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Partition function of a continuous polymer chain: a study of its anomalous behaviour in three dimensions

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Résumé. Les polymères en bon solvants peuvent être représentés par des courbes continues dans un espace continu de dimension $d$ ($d = 3$). Dans ce cas, toutes les quantités physiques peuvent être développées en puissances de l'interaction qui peut être réduite à une constante sans dimension $z$. Cependant, on montre que pour $d = 4 - 2/p$ ($p$ entier), la fonction de partition d’un polymère (ou d’un ensemble de polymères) ne peut pas être développée en puissances de $z$ seul, mais possède un double développement singulier en puissances de $z$ et $\ln z$. On analyse la nature et les effets de cette singularité (qui paraît plus formelle que physique).

Abstract. Polymers in good solvents can be represented by continuous curves in a continuous space of dimension $d$ ($d = 3$). In this case, all physical quantities can be expanded in powers of the interaction which can be reduced to a dimensionless parameter $z$. However it is shown that for $d = 4 - 2/p$ ($p$ integer) the partition function of a polymer cannot be expanded in terms of $z$ alone but has a singular double expansion in powers of $z$ and $\ln z$. The nature and the effects of this singularity (which are apparently more formal than physical) are analysed.

1. Introduction. To derive, in an analytical way, the properties of long polymers in solutions, it is convenient to represent a polymer chain by a continuous curve in a space of dimension $d$. In this case, the number of configurations of a chain is infinite. It is however possible to define finite partition functions by using proper renormalization schemes. Unfortunately the renormalization process itself is sometimes the source of new difficulties.

In the present article, we show that for special values of $d$, namely $d = 4 - 2/p$ where $p$ is an integer, the expansion of a partition function with respect to the «dimensionless coupling constant $z$» [1, 2] contains not only powers of this constant but also an infinite number of logarithmic terms.

We explain the origin of these terms and we analyse the structure of the partition functions for such values of $d$ (for instance for $d = 3$ i.e. $p = 2$). Finally we show that these anomalies do not play any role when we calculate physical quantities. Thus the anomalous terms can be discarded.

The analysis relies on the correspondence which exists [3] between our polymer model and the Landau-Ginzburg field model, when the number of components of the field goes to zero.

2. The model, the elimination of the cut-off and the appearance of logarithmic terms. The position of a point of coordinate $0 < s < S$ along the chain is given in a space of dimension $d$ by the vector $r(s)$. The statistical weight $P$ associated with a chain is a functional of the corresponding function $r(s)$. We shall write:

$$P = \exp \left[ -\frac{1}{2} \int_0^S ds \left( \frac{dr(s)}{ds} \right)^2 - \frac{\delta}{2} \int_0^S ds' \int_0^S ds'' \delta(r(s) - r(s')) \right].$$

This model has been studied in detail in a preceding article [1] (I). It has been shown how it is possible to define a partition function $\mathcal{Z}(S)$, the symbol + indicating that a cut-off is needed; thus to equation (1), we add the restriction $|s' - s''| > s_0$. It has been shown that this cut-off can be eliminated by a simple short range (ultraviolet) renormalization. In this way, we define the partition function $\mathcal{Z}(S)$ which depends only on the dimensionless parameter $z$

$$z = BS^{\varepsilon/2}$$

where $B = b(2\pi)^{-d/2}$ and $\varepsilon = 4 - d$. 

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The same process applies to other « restricted » partition functions and therefore all the physical quantities can be expanded in powers of $z$ as was shown in the classical book by Yamakawa [2].

However for $d = 3$ and, more generally, when $d = 4 - 2/p$ ($p$ = integer), an anomaly occurs: in the expansion of $\mathcal{Z}(S)$, logarithmic terms of the form $z^{q_1}(\ln z)^{q_2}$ appear. This phenomenon is related to the renormalization process, and, in the following, we explain how this occurs.

In I, we have shown that $\mathcal{Z}(S)$ can be expressed as a sum of contributions represented by one-chain diagrams (see Fig. 1). Each polymer segment and each interaction line carries a wave vector; moreover each polymer segment has an « area » $s_j$. To calculate the contribution of a diagram, we have to integrate, over all internal independent wave vectors, a product of terms of the form $e^{-s_j k_j^2}$ where $k_j$ is the wave vector carried by the segment $j$.

In this way, we obtain a function of the « areas » $s_j$ of the polymer segments which appear on the diagram (see Fig. 1). In a one-chain diagram of order $q$, we have $(2q + 1)$ segments of areas $s_1, \ldots, s_{2q+1}$ and we have \( \sum_{j=1}^{2q+1} s_j = S \). Now, we may set $s = s_2 + \cdots + s_{2q}$.

In I, we showed that we could renormalize step by step the internal divergencies. All the integrals are convergent except the last one which is of the form (here $\varepsilon = 4 - d > 0$):

\[
B^q \int_{s_0}^S \frac{ds}{s^{3q/2}}. \tag{3}
\]

This is a direct consequence of the fact that $\mathcal{Z}(S)$ and therefore expression (3) must be dimensionless (see I), and that $B^q \varepsilon^{q/2}$ is dimensionless (see equations (1), (2)).

The interesting part of the preceding integral is

\[
I_q = B^q S \int_{s_0}^S \frac{ds}{s^{3q/2}} \tag{4}
\]

since the remaining part in equation (3) has always a finite limit when $s_0 \to 0$.

Now let us consider various situations. If $\varepsilon q \neq 2$, we may write:

\[
I_q = - \frac{(B S^{q/2})^q}{1 - q\varepsilon/2} + \frac{S}{s_0} \frac{(B S_0^{q/2})^q}{1 - q\varepsilon/2}. \tag{5}
\]

If $\varepsilon q > 2$, the second term vanishes when $s_0 \to 0$; and the first term remains alone.

If $\varepsilon q < 2$, the second term becomes infinite when $s_0 \to 0$, but as was shown in I, the second term can be eliminated by renormalization and the first term remains alone. In both cases, after renormalization, $I_q$ is transformed into $I_{R,q}$ where

\[
I_{R,q} = - \frac{(B S^{q/2})^q}{1 - q\varepsilon/2} = \frac{z_q}{1 - q\varepsilon/2}. \tag{6}
\]

On the contrary, if $\varepsilon q = 2$ (i.e. $d = 4 - 2/p$ and $q = p$), we have:

\[
I_p = B^p \int_{s_0}^S \frac{ds}{s} = B^p S \ln (S/s_0).
\]

Thus setting

\[
z_0 = B s_0^{q/2}
\]

we may write

\[
I_p = pB^p S \ln z - pB^p S \ln z_0.
\]

The second term can be eliminated by renormalization.

In this way, $I_p$ is transformed into $I_{R,p}$

\[
I_{R,p} = p(B S^{q/2})^p \ln z = p z^{q} \ln z \quad (2/\varepsilon = p). \tag{7}
\]

We see now how logarithmic terms appear. We note that, in the diagrams contributing to $\mathcal{Z}(S)$, there are internal parts which are divergent and which must be renormalized step by step. As a consequence, logarithmic terms are now introduced by renormalization and equation (3) should be slightly modified by introducing logarithmic factors. Thus, in this case $\mathcal{Z}(S)$ is represented by a series of terms of the form $z^{q_1}(\ln z)^{q_2}$ where $q_1$ and $q_2$ are integers.

It is however clear that logarithms occur only by accident. We feel that it must be possible to sum up these anomalous terms, and in the following section, we shall find out how this can be done.

3. Perturbation expansions for the polymer model and for the corresponding Landau-Ginzburg model in the non-singular case ($d \neq 2 - 2/p$). — A more precise analysis of the anomalous behaviour of $\mathcal{Z}(S)$ can
be made by examining the situation in the framework of the corresponding Landau-Ginzburg model. This model can be defined by the Lagrangian

\[ f = \frac{1}{2} \sum_{j=1}^{n} \left[ \frac{4}{2} \sum_{i=1}^{d} (\partial_i \varphi_j)^2 + a(\varphi_j)^2 \right] + b \left( \sum_{j=1}^{n} \varphi_j^2 \right)^2. \]  

(8)

Let us call \( g(k; a) \) the Green's function of wave vector \( k \). The corresponding quantity in the polymer model is the Fourier transform \( \overline{g}(k; S) \) of the partition function \( g(r; S) \) of the chains which start from the origin and end at the point of vector \( r \).

In the limit \( n \to 0 \), the correspondence between the polymer model and the Landau-Ginzburg model is given by de Gennes' transformation

\[ \overline{g}(k, a) = \int_0^\infty dS \, e^{-as} \, \overline{g}(k; S) \]  

(9)

\(+ = \text{plus cut-off}.\)

In the following, we shall apply this transformation to the quantities

\[ g(a) = g(0; a) \]

\[ \overline{g}(S) = \overline{g}(0; S). \]

The unperturbed Green's function is

\[ g_0(k; a) = \frac{1}{a + k^2/2} \]  

(10)

and the critical value of \( a \) is \( a_c \), which is cut-off dependent. Thus, it would be very awkward to expand \( g(k; a) \) in terms of the dimensionless parameter \( b(1-a) - v/2 \). It would be better to introduce proper counter terms and to expand \( g(k; a) \) in terms of \( b(a - a_c)^{-v/2} \).

However, the best method consists in introducing adequate counterterms, so as to use, as unperturbed Green's function, the quantity

\[ g_1(a; k) = \frac{1}{a_b + k^2/2} \]  

(11)

where \( 1/a_b = g(0) \) is the exact (bare) value of the Green's function at zero wave vector. In this way all the short range (ultraviolet) divergencies, in the diagrams are eliminated. The expansions are now written in terms of the dimensionless parameter \( B a_b^{-v/2} \). Of course, it is also necessary to find a relation between \( a \) and \( a_b \). Actually, it can be shown \([4]\) that \( da_g/da \) is given by a series of convergent diagrams. This expansion can be written in the form

\[ \frac{da}{da_b} = 1 + \sum_{q=1}^{\infty} A_q \left( B a_b^{-v/2} \right)^q. \]  

(12)

We see immediately that if we have \( qe \neq 2 \) for all \( q \), we may integrate the preceding equation:

\[ a - a_c = a_b \left[ 1 + \sum_{q=1}^{\infty} A_q \left( 1 - qe/2 \right) \left( B a_b^{-v/2} \right)^q \right]. \]  

(13)

This series can be inverted and we may write

\[ \frac{1}{a_b} = \frac{1}{a - a_c} \left[ 1 + \sum_{q=1}^{\infty} 3_q \left( B(a - a_c)^{-v/2} \right)^q \right]. \]  

(14)

Now, we note that \( \overline{g}(S) \) is given by the inverse Laplace transform:

\[ \overline{g}(S) = \frac{1}{\pi} \int_{-\infty}^{\infty} da \, e^{as}(a_b)^{-1} \]  

(15)

(\( c > a_c \)).

In this case we obtain

\[ \overline{g}(S) = e^{a_S} \overline{g}(S) \]

with

\[ \overline{g}(S) = 1 + \sum_{q=1}^{\infty} \frac{\overline{B}_q}{(qe/2)!} (B S^{1/2})^q \]

(16)

i.e. an expansion of \( \overline{g}(S) \) in powers of \( z \). We may recall however that this series is only formal and non-convergent.

4. A study of the anomalous perturbation expansions in the singular case \((d = 4 - 2/p)\). — The situation is completely different, when there exists an integer \( p \) such that \( p \epsilon = 2 \). In particular, this situation occurs for \( d = 3 \) and \( p = 2 \).

Let us examine the situation when

\[ d = 4 - \frac{\epsilon}{p} \]

where \( \eta \) is small.

In this case, equation (13) reads

\[ a - a_c = A_p \frac{B^p a_b^p}{\eta} \]

\[ + a_b \left[ 1 + \sum_{q=1}^{\infty} \frac{A_q}{1 - qe/2} \left( B a_b^{-1/2} \right)^q \right]. \]

We may set

\[ a_0 = a_c + A_p \frac{B^p(1 + \eta)}{\eta}. \]  

(17)

Passing to the limit \( \eta \to 0 \), we find

\[ a - a_0 = A_p B^p \ln(a_b B^{-1/p}) + \]

\[ + a_b \left[ 1 + \sum_{q=1}^{\infty} \frac{A_q}{1 - qe/2} \left( B a_b^{-1/2} \right)^q \right]. \]  

(18)

The effect of the logarithmic term can be properly analysed by using \( a_b \) instead of \( a \) as the integration variable in the expression of \( \overline{g}(S) \). Thus, equation (15) will be written as follows

\[ \overline{g}(S) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{da_b}{a_b} \left( \frac{da}{da_b} \right) e^{a_S} \]
or after partial integration

\[ +Z(S) = \frac{1}{2\pi i} \int_{cB-i\infty}^{cB+i\infty} \frac{daB}{S^2aB} e^{SaB}. \]

In this integral, let us express « a » as a function of « aB »:

\[ +Z(S) = e^{S\theta_0} \sum_{q=1}^{\infty} \frac{A_q}{1-q\theta/p} \times \exp \left\{ SA_B \left[ 1 + \sum_{q=1}^{\infty} \frac{A_q}{1-q\theta/p} (BA_B^{-1}p)^q \right] \right\}. \quad (19) \]

Noting that, in this case \( z = BS^1/p \), we define a renormalized partition function \( \bar{Z}(S) \) by setting

\[ +Z(S) = e^{S\theta_0} z^{-pA_B z^p} \bar{Z}(S). \quad (20) \]

We obtain from equation (19):

\[ \bar{Z}(S) = \frac{1}{2\pi i} \int_{cB-i\infty}^{cB+i\infty} \frac{d\theta}{\theta^2} e^{pA_B z^p} \times \exp \left\{ \theta + \sum_{q=1}^{\infty} \frac{A_q}{1-q\theta/p} \theta^{1-q/p} \right\}. \quad (21) \]

In this way, the anomalous part of \( +Z(S) \) can be isolated. Unfortunately, equation (21) is not very satisfactory. To find an expansion of \( \bar{Z}(S) \), we might be tempted to expand the term

\[ \exp \left\{ \sum_{q=1}^{\infty} \frac{A_q}{1-q\theta/p} \theta^{1-q/p} \right\} \]

in powers of \( \theta \). However, the preceding exponential contains positive powers of \( \theta \) namely \( A_1 \theta^{1-1/p}, ..., A_{p-1} \theta^{1-(p-1)/p} \) which are unpleasant. By expanding the exponential of the sum of these terms, we generate powers of \( \theta^n \) (with \( n \geq 0 \)), where \( n \) may be very large, and strictly speaking, these terms have no Laplace transforms.

Therefore an expansion of this kind cannot be used for transforming equation (21).

The appearance of unpleasant terms in the exponential is not related to the anomaly. By applying the same method to the normal case \( (d \neq 4 - 2/p) \), we find the equation:

\[ +Z(S) = e^{S\theta_0} \int_{cB-i\infty}^{cB+i\infty} d\theta \theta^{-2} \times \exp \left\{ \theta + \sum_{q=1}^{\infty} \frac{A_q}{1-q\theta/p} \theta^{1-q/2} \right\} \]

which has the same defects.

To avoid this difficulty, we may transform equation (20) again, in order to obtain an expression similar to the initial formula.

We set

\[ \theta = \theta(t) \]

where \( \theta(t) \) is defined by the implicit formula

\[ t = \theta(t) = \theta \left[ 1 + \sum_{q=1}^{\infty} A_q z^{q\theta/p} \right]. \quad (22) \]

By partial integration, equation (21) gives:

\[ \bar{Z}(S) = \frac{1}{2\pi i} \int_{cB-i\infty}^{cB+i\infty} \frac{d\theta}{1-A_p z^p} \times \exp[t(\theta)]. \]

and by changing the integration variable

\[ \bar{Z}(S) = \int_{cB-i\infty}^{cB+i\infty} dt e^{\theta(t)}, \quad (23) \]

This equation is somewhat similar to equation (15).

By inverting equation (22), we can calculate a series expansion of \( \theta(t) \) with respect to \( t \). Finally, we may write

\[ [\theta(t)]^p z^t - 1 = t^p z^t - 1 \left[ 1 + \sum_{q=1}^{\infty} C_q z^{q\theta/p} \right]. \quad (24) \]

We know that

\[ \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} dt e^{t} t^{-n-1} = \frac{1}{n!}. \]

Therefore equations (23) and (24) give

\[ \bar{Z}(S) = \int_{cB-i\infty}^{cB+i\infty} dt e^{\theta(t)}, \quad (25) \]

All factorials can be expanded in powers of \( z^p \). Thus \( \bar{Z}(S) \) is given in terms of \( z \) by a power series.

We recall now that the unrenormalized partition function \( +Z(S) \) is given by:

\[ +Z(S) = e^{S\theta_0} z^{-pA_B z^p} \bar{Z}(S) \]

\[ = e^{S\theta_0} (B^p S)^{-pA_B z^p} \bar{Z}(S). \quad (26) \]

This formula determines the singularity of \( +Z(S) \) for small values of \( z \) when \( d = 4 - 2/p \).
On the other hand, in section 2, we described a renormalization process which applies when \( d = 4 - 2/p \); this process transforms \( \mathcal{Z}(S) \) into a renormalized partition function \( \mathcal{Z}(S) \) which is given by

\[
\mathcal{Z}(S) = z^{-p A_{a} x^{p}} \mathcal{Z}_{r}(S). \tag{27}
\]

5. Discussion and conclusion. — In this article, we have shown that for \( d = 4 - 2/p \) (\( p \) = integer), \( \mathcal{Z}(S) \) has a singularity which is given by equation (27) and that the existence of this singularity is related to a short range renormalization process which is described in (I) as the second renormalization. This renormalization does not apply only to \( \mathcal{Z}(S) \) but to all partition functions of a polymer or of a set of polymers. Let us consider for instance \( p \) polymers of areas \( S_1, ..., S_N \) and let us assume that they are subjected to a constraint \( C \). We may expect that the corresponding « restricted partition » functions \( \mathcal{Z}(C; S_1, ..., S_N) \) has the same singularities as the product \( \mathcal{Z}(S_1) ... \mathcal{Z}(S_N) \).

This explains why the anomaly should not appear in physical quantities because these quantities always depend on expressions of the form:

\[
\frac{\mathcal{Z}(C; S_1, ..., S_N)}{\mathcal{Z}(S_1) ... \mathcal{Z}(S_N)}.
\]

Thus, in the book by Yamakawa [2], various physical quantities are expanded with respect to the interaction for \( d = 3 \), and we verify that, in all cases, these quantities are represented by simple power series in \( z \) (without logarithms).

Finally we remark that several expansions concerning Landau-Ginzburg theory, have been calculated directly [4] for \( d = 3 \); until now these results have been used in polymer physics only to derive critical exponents; other applications are possible and the present analysis may be helpful in this respect.

References
