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Long polymers in good solvent : ε -expansion of the ratio of the radius of gyration to the end to end distance

M. Benhamou and G. Mahoux

Service de Physique Théorique, CEN-Saclay, 91191 Gif-sur-Yvette Cedex, France

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Résumé. — Le rapport du rayon de giration à la distance carrée moyenne bout à bout pour une longue chaîne isolée est donné au second ordre en $\varepsilon = 4 - d$, où d est la dimension de l'espace. Notre méthode de calcul est basée sur le concept de renormalisation directe introduit par J. des Cloizeaux. A trois dimensions ($\varepsilon = 1$), notre résultat peut être comparé au résultat numérique obtenu par C. Domb et F. F. Hioe.

Abstract. — The ratio of the radius of gyration to the mean square end to end distance of an isolated long chain is given to second order in $\varepsilon = 4 - d$, where d is the space dimension. Our method of calculation is based on the direct renormalization idea introduced by J. des Cloizeaux. In dimension three ($\varepsilon = 1$), our result can be compared with the result of computer experiments made by C. Domb and F. F. Hioe.

1. Introduction.

The ratio of the radius of gyration to the mean square end to end distance of an isolated chain is a finite quantity having a universal character in the long chain limit. Our aim here, is to calculate this ratio to second order in $\varepsilon = 4 - d$. The strategy consists in making the calculation near dimension four, and extending the result to dimension three ($\varepsilon = 1$). The model is the continuous one [1, 2, 3] in which a polymer in a good solvent is represented by a Brownian chain with local interaction. In the framework of this model, a chain is considered as a continuous curve in a continuous space of dimension d . A point on the chain is given by a vector $\mathbf{r}(s)$ ($0 < s < S$), where the parameter s marks the position of this point on the chain (in terms of discrete chain s is proportional to the number of links), and the quantity S is the area of the Brownian chain.

The mean square end to end distance of an isolated chain is defined by

$$R^2 = \langle [\mathbf{r}(S) - \mathbf{r}(0)]^2 \rangle$$

and the radius of gyration by :

$$R_G^2 = \frac{1}{2S^2} \int_0^S ds_1 \int_0^S ds_2 \langle [\mathbf{r}(s_2) - \mathbf{r}(s_1)]^2 \rangle$$

2. Calculations and result.

The mean values which appear in the above formulae can be expressed in terms of partition functions as follows :

$$\langle [\mathbf{r}(S) - \mathbf{r}(0)]^2 \rangle = \frac{-2d}{Z(S, b)} \frac{\partial}{\partial k^2} Z(\mathbf{k}, -\mathbf{k}; S, b) |_{\mathbf{k}=\mathbf{0}},$$

$$\langle [\mathbf{r}(s_1) - \mathbf{r}(s_2)]^2 \rangle = -\frac{2d}{Z(S, b)} \frac{\partial}{\partial k^2} Z(\mathbf{k}, -\mathbf{k}; s_1, s_2; S, b) |_{\mathbf{k}=\mathbf{0}}.$$

Here, $Z(S, b)$ is the partition function of one polymer; $Z(\mathbf{k}, -\mathbf{k}; S, b)$ is the partition function of one polymer with two insertions of wave vectors \mathbf{k} and $-\mathbf{k}$ respectively at the origin and extremity of the chain; $Z(\mathbf{k}, -\mathbf{k}; s_1, s_2; S, b)$ has the same definition as $Z(\mathbf{k}, -\mathbf{k}; S, b)$, except that the wave vectors \mathbf{k} and $-\mathbf{k}$ are injected at two points of coordinates s_1 and s_2 along the chain.

The three partition functions $Z(S, b)$, $Z(\mathbf{k}, -\mathbf{k}; S, b)$ and $Z(\mathbf{k}, -\mathbf{k}; s_1, s_2; S, b)$ are expanded with respect to the coupling constant b . The diagrams that contribute up to second order in b to the two first partition functions are exhibited in figure 1. To the same order in b , the diagrams that contribute to the third partition function are those of figure 1 modified by two insertions in all possible positions.

Actually, we need the perturbation expansion of $Z(S, b)$ only to first order. We write :

$$Z(S, b) = 1 + Z_1(z) + \mathbf{O}(z^2),$$

where z is the dimensionless parameter

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

Similarly, R^2 and R_G^2 can be written :

$$R^2 = dS [1 - I_1 - I_2 - I_3 - I_4 + Z_1 I_1 + \mathbf{O}(z^3)],$$

$$R_G^2 = dS \left[\frac{1}{6} - J_1 - J_2 - J_3 - J_4 + Z_1 J_1 + \mathbf{O}(z^3) \right],$$

where the 8 quantities $I_1, \dots, I_4, J_1, \dots, J_4$, functions of the only parameter z , have an index running from 1 to 4, referring to one of the 4 diagrams of figure 1.

One knows that at any (non necessarily integer) dimension d less than 4, R^2 and R_G^2 are divergenceless quantities. Accordingly, we need not introduce any cut-off in our calculation as long as

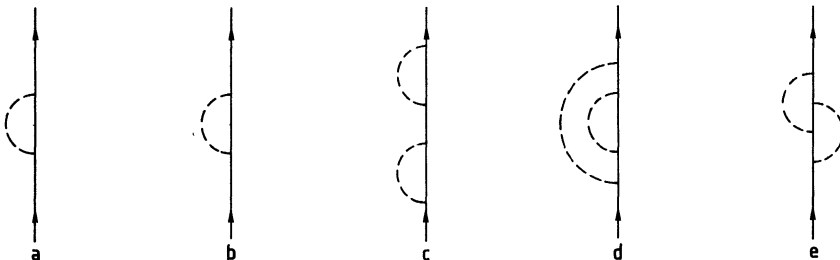


Fig. 1. — Diagrams of first and second order contributing to $Z(S, b)$ and $Z(\mathbf{k}, -\mathbf{k}; S, b)$.

$d < 4$. However, Z_1, I_2, I_3, J_2 and J_3 exhibit simple poles at $d = 2$. We have checked that the particular combinations $I_2 + I_3 - Z_1 I_1$ and $J_2 + J_3 - Z_1 J_1$ that enter the expressions of R^2 and R_G^2 are pole free, as expected.

The ratio R_G^2/R^2 now reads

$$\frac{R_G^2}{R^2} = \frac{1}{6} \left\{ 1 + \sum_{D=1}^4 (I_D - 6 J_D) + (I_1 - Z_1)(I_1 - 6 J_1) + \mathbf{O}(z^3) \right\}. \tag{1}$$

The 3 first order quantities Z_1, I_1 and J_1 have a simple pole at $d = 4$, whereas the 6 second order ones, I_2, \dots, J_4 , have double poles. We have observed that the combinations $I_D - 6 J_D (D=2, 3, 4)$ have only simple poles at $d = 4$, and that $I_1 - 6 J_1$ is pole free. For the various quantities appearing in equation (1), we have obtained the following $\varepsilon (= 4 - d)$ expansions :

$$\begin{aligned} I_1 - Z_1 &= -\frac{4z}{\varepsilon} + \mathbf{O}(\varepsilon), \\ I_1 - 6 J_1 &= -\frac{z}{12} \left[1 - \frac{5\varepsilon}{12} + \mathbf{O}(\varepsilon^2) \right] \\ I_2 - 6 J_2 &= z^2 \left[\frac{1}{3\varepsilon} - \frac{17}{18} + \mathbf{O}(\varepsilon) \right], \\ I_3 - 6 J_3 &= z^2 \left[-\frac{1}{2\varepsilon} + \frac{11}{12} + \mathbf{O}(\varepsilon) \right], \\ I_4 - 6 J_4 &= z^2 \left[\frac{1}{2\varepsilon} - \frac{1}{24} - \frac{5\xi}{6} + \mathbf{O}(\varepsilon) \right], \end{aligned}$$

where ξ is defined by

$$\begin{aligned} \xi &= \frac{2\pi}{\sqrt{3}} \log \frac{4}{3} - 6 \int_0^1 du \frac{\log(1-u^2)}{1+3u^2} \\ &= 2.343\ 907\ 235\dots \end{aligned}$$

This gives for the ratio R_G^2/R^2 the following double expansion :

$$\frac{R_G^2}{R^2} = \frac{1}{6} [1 + A_1 z + A_2 z^2 + \mathbf{O}(z^3)], \tag{2}$$

with

$$\begin{aligned} A_1 &= -\frac{1}{12} \left[1 - \frac{5}{12} \varepsilon + \mathbf{O}(\varepsilon^2) \right], \\ A_2 &= \frac{2}{3\varepsilon} - \frac{5}{6} \left(\xi + \frac{1}{4} \right) + \mathbf{O}(\varepsilon). \end{aligned} \tag{3}$$

We note that A_2 is singular at $\varepsilon = 0$.

Now, the renormalization strategy consists in dropping the variable z to the benefit of a more physical quantity g , which is (essentially) the second virial coefficient. This can be done by using the expansion of z in terms of g [3] :

$$z = g + \frac{g^2}{\varepsilon} [8 - (2 + 4 \text{Ln } 2) \varepsilon] + \mathbf{O}(g^3).$$

This expansion is also singular at $\varepsilon = 0$. Inserting it in equations (2) and (3), we obtain :

$$\frac{R_G^2}{R^2} = \frac{1}{6} \left[1 - \frac{1}{12} \left(1 - \frac{5\varepsilon}{12} \right) g + \frac{1}{6} \left(\frac{17}{12} + 2 \text{Ln } 2 - 5\xi \right) g^2 + \mathbf{O}(g^3) \right]$$

and we observe that the singularity at $\varepsilon = 0$ has now disappeared.

This is in agreement with the fact that relations between physical quantities should remain meaningful up to dimension 4.

Finally, when $z \rightarrow \infty$ (Kuhnian chain limit), $g \rightarrow g^*$, with [3]

$$g^* = \frac{\varepsilon}{8} + \frac{\varepsilon^2}{16} \left(\frac{25}{16} + \text{Ln } 2 \right) + \mathbf{O}(\varepsilon^3).$$

In this limit the ratio R_G^2/R^2 becomes

$$\frac{R_G^2}{R^2} = \frac{1}{6} \left[1 - \frac{\varepsilon}{96} - 0.0306 \varepsilon^2 + \mathbf{O}(\varepsilon^3) \right]. \quad (4)$$

3. Comments.

The two first terms of the ε -expansion of the ratio R_G^2/R^2 (Eq. (4)) have already been found by J. Des Cloizeaux [3] and by T. A. Witten *et al.* [4] who used the $n = 0$ limit of an n -component ϕ^4 field theory. For $d = 3$ ($\varepsilon = 1$) the ε^2 correction to R_G^2/R^2 gives a value of 0.159 which is to be compared to 0.165 in first order. Notice that the value of computer experiments obtained by C. Domb *et al.* [5] is equal to 0.155. The ε^2 correction provides an improvement of the first order calculation, since it yields a result closer to the value of the numerical simulation. We represent on figure 2, with respect to ε , the variation of $6 R_G^2/R^2$.

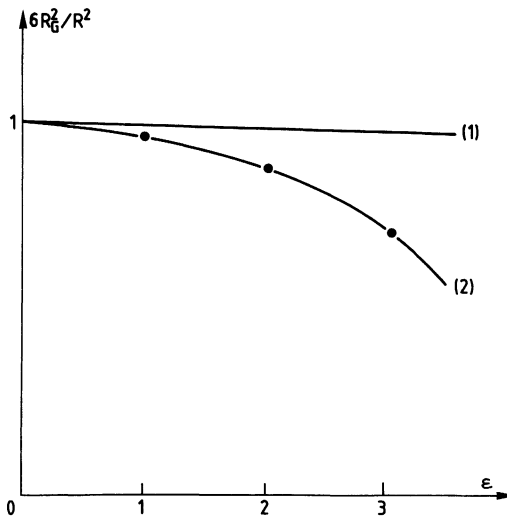


Fig. 2. — (1) The variation of $6 R_G^2/R^2$ at first order with respect to ε . (2) The variation of $6 R_G^2/R^2$ at second order with respect to ε .

Concerning this subject, we recall that Peterlin [6], Benoit [7] and Ptitsyn [8] using a simple assumption (the swelling law is uniform on the chain) have derived an approximate expression of R_G^2/R^2 :

$$\begin{aligned} \frac{R_G^2}{R^2} &= \int_0^1 dt (1-t) t^{2\nu} \\ &= \frac{1}{(2\nu+1)(2\nu+2)}. \end{aligned}$$

On the other hand the exponent ν is given by [3] :

$$\nu = \frac{1}{2} \left[1 + \frac{\varepsilon}{8} + \frac{15}{256} \varepsilon^2 + \mathbf{O}(\varepsilon^3) \right].$$

This leads to the result :

$$\frac{R_G^2}{R^2} = \frac{1}{6} \left[1 - \frac{5}{48} \varepsilon - \frac{187}{4608} \varepsilon^2 + \mathbf{O}(\varepsilon^3) \right]$$

which is really different from equation (4) and gives the value of 0.142 at $d = 3$ ($\varepsilon = 1$). Of course, we cannot believe this result since it relies on an unrealistic assumption.

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