}_L}, \quad (15)$$

where $\hat{\sigma}_L$ is a new (irreducible) critical exponent, associated with the L-leg vertex. Thus, using (11) to (15) we find the basic new hyperscaling relations

$$\gamma_G - 1 = \sum_{L\geq 1} n_L\hat{\sigma}_L - \nu d\mathcal{L}, \quad (16a)$$

$$\sigma_G = \sum_{L\geq 1} n_L\hat{\sigma}_L - (2\nu-1)(d/2)\mathcal{L}. \quad (16b)$$

Let us first consider the Wilson-Fisher $d=4-\epsilon$ expansion. I have calculated $Z(\mathcal{S}_L,z,d)$, using dimensional regularization. We find to first order (Fig. 3)

$$Z(\mathcal{S}_L,z,\epsilon) = 1 + z\{(2/\epsilon)[L-\tfrac{1}{2}L(L-1)] + O(1)\} + O(z^2). \quad (17)$$

Therefore $\hat{Z}_L$ (15) equals

$$\hat{Z}_L(z,\epsilon) = 1 + z/\epsilon(2-L)L + \ldots, \quad (18)$$

and the critical index $\hat{\sigma}_L$ is obtained as[8,9]

$$\hat{\sigma}_L = \frac{\epsilon}{2} z \ln\hat{Z}_L/\partial z = (2-L)(L/2)z + O(z^2) = (2-L)(L/2)z_R + O(z_R^2), \quad (19)$$

where we substituted to z the dimensionally *renormalized* Zimm-Yamakawa parameter z_R, defined in Ref. 9 in terms of which $\hat{\sigma}_L[z_R,\epsilon]$ is finite to all orders in z_R, ϵ, and $1/\epsilon$ pole free. Its fixed point value for $z\rightarrow\infty$ is[9] $z_R^* = \epsilon/8 + O(\epsilon^2)$. Thus (19) reads in the excluded volume limit

$$\hat{\sigma}_L = (2-L)L\,\epsilon/16 + O(\epsilon^2). \quad (20)$$

Therefore, using also[1] $2\nu-1=\epsilon/8+O(\epsilon^2)$, we find from (16b)

$$\sigma_G = \frac{\epsilon}{8}\left[\sum_{L\geq 1} n_l\tfrac{1}{2}(4-L^2) - 2\right] + O(\epsilon^2), \quad (21)$$

where I used (3). For stars, this agrees exactly with $O(\epsilon)$ results of Ref. 5.

Let us now consider *two dimensions*. The values of γ and ν have been conjectured by Nienhuis[3] to be

$$\gamma = \tfrac{43}{32}, \quad \nu = \tfrac{3}{4}. \quad (22)$$

Quite recently, by studying conjectures of Dotsenko and Fateev[11] on magnetic and thermal operators in critical conformal invariant theories in 2D, and from numerical calculations on 2D strips, Saleur[10] has given a conjecture for the number $\bar{\omega}$ of self-avoiding configurations of L nearly identical polydisperse polymer chains on a lattice, tied together at their extremities (Fig. 4) and having a fixed *total* length l: $\bar{\omega} \sim \mu^l\, l^{(20-9L^2)/32}$. I have to adapt this result to the case where all chain lengths are fixed (and equal). The number ω of configurations of L attached chains with fixed lengths l is smaller than the number $\bar{\omega}$ of L nearly identical chains $l_1,\ldots,l_L$, with total length l, by a simple constraint factor

$$\int_0^\infty \prod_{a=1}^{L} dl_a \delta\left(l - \sum_{a=1}^{L} l_a\right) \sim l^{L-1}.$$

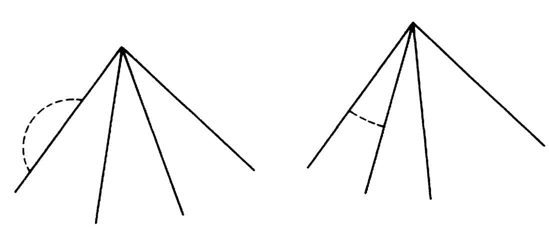

FIG. 3. First-order diagrams contributing to $Z(\mathcal{S}_L)$. The dotted lines correspond to interaction b.

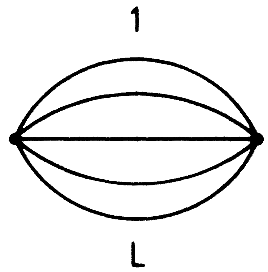

FIG. 4. The "watermelon" network of L-polymer chains attached by their extremities.

Therefore for the configuration of Fig. 4 with individual fixed lengths, I obtain the exact index

$$\gamma_L - 1 = (20 - 9L^2)/32 - (L-1). \qquad (23)$$

[For $l=1$, (23) agrees with Nienhuis's (22).] Identifying (23) with (16a) for $n_L = 2$, $n_{l'} = 0$ $(L' \neq L)$, $\mathcal{L} = L - 1$, and using (3) and (22) we find the key result

$$\hat{\sigma}_L = (2-L)(9L+2)/64. \qquad (24)$$

By insertion of (24) into (16a), use of (3) and (22) gives exactly (1), Q.E.D. Let me stress that γ_G (1) is valid in 2D for all network topology respecting the planarity condition.[13] γ_G (1) does not depend on the irrelevant number n_2 of two-leg vertices. For a simple closed loop $\mathcal{L}$, $n_L = 0$, $\forall L \geqslant 1$; hence $\gamma_{\mathcal{L}} = -\frac{1}{2} \equiv 1 - \nu d$. Usually, one gives $\gamma'_{\mathcal{L}} = -\nu d = -\frac{3}{2}$. This is simple because one then divides by the circular reptation symmetry factor S^{-1}, not taken into account here for a general (nonsymmetrical) network. It is also very interesting to consider (1a) for the L-arm star $\mathcal{S}_L$ in 2D. For $L = 3,4$, this gives $\gamma_{\mathcal{S}_3} = 1\frac{1}{16} = 1.0625$, and $\gamma_{\mathcal{S}_4} = \frac{1}{2}$. This can be seen to be in excellent agreement with the recent numerical results by Lipson *et al.*[7] on 2D lattices. These authors did not know the exact values, but I think that their results (see triangular lattices in Fig. 1 of Ref. 7) actually converge to the above values. A last striking fact can be seen in the critical exponent σ_G (16b) which is the excluded volume part of $\gamma_G - 1$. Insertion of (3) and (24) into (16b) gives in 2D

$$\sigma_G = \frac{9}{64} \sum_{L \geqslant 1} n_L (4 - L^2) - \frac{1}{2}. \qquad (25)$$

Comparing (25) with (21) shows that the polynomial dependence on L is exactly the same in $d=2$ and $d = 4 - \epsilon$, to $O(\epsilon)$. Furthermore, for $\epsilon = 2$, (21) is extremely close to (25): The only difference is a coefficient $\frac{1}{8}$ approximating the exact $\frac{9}{64}$.

Note added.—The last numerical results on star polymers by Wilkinson *et al.*[14] agree remarkably with formula (1a).

[1]P. G. de Gennes, Phys. Lett. **38A**, 339 (1972), and *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979), and references therein.

[2]J. L. Cardy and H. W. Hamber, Phys. Rev. Lett. **45**, 499 (1980).

[3]B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982), and J. Stat. Phys. **34**, 731 (1984).

[4]G. Parisi and N. Sourlas, Phys. Rev. Lett. **46**, 871 (1981).

[5]D. S. Gaunt, J. E. G. Lipson, G. M. Torrie, S. G. Whittington, and M. K. Wilkinson, J. Phys. A **17**, 2843 (1984), and references therein.

[6]A. Miyake and K. F. Freed, Macromolecules **16**, 1228 (1983).

[7]J. E. G. Lipson, S. G. Whittington, M. K. Wilkinson, J. L. Martin, and D. S. Gaunt, J. Phys. A **18**, L469 (1985).

[8]J. des Cloizeaux, J. Phys. (Paris) **42**, 635 (1981).

[9]B. Duplantier, J. Phys. (Paris) **47**, 569 (1986).

[10]H. Saleur, Saclay Report No. PhT 86/022, 1986 (unpublished).

[11]V. L. S. Dotsenko and V. A. Fateev, Nucl. Phys. **B240**, 312 (1984).

[12]S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

[13]In 2D, nonplanar networks would have the same exponent γ, but the amplitude of $\mathcal{Z}(G)$ then vanishes, since there is no possible self-avoiding configuration.

[14]M. K. Wilkinson, D. S. Gaunt, J. E. G. Lipson, and S. G. Whittington, J. Phys. A **19**, 789 (1986).