Partition function of an isolated polymer with excluded volume interactions in dimension four

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Partition function of an isolated polymer with excluded volume interactions in dimension four

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Abstract. We have calculated the number of total configurations C of a polymer chain up to third order in the excluded volume parameter u. The results support that close to the dimensionality $d=4$ the perturbation series sums up to a simple expression which can be determined from second-order perturbation theory. The good solvent behaviour, where the statistical quantities characterising the polymer molecule show a power law dependence on the molecular weight N, is deduced from this solution. Though the critical exponents are independent of u, the prefactors depend on it. The meaning of the fixed point as that point where the exponents can be evaluated relatively easily can also be seen. The proposed expressions for C and the size of the macromolecule also describe the chain for small negative u (poor solvent) where the chain starts to shrink.

1. Introduction

The parameter $uN^{(4-d)/2}$ ($N \sim$ molecular weight of the chain) which expresses the non-idealities in the behaviour of a polymer chain decreases as the dimensionality of the system increases and the fact that $d=4$ is a critical dimensionality above which the non-idealities disappear is well established (Wilson and Kogut 1974). With the reduction of the non-idealities the difficulty in searching for a complete solution to the problem by summing up for example all perturbation order terms in u (Edwards 1975, Lax *et al* 1978) also decreases. However, the advantages from a solution at $d=4-\varepsilon$ (ε small) are large, since the continuous character of d permits the transfer of the properties of the solution to smaller realistic dimensionalities (Kosmas and Freed 1978).

In previous work we have calculated C up to second order in u at $d=4-\varepsilon\,(\varepsilon \ll 1)$ determining the critical exponents (Kosmas 1981a) as well as other properties of the coil (Kosmas 1981b). In the present work we make third-order calculations on the quantity C, the total number of configurations, which is related to the partition function and the free energy of the macromolecule, trying to see the overall behaviour of the expansion. Second-order perturbation theory at $d=4$ gives for C the expression (Kosmas 1981a)

$$C=[1-2uN+(\tfrac{1}{2})(2uN)^2-\ldots][1+2(u\ln N)-6(u\ln N)^2+\ldots]. \tag{1.1}$$

Recent results on an easier problem (Kosmas 1981c) have shown that the series in $u\ln N$ sums up exactly to a simple expression of the general form $[1+a(u\ln N)]^b$.

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For the present excluded volume problem a and b can be uniquely determined from a second-order perturbation theory. Using relation (1.1) we take that $a=8$ and $b=\frac{1}{4}$. The purpose of the present work is to check the validity of the above summation by evaluating the next third-order term of the general expression

$$C=\exp(-2uN)[1+8(u\ln N)]^{1/4}. \tag{1.2}$$

Thus one can check if the third-order perturbation results yield the third-order expansion term of the expression $[1+a(u\ln N)]^b$, $a=8$, $b=\frac{1}{4}$, which is

$$b(b-1)(b-2)a^3(u\ln N)^3/6=28(u\ln N)^3.$$

The results come out exactly as expected and the calculations are presented in § 2. In § 3 we propose an expression for the mean end-to-end square distance $\langle R^2\rangle$ and we present the conclusions of the present work. Finally in the appendix we demonstrate the evaluation of third-order diagrams.

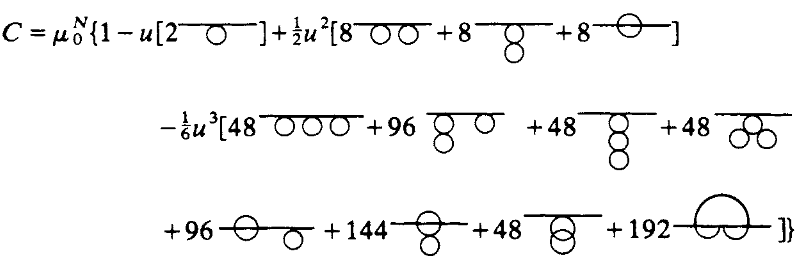
2. The total number of configurations C

The model which we are going to employ is a discrete model equivalent to the continuous model extensively used before (Edwards 1965, Freed 1972). The polymer chain consists of N beads located at positions defined by the vectors $\{\boldsymbol{r}_i, i=1,2,\ldots,N\}$ and the total number of configurations related to the partition function and the free energy of the system is given by a multiple integral over all the positions of the beads

$$C=\int\prod_{i=1}^{N}\mathrm{d}^d\boldsymbol{r}_i\exp\Big(-(d/2\pi l^2)\sum_{i=1}^{N}(\boldsymbol{r}_i-\boldsymbol{r}_{i+1})^2-\tfrac{1}{2}B\sum_{\substack{i=1\\i\neq j}}^{N}\sum_{j=1}^{N}V(\boldsymbol{r}_i-\boldsymbol{r}_j)\Big). \tag{2.1}$$

In this expression l is an effective unit length which, for simplicity, will be taken to be equal to unity and B is proportional to the inverse of the temperature. The first term in the Boltzmann factor is a connectivity term guaranteeing that all polymeric beads are connected to a chain while the second potential term represents the two-body interactions between all pairs of beads. As is customary it will be approximated by $\frac{1}{2}BV(\boldsymbol{r}_i-\boldsymbol{r}_j)=u\delta^d(\boldsymbol{r}_i-\boldsymbol{r}_j)$ (Fixman 1955, Yamakawa 1971) where u, the excluded volume parameter, is the binary cluster integral.

Expanding expression (2.1) in powers of u and using the same diagrammatic language used before (Kosmas 1981a), we work up to third order in u so that

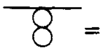


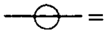
(2.2)

with μ_0 a normalisation factor representing the activity of an ideal chain. The diagrams up to second order in u have been previously evaluated at $d=4$ and for large N (Kosmas 1981a) and are

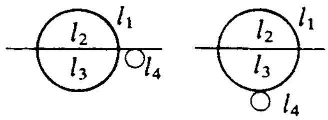
 $$= N - \ln N \tag{2.3a}$$

 $$= \tfrac{1}{2}N^2 - 2N\ln N + \ln^2 N \tag{2.3b}$$

 $$= \quad N\ln N - \ln^2 N \tag{2.3c}$$

 $$= \quad -\tfrac{3}{2}\ln^2 N. \tag{2.3d}$$

There are eight different third-order diagrams (Barrett and Domb 1979). They are given in equation (2.2) together with their multiplicity. Each one represents a six-fold summation coming from the three delta functions of the u^3 term. The expression, to be summed up as the expansion of equation (2.1) implies, is the number of total configurations of Gaussian chains with three contacts. Each expression depends on the topology of each diagram. For the first four diagrams consisting of three loops of lengths l_1, l_2 and l_3 the contribution from each loop is $1/(\text{its length})^{d/2}$ giving for the final expression $1/(l_1l_2l_3)^{d/2}$. The diagrams



have a loop of length l_4 and three other characteristic segments of lengths l_1, l_2 and l_3 yielding the expression (Kosmas 1981a) $1/l_4^{d/2}(l_1l_2+l_1l_3+l_2l_3)^{d/2}$. The two last diagrams have five characteristic segments each. The diagram

has an expression to be summed equal to $1/[l_1l_2l_3+(l_4+l_5)(l_1l_2+l_1l_3+l_2l_3)]^{d/2}$ where l_4 and l_5 are the lengths of the AB and AC segments and l_1, l_2 and l_3 are the lengths of the three segments from B to C. Finally the diagram

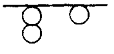
yields the expression

$$1/[l_1l_2(l_3+l_4)+l_3l_4(l_1+l_2)+l_5(l_1+l_2)(l_3+l_4)]^{d/2}$$

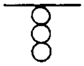
with l_5 the length of the AB segment, l_1 and l_2 the lengths of the two AC segments and l_3 and l_4 the lengths of the other two CB segments. After these remarks the third-order diagrams can be written as

 $$= \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N-1}\sum_{l=k+1}^{N}\sum_{m=l}^{N-1}\sum_{n=m+1}^{N} 1/(l_1l_2l_3)^{d/2}$$

$$l_1=j-i \qquad l_2=l-k \qquad l_3=n-m \tag{2.4a}$$

 $$= \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N}\sum_{l=1}^{i}\sum_{m=k}^{N-1}\sum_{n=m+1}^{N} 1/(l_1l_2l_3)^{d/2}$$

$$l_1=j-i \qquad l_2=k-l-j+i \qquad l_3=n-m \tag{2.4b}$$

 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N}\sum_{l=1}^{i}\sum_{m=1}^{l}\sum_{n=k}^{N}1/(l_1l_2l_3)^{d/2}$$

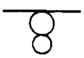
$$l_1=j-i \qquad l_2=k-l-j+i \qquad l_3=n-m-k+l \tag{2.4c}$$

 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N-1}\sum_{l=k+1}^{N}\sum_{m=1}^{i}\sum_{n=l}^{N}1/(l_1l_2l_3)^{d/2}$$

$$l_1=j-i \qquad l_2=l-k \qquad l_3=n-m-j+i-l+k \tag{2.4d}$$

 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j+1}^{N}\sum_{l=i}^{j}\sum_{m=2}^{i}\sum_{n=1}^{m-1}1/l_4^{d/2}(l_1l_2+l_1l_3+l_2l_3)^{d/2}$$

$$l_1=j-l \qquad l_2=l-i \qquad l_3=k-j \qquad l_4=m-n \tag{2.4e}$$

 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N-1}\sum_{l=k+1}^{N}\sum_{m=l}^{N}\sum_{n=i}^{j}1/l_4^{d/2}(l_1l_2+l_1l_3+l_2l_3)^{d/2}$$

$$l_1=j-n \qquad l_2=n-i \qquad l_3=m-j-l+k \qquad l_4=l-k \tag{2.4f}$$

 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N}\sum_{l=i}^{j-1}\sum_{m=1}^{i}\sum_{n=k}^{N}1/[l_1l_2l_3+(l_4+l_5)(l_1l_2+l_1l_3+l_2l_3)]^{d/2}$$

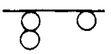
$$l_1=k-j \qquad l_2=l-j \qquad l_3=j-l \qquad l_4=i-m \qquad l_5=n-k \tag{2.4g}$$

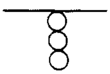
 $$=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{k=j}^{N-1}\sum_{l=k+1}^{N}\sum_{m=i}^{j}\sum_{n=k}^{1}1/[l_1l_2(l_3+l_4)+l_3l_4(l_1+l_2)+l_5(l_1+l_2)(l_3+l_4)]^{d/2}$$

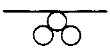
$$l_1=m-i \qquad l_2=j-m \qquad l_3=l-n \qquad l_4=n-k \qquad l_5=k-j. \tag{2.4h}$$

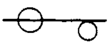
The summations are approximated with integrations and the values of the diagrams are found to be

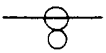
 $$=\tfrac{1}{6}N^3-\tfrac{3}{2}N^2\ln N+3N\ln^2N-\ln^3N \tag{2.5a}$$

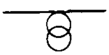
 $$=\tfrac{1}{2}N^2\ln N-2N\ln^2N+\ln^3N \tag{2.5b}$$

 $$=N\ln^2N-\ln^3N \tag{2.5c}$$

 $$=\mathrm{O}(N^3,N^2\ln N,N\ln^2N,\ln^3N) \tag{2.5d}$$

 $$=-\tfrac{3}{2}N\ln^2N+\tfrac{3}{2}\ln^3N \tag{2.5e}$$

 $$=\tfrac{1}{2}N\ln^2N-\tfrac{1}{2}\ln^3N \tag{2.5f}$$

 $$=-\ln^3N \tag{2.5g}$$

 $$=-\ln^3N. \tag{2.5h}$$

Examples of the evaluation of third-order diagrams are given in the appendix.

Putting the values of the diagrams in equation (2.2) we end up with the expression

$$C=\mu_0^N[1-u(2N-2\ln N)+u^2(2N^2-4N\ln N-6\ln^2 N)$$
$$-u^3(\tfrac{4}{3}N^3-4N^2\ln N-12N\ln^2 N-28\ln^3 N)+\ldots]$$
$$=\mu_0^N[1-2uN+(\tfrac{1}{2})(2uN)^2-(\tfrac{1}{6})(2uN)^3+\ldots]$$
$$\times[1+2(u\ln N)-6(u\ln N)^2+28(u\ln N)^3-\ldots]$$
$$=\mu_0^N\exp(-2uN)[1+8(u\ln N)]^{1/4}\qquad d=4. \tag{2.6}$$

Notice that the numbers 8 and $\frac{1}{4}$ are uniquely determined from second-order perturbation results and that the third-order calculation is a check to the validity of the summation of the series into the proposed closed expression. Calculations are also possible for dimensionalities less than four and, as can be seen from the first diagrams at $d=4-\varepsilon$ ($\varepsilon \ll 1$), the only alteration to the closed expression equation (2.6) is just the replacement of $\ln N$ with $(2/\varepsilon)(N^{\varepsilon/2}-1)$. This replacement gives, for the total number of configurations C, the expression

$$C=\mu_0^N\exp(-2uN)[1+8u(2/\varepsilon)(N^{\varepsilon/2}-1)]^{1/4} \tag{2.7}$$

which can be used for deriving useful conclusions. We shall postpone these conclusions to the next section where we shall give the corresponding expression for the mean end-to-end square distance $\langle R^2\rangle$ expressing the size of the macromolecule.

3. Mean end-to-end square distance and conclusions

Second-order perturbation theory can be used to determine a closed algebraic expression for the mean end-to-end square distance $\langle R^2\rangle$ of the coil. Previous results (Kosmas 1981a) and the above analysis imply that

$$\langle R^2\rangle=N[1+8u(2/\varepsilon)(N^{\varepsilon/2}-1)]^{1/4}\qquad d=4-\varepsilon\qquad \varepsilon\ll 1. \tag{3.1}$$

Several conclusions can be derived from this expression for the size of the macromolecule.

(i) At the limit of large N and in the $u>0$ region the power law

$$\langle R\rangle^2=(16u/\varepsilon)^{1/4}N^{1+\varepsilon/8}=(16u/\varepsilon)^{1/4}N^{2\nu_{4-\varepsilon}} \tag{3.2}$$

is obtained where we see that the meaning of an exponent $2\nu_{4-\varepsilon}=1+\frac{1}{8}\varepsilon$ is valid (de Gennes 1972) in agreement with previous findings (des Cloizeaux 1981). The prefactor in expression (3.2) depends on u giving a dependence of the size of the polymer on the temperature and other characteristics of the polymer and the solvent.

(ii) The fixed point, as a special point where the exponents can be determined relatively easily, is represented by the point at which u becomes equal to $u^*=\varepsilon/16$ (Kosmas 1981a). For this value of u the other constants in equation (3.1) cancel exactly leaving a pure power law.

(iii) Expression (3.1) also describes the size of the polymer for small negative u (poor solvent) (Lifshitz *et al* 1978, Moore and Al-Noaimi 1978, Duplantier 1980). The quantity $(2/\varepsilon)(N^{\varepsilon/2}-1)$ takes large values so that negative u reduce $\langle R^2\rangle^{1/2}$ to values smaller than the ideal Θ size implying shrinking of the coil.

Acknowledgments

I should like to thank Professor S F Edwards for his support and hospitality during the course of this work. I am also grateful to him for his comments on the present manuscript.

Appendix

In this appendix we are going to demonstrate a way of evaluating the third-order diagrams. As a first example we will find the value of the diagram given by equation (2.4*a*). Converting the summations of equation (2.4*a*) into integrations and introducing the natural variables l_1, l_2 and l_3 we end up with the expression

$$= \int_1^N \mathrm{d}l_1 \int_1^{N-l_1} \mathrm{d}l_2 \int_1^{N-l_1-l_2} \mathrm{d}l_3 \int_1^{N-l_1-l_2-l_3} \mathrm{d}i \int_{l_1+i}^{N-l_2-l_3} \mathrm{d}k \int_{l_2+k}^{N-l_3} \mathrm{d}m \; 1/l_1^2 l_2^2 l_3^2$$

$$d=4. \tag{A1}$$

The integrations over i, k and m are easy because there is no dependence of the function to be integrated on them. Equation (A1) then gives

$$= \tfrac{1}{6} \int_1^N \mathrm{d}l_1 \int_1^{N-l_1} \mathrm{d}l_2 \int_1^{N-l_1-l_2} \mathrm{d}l_3 \, (N-l_1-l_2-l_3)^3 / l_1^2 l_2^2 l_3^2. \tag{A2}$$

Expanding $[(N-l_1-l_2)-(l_3)]^3$ in powers of l_3 and integrating over l_3, two terms survive in the limit of large chain lengths giving

$$= \tfrac{1}{6} \int_1^N \mathrm{d}l_1 / l_1^2 \int_1^{N-l_1} \mathrm{d}l_2 \, [(N-l_1-l_2)^3 - \ln N (N-l_1-l_2)^2] / l_2^2. \tag{A3}$$

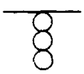
The double integrations over the two parts of equation (A3) are straightforward and yield in the limit of $N \to \infty$ the results

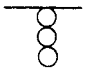
$$\int_1^N \mathrm{d}l_1 / l_1^2 \int_1^{N-l_1} \mathrm{d}l_2 \, (N-l_1-l_2)^3 / l_2^2 = N^3 - 6N^2 \ln N + 6N \ln^2 N \tag{A4}$$

and

$$\int_1^N \mathrm{d}l_1 / l_1^2 \int_1^{N-l_1} \mathrm{d}l_2 \, (N-l_1-l_2)^2 / l_2^2 = N^2 - 4N \ln N + 2 \ln^2 N. \tag{A5}$$

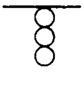
Putting these results back in equation (A3) we find the final value of the diagram which we quote in equation (2.5*a*).

The corresponding three-fold integral on the length variables l_1, l_2 and l_3 for the diagram  comes out to be



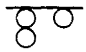
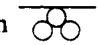
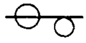
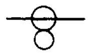
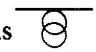
$$= \int_1^N \mathrm{d}l_1 \int_1^{N-l_1} \mathrm{d}l_2 \int_1^{N-l_1-l_2} \mathrm{d}l_3 \, (N-l_1-l_2-l_3) l_1 l_2 (l_1 l_2 l_3)^{-2}. \tag{A6}$$

Performing the l_3 integration we find



$$= \int_1^N \mathrm{d}l_1/l_1 \int_1^{N-l_1} \mathrm{d}l_2 \{(N-l_1-l_2)[-1/(N-l_1-l_2)+1] - \ln(N-l_1-l_2)\}/l_2. \tag{A7}$$

The part of equation (A7) which includes the $-1/(N-l_1-l_2)$ ratio gives insignificant terms in the limit of large N while the $\ln(N-l_1-l_2)$ part yields $\ln N$. The double integrations are straightforward yielding the result quoted in equation (2.5c).

In a similar way the diagram  can be evaluated while the diagram  gives zero contribution in the limit of large N. Lengthier calculations are needed for the diagrams  and  where we have four lengths and even lengthier for the last two diagrams  and  where five lengths appear. Their contributions are given in equation (2.5).

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