Flory formula as an extended law of large numbers

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A new derivation of the Flory formula for self-avoiding walks (SAW's) is proposed. It relies on purely statistical arguments concerning sums of long-range correlated random variables, and does not involve any free-energy minimization. It allows unambiguous generalization to several other problems: in particular, the correct Flory-type formulas for SAW's and TSAW's on fractals are obtained.

The aim of this Brief Report is to present a new physical picture of the self-avoiding walk (SAW) problem. The first outcome of this picture is to provide for the first time a crystal-clear interpretation of the Flory approximation[1] for the exponent relating the end-to-end distance of a polymer to the number of its monomers. Usually, the Flory formula is found by balancing two terms of the polymer free energy: the elastic energy (sometimes called entropic term) and the repulsive energy, both estimated in a "mean-field" way. Though the resulting formula is amazingly successful, this derivation suffers from several flaws: both terms are grossly overestimated,[2] one deals in fact with subdominant terms,[3] and the resulting free energy has the wrong sign.[3] Attempts to account for its success have been proposed, in particular in Refs. 4–7.

We want to show here that the Flory formula can be obtained on statistical grounds: it can be viewed as a self-consistent way of estimating sums of correlated random variables. No free energy is involved in our derivation, which can be unambiguously generalized to many other situations, as will be shown on several examples: self-avoiding Levy flights, SAW's on fractals, "true" SAW (Ref. 8), etc.

Taking this picture seriously suggests an alternative field-theoretical representation for polymers which happens to give back the $n=0$ result at first order in $\epsilon=4-d$.

The physical picture we propose is the following: a polymer is a random walk with a *long-range correlation* between the elementary displacements, which is induced by the self-avoiding constraint. It can be seen as a random walk in a correlated environment, the structure of which is generated by the past motion of the polymer it self.

Let us first show how to deal with such a sum of correlated random variables ($\langle x_i \rangle = 0$):

$$R_N = \sum_{i=1}^{N} x_i \,, \tag{1}$$

where we assume that the correlation function $C(n) = \langle x_i x_{i+n} \rangle$ depends only on the difference n (stationary process). The mean square of R_N is given by

$$\langle R_N^2 \rangle = NC(0) + 2\sum_{n=1}^{N} (N-n)C(n) \,. \tag{2}$$

Thus, one must distinguish between two cases.

(1) The sum $\sum_{n=1}^{N} C(n)$ converges when N becomes large [i.e., in practice, when $C(n)$ decreases faster than $1/n$] and then $R_N^2 \sim N$ behaves as a Brownian (uncorrelated) walk, the prefactor only being modified: correlations are in this sense "irrelevant."

(2) The sum diverges, and in this case *correlations are relevant*: suppose that $C(n)$ decreases for large n as $1/n^y$ with $0 < y < 1$. One gets a modified "stretched" behavior of the walk:

$$\langle R_N^2 \rangle \sim N^{(2-y)} \,. \tag{3}$$

The statistical meaning of this analysis is the following:

$$N_{id} = \sum_{n=1}^{N} C(n) \sim \begin{cases} \text{const} & \text{if } y > 1, \\ N^{(1-y)} & \text{if } 0 < y < 1 \end{cases} \tag{4}$$

is proportional to the number of times the variable x_i is essentially identical to x_1, and thus N/N_{id} can be thought of as the number of *effectively independent* variables ($\hat{x}_i$) in the process. R_N can now be estimated by rewriting it under the form

$$R_N = N_{id} \sum_{N/N_{id} \text{ terms}} \hat{x}_i \,, \tag{5}$$

where the central limit theorem in its usual form can now be applied to the sum. This leads to $R_N \sim N_{id}(N/N_{id})^{1/2}$ and (3) is recovered.

For the SAW problem, the exponent y governing the correlations between displacements may be estimated as follows. Consider the nth monomer of the chain: its displacement x_n is strongly correlated to *all* the preceding ones, $x_1, \ldots, x_{n-1}$, by the fact that if this nth monomer happens to be close to one of the preceding ones, the displacement x_n has to be chosen so as to expand the chain radially, thus reducing the occurrence of further intersec-

tions. Assuming perfect transmission of the correlations at the contact points (that is, $\sum_{i=1}^{N_c}\hat{x}_i \sim N_c$, where the sum is restricted to contact points only), the integral N_{id} of the correlation $C(n)$ must scale as the number of contacts N_c, which can be estimated in the usual mean-field spirit as $n^{2-\nu d}$. This estimation yields a decrease $C(n)\sim 1/n^{\nu d-1}$, where ν is the exponent of the end-to-end distance R_N itself. Note that, since $r\sim n^{\nu}$, this amounts to a decay $1/r^{d-1/\nu}$ with distance, which is simply the behavior of the correlation function of the polymer itself.

Thus $y=\nu d-1$. Correlations are thus relevant as long as $d<2/\nu$; since $\nu>\frac{1}{2}$, this yields the upper critical dimension $d_c=4$. When $d<4$ ($y<1$), self-consistency requires from (3)

$$2\nu=2-(\nu d-1)$$

or

$$\nu=3/(2+d)\,, \tag{6}$$

which is precisely Flory's formula. ($y=1$ for $d=4$ implies logarithmic correctins to $R^2=N$, which indeed exist at the critical dimension. This is out of reach of the conventional Flory approach.) This formula has thus a statistical content; as such, it is quite insensitive to "details:" in particular, only the limiting behavior of the correlation function is of any relevance. This again emphasizes the link, suggested by Jona Lasinio,[9] between critical phenomena and sums of correlated random variables. Further investigations along these lines are, in our opinion, highly desirable.

The above derivation shows very clearly that Flory's formula combines an exact result on some correlated random variables [Eq. (3)], and an *approximate* way of estimating the decay of the correlation $C(n)$, based on a mean-field counting of the number of contacts and a "perfect correlation transmission" hypothesis. [Weaker correlations through contacts characterized by a slower power law $\sum_{i=1}^{N_c}\hat{x}_i\sim N_c^{\beta}$, $\beta\leq 1$ would lead to a "generalized Flory formula" $\nu=(2\beta+1)/(2+\beta d)$. The self-consistent choice $\beta=\nu$ yields a Flory-type formula $\nu=1/\sqrt{d}$ which, remarkably, is exact at first order in $1+\epsilon$ and $4-\epsilon$.] The estimate $C(n)\sim 1/n^{\nu d-1}$ corresponds, in more familiar terms, to the repulsive term N^2/R^d in the free energy. One can think of improving this estimation by multiplying $C(n)$ by the correction factor $1/n^{\gamma-1}$ which takes into account the depletion of the end-to-end probability distribution near the origin. This leads to a modified formula:

$$\nu=(4-\gamma)/(2+d)\,, \tag{7}$$

which again is exact for $d=4$ and $d=1$ and has the remarkable property to yield the correct first order term in an $\epsilon=4-d$ expansion.

One of the main interest of this statistical interpretation is that it allows unambiguous generalizations to many other problems: we now give four illustrative examples.

(a) *Directed SAW's.* As soon as an average drift is imposed to the walk, the correlation $C(n)$ will decrease exponentially, and it is thus obvious that one recovers the exponent $\nu=\frac{1}{2}$ for the transverse spreading.

(b) *"True" SAW.* For the "true" SAW (TSAW),[8] self-intersections are not strictly forbidden; instead, the direction of an elementary displacement is given a weight which favors neighboring sites with a low occupation number. The correlation has thus a *local* nature: it simply decreases as the probability for the last monomer to coincide with the first one, i.e., as $1/n^{\nu d}$, and thus $y=\nu d$. Self-consistency now yields

$$2\nu=2-\nu d \quad \text{or} \quad \nu=2/(2+d)\,, \tag{8}$$

which is the expression proposed by Pietronero,[10] again very close to numerical results in $d=1$ (Refs. 11 and 12), and possibly exact.

(c) *Self-avoiding Levy flights.* If the elementary displacements have a broad distribution behaving as

$$\rho(x)\sim 1/x^{1+\sigma} \tag{9}$$

for large x, $\sigma>0$, then, writing R_N as in (5),

$$R_N=\sum_{N/N_{id}\ \text{terms}}\ \sum_{N_{id}\ \text{terms}} x_i\,. \tag{10}$$

The internal sum then behaves as $(N_{id})^{1/\sigma}\hat{x}_i$ if $0<\sigma<1$ and as $N_{id}\hat{x}_i$ if $\sigma>1$, where the $\hat{x}_i$'s are effectively independent random variables, still distributed as (9).[13] The remaining sum behaves as $(N/N_{id})^{1/\sigma}$ if $\sigma<2$ and as $\sqrt{N/N_{id}}$ for $\sigma>2$. The same self-consistency argument as above (with $N_{id}\sim N^{1-y}$, $y=d\nu-1$) thus leads [for $d<\min(2\sigma,4)$] to

$$\nu=\begin{cases}\dfrac{1}{\sigma}, & 0<\sigma<1 \quad \text{(unperturbed Levy flight)},\\[2ex] \dfrac{2\sigma-1}{\sigma(d+1)-d}, & 1<\sigma<2,\\[2ex] \dfrac{3}{2+d}, & \sigma>2 \quad \text{(normal SAW)},\end{cases} \tag{11}$$

which are the results obtained in Ref. 14 through the usual free-energy minimization (see Ref. 15 for the complete phase diagram). Note that in this case the elastic part of this free energy is rather subtle to obtain: it is *not* related to the probability distribution of the free walk.[15]

(d) *Self-avoiding walks on fractals.* Walking on a fractal network (of dimension d_F) introduces two features at variance with the Euclidean case.

(1) The statistical behavior of the sum of N/N_{id} independent random displacements is modified by the fractal geometry.[16] It behaves as

$$(N/N_{id})^{d_s/2d_F}\,, \tag{12}$$

where d_s is the spectral dimension of the lattice.

(2) Performing N_{id} identical displacements on the lattice results in a Euclidean distance from the starting point scaling as

$$(N_{id})^{\hat{d}/d_F}\,, \tag{13}$$

where $\hat{d}$ is the spreading dimension (see, e.g., Ref. 17). Taking these modifications into account (together with $y=\nu d_F-1$) leads to a generalized Flory formula for

SAW's on fractals:

$$\nu d_F = \frac{4\hat{d} - d_s}{2 + 2\hat{d} - d_s} . \tag{14}$$

This expression differs from a number of previously proposed ones[7,18,19] generally obtained through rather heuristic arguments. Note that formula (14) satisfies three necessary requirements: (i) $d_s < 4$ appears as the criterion for the relevance of the self-avoiding constraint, independently of d_F and $\hat{d}$. (ii) νd_F is independent of d_F itself and thus depends only on the intrinsic quantities d_s and $\hat{d}$ (see Ref. 20). (iii) $\nu d_F = 1$ if $\hat{d} = 1$, independently of d_s. Comparison with exact or numerical results are summarized in Table I for several fractals. The agreement is quite satisfactory (which anyhow is also the case of most of the formulas referred to above). Nevertheless, we wish to emphasize that formula (14) has been derived on clear statistical grounds. [Note that formula (14) can also be obtained[23] by identifying the elastic energy with the logarithm of the recently derived probability distribution for random walks on fractals.[24]] For TSAW's on fractals, one obtains in the same way ($y = d_F \nu$)

$$\nu d_F = \frac{2\hat{d}}{2 + 2\hat{d} - d_s} . \tag{14'}$$

We have considered along these lines[25,26] the case of self-avoiding manifolds of internal dimension D (Ref. 27) for which $y = \nu d / D - 1$; using

$$\sum_{i=1}^{N} x_i \sim N_{id} \left(\frac{N}{N_{id}} \right)^{1 - D/2} \tag{15}$$

one finds the generalized "Flory formula:"

$$\nu = (2 + D)/(2 + d) , \tag{16}$$

which, interestingly enough, coincides with the one proposed in Ref. 27.

This picture of a SAW as a random walk with a self-induced correlation naturally suggests study of the problem of a random walk in a random environment, described by the following Langevin equation:

$$\frac{d\mathbf{R}_N}{dN} = \mathbf{F}(\mathbf{R}_N) + \eta(N) , \tag{17}$$

where $\mathbf{F}(\mathbf{R})$ denotes a quenched random force with long-range correlations decaying as $\langle F_\mu(R) F_\nu(R') \rangle \sim \delta_{\mu\nu} (R - R')^{-a}$. This problem has been addressed in Ref. 30 through a renormalization-group analysis, where we have shown that disorder is relevant for $a < 2$ and that the modified diffusion exponent ν reads, at first order in $\delta = 2 - a$,

$$\nu = \frac{1}{2} + \frac{1}{8} \frac{d-2}{d-1} \delta + \cdots . \tag{18}$$

Note that the self-consistent method explained above would lead to $\nu = 2/(2 + a)$ for this problem, which, at first order in $2 - a$, coincides with (18) in the $d \to \infty$ limit.

Coming back to the SAW problem, one can imagine that the self-avoiding constraint can be implemented through a centrifugal force associated with each monomer, the correlations of which thus decrease as those of the density itself. This suggests the choice of the value $a = d - 1/\nu$. Remarkably, matching the expansions of both sides of (18) in $\epsilon = 4 - d$, yields

$$\nu = \frac{1}{2} + \frac{\epsilon}{16} + \cdots , \tag{19}$$

which is precisely the well-known $n = 0$ result at one-loop order. Note that this field theory also allows the recovery of the exact asymptotic behavior of the end-to-end distance distribution $P(R,N) \sim \exp[-(R/N^\nu)^b]$ with $b = (1 - \nu)^{-1}$. At higher orders, the detailed structure of the force correlations comes into play, and one presumably cannot carry on with a quenched picture, but instead introduce some nonstationarity, much as in Edwards formulation of the SAW problem.[4,29,30]

As a conclusion, this work emphasizes the link between Flory-type approximations and statistical limit behaviors. As such it has a large degree of generality, and it would be interesting to extend similar ideas to other problems such as lattice animals or $O(n)$ spin models.

TABLE I. Exponent ν for SAW's and TSAW's on different fractal lattices: comparison between numerical (or exact) values and formulas (14) in text.

		ν: numerical or exact	ν: approximation [Eqs. (14) in the text]
	Sierpiński gasket		
$d=2$	SAW	0.798 (Ref. 19)	0.825
	TSAW	0.51 (Ref. 21)	0.53
$d=3$	SAW	0.675 (Ref. 19)	0.724
	TSAW		0.45
	Percolation cluster (backbone)		
$d=2$	SAW	0.767 (Ref. 22)	0.76
	TSAW		0.48
$d=3$	SAW	0.65 (Ref. 18)	0.67
	TSAW		0.44
Koch curve		0.891 (Ref. 19)	0.855

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[1]P. J. Flory, in *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1971), Chap. 12; see also M. Fisher, J. Phys. Soc. Jpn. Suppl. **26**, 44 (1969).
[2]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1985).
[3]J. des Cloiseaux, J. Phys. (Paris) **31**, 715 (1970).
[4]S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).
[5]S. P. Obukhov, J. Phys. A **17**, L965 (1984).
[6]L. Peliti and L. Piliti, Riv. Nuovo Cimento **6**, 1 (1987).
[7]R. Dekeyser, A. Maritan, and A. Stella, Phys. Rev. A **36**, 2338 (1987).
[8]D. Amit, G. Parisi, and L. Peliti, Phys. Rev. A **27**, 1635 (1983).
[9]G. Jona Lasinio, Nuovo Cimento **26B**, 99 (1975); M. Cassandro, G. Jona Lasinio, Adv. Phys. **27**, 913 (1978).
[10]L. Pietronero, Phys. Rev. B **27**, 5887 (1983).
[11]R. Rammal, J. C. Angles, d'Auriac, and A. Benoit, J. Phys. (Paris) Lett. **17**, L9 (1984).
[12]J. Bernasconi and L. Pietronero, Phys. Rev. B **29**, 5196 (1984).
[13]See, for example, B. V. Gnedenko and A. N. Kolmogorov, *Limit Theorems for Sums of Independent Random Variables* (Addison-Wesley, Cambridge, 1954).
[14]P. G. de Gennes, in *Directions in Condensed Matter Physics, Memorial Volume in Honour of S. K. Ma,* edited by J. Grinstein and E. Mazenko (World-Scientific, Philadelphia, 1986).
[15]E. Bouchaud and M. Daoud, J. Phys. A **20**, 1463 (1987); E. Bouchaud, thesis, Université d'Orsay, 1988 (unpublished).
[16]S. Alexander and R. Orbach, J. Phys. (Paris) Lett. **43**, L625 (1982); R. Rammal and G. Toulouse, *ibid.* **44**, L13 (1983).
[17]J. Vannimenus, in *Physics of Finely Divided Matter,* edited by N. Boccara and M. Daoud (Springer-Verlag, Berlin, 1985).
[18]K. Kremer, Z. Phys. B **45**, 148 (1981).
[19]R. Rammal, G. Toulouse, and J. Vannimenus, J. Phys. (Paris) **45**, 389 (1984).
[20]J. Vannimenus, J. Phys. (Paris) Lett. **45**, L1701 (1984).
[21]J. C. Angles D'Auriac and R. Rammal, J. Phys. A **17**, L15 (1984).
[22]P. M. Lam and Z. Q. Zhang, Z. Phys. B **56**, 155 (1984).
[23]S. Havlin, D. Ben Avraham, Adv. Phys. **36**, 695 (1987); A. Aharony and A. B. Harris, J. Stat. Phys. (to be published).
[24]A. Aharony and A. Brook Harris, Europhys. Lett. **4**, 1355 (1987); F. Delyon, Y. Levy, and B. Souillard (unpublished).
[25]E. Bouchaud and J. P. Bouchaud, J. Phys. (Paris) (to be published).
[26]J. P. Bouchaud and A. Georges, Phys. Rep. (to be published).
[27]Y. Kantor, M. Kardar, and D. Nelson, Phys. Rev. Lett. **57**, 791 (1986).
[28]J. P. Bouchaud, A. Comtet, A. Georges, and P. Le Doussal, J. Phys. (Paris) **48**, 1445 (1987); **49**, 369(E) (1988).
[29]S. F. Edwards and P. Singh, Faraday Trans. 2 **75**, 1001 (1979).
[30]M. K. Kosmas and K. M. Freed, J. Chem. Phys. **68**, 4878 (1978).