# Flory Approach to the Enhancement Factor in Polymer Statistics

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Using the new concept of survival probability we generalize the Flory approach to compute the second independent exponent in polymer statistics with excluded volume. We obtain $\gamma = 3 - d\nu$; and for the $\theta$ point, $\gamma^{\theta} = 2(2 - \nu^{\theta} d)$. These results bring to completion the mean-field theory for the exponents of polymer statistics.

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The Flory approach is a very successful method for the calculation of the exponent $\nu$ in polymer statistics with excluded volume.[1] This exponent relates the mean end-to-end distance $R$ to the number of monomers $N$: $R \sim N^{\nu}$. The self-consistent approach of Flory gives $\nu_F = 3/(d+2)$, where $d$ is the space dimension. This result produces the correct critical dimension $d_c = 4$ and also gives extremely good values for $\nu$ at lower dimensions. For $d = 2$, $\nu_F = \frac{3}{4}$ is considered to be the exact value[2] while for $d = 3$, $\nu_F = \frac{3}{5}$ overestimates the best numerical values by about 2%.[3] Even after de Gennes has shown that the self-repelling chain (SRC) problem (also called the self-avoiding walk) belongs to the class of problems known as critical phenomena,[1] several questions remain open about the origin of the striking success of the simple Flory scheme for such a complex problem.[4] This situation is unique because no other critical exponent can be approached successfully with similar methods. In particular, considering the SRC as a critical problem there are actually two independent exponents, while the Flory approach only gives $\nu$. In this Letter we formulate a generalized Flory approach for the enhancement factor of polymer statistics from which an expression for the second independent exponent $\gamma$ can be derived. The approach is inspired by the new concepts recently introduced in kinetic walk problems[5] and polymer statistics.[6,7] We obtain $\gamma = 3 - d\nu$, and for the $\theta$ point, $\gamma^{\theta} = 2(2 - \nu^{\theta} d)$. These results provide the first complete picture for the exponents of the SRC in terms of a self-consistent Flory approach. Their validity and their implications with respect to the approximations involved in self-consistent methods for critical phenomena will be briefly discussed.

The total number of self-repelling chains of $N$ steps has the asymptotic form (at large $N$)[1]

$$Z_N \simeq \tilde{z}^N N^{\gamma - 1}. \tag{1}$$

The term $\tilde{z}$ represents the "effective" number of available neighbors at each step. The factor $N^{\gamma-1}$ is called the enhancement factor and represents a correction to the leading term $\tilde{z}^N$. The interesting feature about this correction term is that its behavior is governed by the universal exponent $\gamma \geq 1$ while the term $\tilde{z}$ in the leading factor is not universal.

In the following we are going to describe Eq. (1) in terms of the survival probability of random walks. This means that we consider all the possible unrestricted random walks of $N$ steps and then we select only those that do not contain any self-intersection.[6,7] The total number of random walks of $N$ steps is (in a lattice with coordination $z$) $z^N$. The survival probability for a walk of $N$ steps is then

$$S_N \simeq (1/z^N) Z_N \simeq (\tilde{z}/z)^N N^{\gamma - 1}. \tag{2}$$

Within the assumption of a single relevant scaling length $R \sim N^{\nu}$, the probability distribution for the end-to-end distance $r$ of a generalized random walk can be written, with the use of standard notations, as[1]

$$P_N(r) \simeq (1/R^d) f_p(r/R), \tag{3}$$

$$f_p(x) \simeq f_1(x) e^{-x^{\delta}}, \quad \delta = (1-\nu)^{-1}, \tag{4}$$

and

$$\lim_{x \to 0} f_1(x) \simeq x^g. \tag{5}$$

The exponent $g$ is linked to $\gamma$ and $\nu$ by the des Cloiseaux relation[1]

$$g = (\gamma - 1)/\nu. \tag{6}$$

Consider a walk that has survived $N$ steps; the probability to be trapped at the next step is given by the product of the probability to encounter another portion of the walk and the conditional probability that this encounter leads to a trap. For scaling properties only the encounter probability is of relevance; the other term plays essentially the role of an irrelevant prefactor.[6] The probability that addition of one step to a walk that has survived $N$ steps leads to an encounter with a portion of the walk that is distant exactly $\tilde{N}$ steps ($1 \leq \tilde{N} \leq N$) from the tip is given by the probability to return to the origin for a reduced walk of $\tilde{N}$ steps. From Eq. (3) this probability is

$$P_{\tilde{N}}(r=1) \simeq (1/\tilde{R}^d) f_p(1/\tilde{R}), \quad \tilde{R} \simeq \tilde{N}^\nu, \tag{7}$$

and since $1/\tilde{R} \ll 1$, we can use the asymptotic expression of Eq. (5) to obtain

$$P_{\tilde{N}}(1) \simeq \tilde{N}^{-\nu(d+g)}. \tag{8}$$

The probability $p(N)$ to encounter some portion of the walk, no matter at what distance $\tilde{N}$ from the tip, is then given by the sum of $P_{\tilde{N}}(1)$ over all the possible values of $\tilde{N}$:

$$p(N) = \sum_{\tilde{N}=1}^{N} P_{\tilde{N}}(1) \simeq \int_1^N d\tilde{N}\, P_{\tilde{N}}(1) \simeq [-N^{-\nu(d+g)+1}]_1^N, \tag{9}$$

where the minus sign as the prefactor of the right-hand side is due to the fact that $-\nu(d+g)+1<0$. We can check at the end that this is consistent with the results obtained.

We can rewrite Eq. (9) in the more convenient form

$$p(N) = p(\infty) - \Delta p(N), \tag{10}$$

where

$$p(\infty) = \int_1^\infty d\tilde{N}\, P_{\tilde{N}}(1) \tag{11}$$

is an asymptotic encounter probability of order of unity, and

$$\Delta p(N) = \int_N^\infty d\tilde{N}\, P_{\tilde{N}}(1) \simeq N^{-\nu(d+g)+1}. \tag{12}$$

The physical meaning of these two terms is the following: The term $p(\infty)$ refers to the encounter probability for a walk of infinite length, while $\Delta p(N)$ *gives the correction due to the fact that the length of the walk is actually N.* We are going to see in the following how the enhancement factor is directly linked to this correction.

We now follow a walk from its start $n=1$ until it reaches $n=N$ and compute its total survival probability. At a given length $n$ the encounter (and trapping) probability is of order $p(n)$ so that the survival probability is $1-p(n)$. The total survival probability $S_N$ is then the product of all these terms:

$$S_N = \prod_{n=1}^{N} [1-p(n)] = \prod_{n=1}^{N} [1-p(\infty)+\Delta p(n)]. \tag{13}$$

It is convenient to introduce $x(n)$ such that

$$[1-p(\infty)]x(n) = [1-p(\infty)+\Delta p(n)]; \tag{14}$$

this gives

$$x(n) = 1 + \Delta p(n)/[1-p(\infty)]. \tag{15}$$

Equation (13) can then be written as

$$S_N = \prod_{n=1}^{N} [1-p(\infty)]x(n) = [1-p(\infty)]^N \prod_{n=1}^{N} x(n), \tag{16}$$

and in the limit $N \gg 1$ we have

$$S_N \simeq e^{-p(\infty)N} \prod_{n=1}^{N} x(n). \tag{17}$$

By comparing Eq. (17) with Eq. (2) we can make the identification

$$p(\infty) = \ln(z/\tilde{z}), \tag{18}$$

which enlightens the asymptotic meaning of $\tilde{z}$: The use of the same $\tilde{z}$ at each step corresponds to the "effective" number of available sites for an infinite chain. The term

$$f_N = \prod_{n=1}^{N} x(n) \simeq N^{\gamma-1} \tag{19}$$

corresponds to the enhancement of the survival probability due to the fact that the chain is actually finite at each step. The requirement that $f_N$ behaves asymptotically as a power law implies that

$$df_N/dN \simeq (1/N) f_N \simeq f_{N+1} - f_N \tag{20}$$

and from Eq. (19) we have

$$f_{N+1} - f_N = f_N [x(N+1)-1] = f_N \frac{\Delta p(N+1)}{[1-p(\infty)]}. \tag{21}$$

This implies the scaling condition

$$\Delta p(N) \sim N^{-1}, \tag{22}$$

which together with Eq. (12) leads to the relation

$$\nu(d+g) = 2, \tag{23}$$

which corresponds to $g = \alpha/\nu$, where $\alpha$ is the characteristic exponent of closed self-avoiding loops.[1] By using the des Cloiseaux relation [Eq. (6)] we can rewrite Eq. (23) as

$$\gamma = 3 - d\nu, \tag{24}$$

which is our main result. We first note that this expression shows the correct behavior at the critical dimension. In fact for $d = d_c = 4$ and $\nu = \frac{1}{2}$, Eq. (24) gives $\gamma = 1$. For lower dimensions we can use $\nu \simeq \nu_F = 3/(2+d)$ to obtain

$$g_F = (4-d)/3, \tag{25}$$

and

$$\gamma_F = 2\nu_F = 6/(2+d). \tag{26}$$

We can see that for $d=3$ these expressions give extremely good values: $g_F(d=3)=\frac{1}{3}$ corresponds to the best numerical estimates[1] and $\gamma_F(d=3)=1.2$ is about 3% larger than the best numerical estimates.[1] The situation is not as good for $d=2$ because $\gamma_F(d=2)=1.5$ is about 10% larger than the conjectured exact value $\gamma=\frac{43}{32}$.[2] From the point of view of critical phenomena we note that Eq. (26) corresponds to $\eta=0$, where $\eta$ is the correlation-function exponent.[1] This fact may help in clarifying the limits of self-consistent approaches for critical phenomena, a point that we intend to discuss in more detail elsewhere.[8]

The previous concepts can be used also to derive $\gamma^\theta$ corresponding to the $\theta$ point. To this purpose it is useful first to rederive Eq. (24) with the explicit use of the coil density $\rho(N)$:

$$\rho(N) \simeq N/V \simeq NR^{-d} \simeq N^{1-\nu d}. \tag{27}$$

Given a walk that has survived $N$ steps we make $\Delta N$ more steps. We assume that in each step the correction for using $p(\infty)$ instead of $p(N)$ is of the order of $\rho(N)$.[9] This gives for the enhancement factor

$$f_{N+\Delta N} = f_N[1+\rho(N)]^{\Delta N} \simeq f_N[1+\rho(N)\Delta N] \tag{28}$$

and

$$\Delta f_N = (df_N/dN)\Delta N \simeq \rho(N)\Delta N, \tag{29}$$

so that

$$df_N/dN \simeq \rho(N). \tag{30}$$

This relation can be used in two ways: (a) From Eqs. (20) and (21) we have

$$df_N/dN \simeq f_N \Delta p(N) \simeq \rho(N). \tag{31}$$

Using $f_N \simeq N^{\gamma-1}$, $\Delta p(N) \simeq N^{-\nu(d+g)+1}$, and $\rho(N) \simeq N^{1-\nu d}$, we recover the des Cloiseaux relation $g=(\gamma-1)/\nu$. (b) From Eq. (19) we also have

$$df_N/dN \simeq N^{\gamma-2}, \tag{32}$$

which, when used in Eq. (30), gives us back $\gamma = 3-d$.

At the $\theta$ point the effect of first-order encounters is exactly canceled by the attractive interaction. The "effective" encounter probability is then proportional to $\rho^2(N)$ instead of $\rho(N)$.[6,9] This changes Eq. (30) into

$$df_N/dN \simeq \rho^2(N) \tag{33}$$

and therefore

$$N^{\gamma-2} \simeq \rho^2(N). \tag{34}$$

This relation leads to

$$\gamma^\theta = 2(2-\nu^\theta d). \tag{35}$$

Also here we obtain the correct behavior at the critical dimensionality which for the $\theta$ point is $d_c=3$: $\gamma^\theta(d=3)=1$. For $d=2$ and for $\nu_F^\theta(d=2)=\frac{2}{3}$ we obtain $\gamma^\theta(d=2)=\frac{4}{3}$ which, in view of the discussion following Eq. (26), should be considered as an upper limit for the real value. This is true because also in this case our relation corresponds to $\eta^\theta=0$.

In summary, we have shown that the concept of survival probability allows one to frame a Flory approach to the enhancement factor, bringing to completion the mean-field picture for the exponents of polymer statistics. This will hopefully enlighten the roots of these types of approximation also with respect to their applications to other physical phenomena.

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[9]The first-order trapping probability is of the order of $\rho$ as discussed in Ref. 6. The assumption here is that the correction term is related to a fraction of this probability, and so it is still of order $\rho$. At the $\theta$ point the situation is analogous with respect to the second-order trapping probability that is of the order of $\rho^2$.