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1984 J. Phys. A: Math. Gen. 17 L965

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## LETTER TO THE EDITOR

# The efficiency of the Flory approximation

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Received 17 September 1984

**Abstract.** The Flory approximation for the self-avoiding chain problem is compared with a conventional perturbation theory expansion. While in perturbation theory each term is averaged over the unperturbed set of configurations, the Flory approximation is equivalent to the perturbation theory with the averaging over the stretched set of configurations. This imposes restrictions on the integration domain in higher-order terms and they can be treated self consistently. The accuracy  $\delta\nu/\nu$  of the Flory approximation for self-avoiding chain problems is estimated to be  $10^{-1}$ - $10^{-2}$  for  $1 < d < 4$ .

The Flory method is widely used for the calculation of critical exponents in many problems of configurational statistics. Originally, it was proposed for the problem of the linear polymer with excluded volume (Flory 1971, Fisher 1969), but its simplicity and unexpected accuracy stimulated its application to various problems: branched polymer problem—animals, percolation (Isaacson and Lubensky 1980), directed animals and directed percolation (Redner and Coniglio 1982), the true self-avoiding walk problem (Pietronero 1983) and the problem of multicritical behaviour of linear chains (Majid *et al* 1984) etc.

There were attempts to apply this method in a modified form to a phenomenon of the irreversible aggregation: cluster-particle aggregation (Muthukumar 1983), and cluster-cluster aggregation (Kolb 1984, Obukhov 1984). See also the application of Flory theory for irreversible kinetic gelation (Pandey 1984).

Nonetheless, this effectiveness of the Flory method remained as yet unexplained and no control of its accuracy is possible. Below we shall consider the accuracy of this approximation for the case of the linear polymer problem. This consideration can easily be extended to other problems of configurational statistics.

The Flory method consists of calculation of the 'free energy' as a function of size of the polymer coil. This free energy consists of two terms. The first one is the elastic energy which is needed to stretch up to the size  $R$  the coil with unperturbed radius  $R_0 \sim N^{1/2}$  (where  $N$  is the length of the polymer)

$$F_{el} = c_1 R^2/N. \quad (1)$$

The second term is the repulsive energy of  $N$  monomers distributed uniformly in a volume  $R^d$ :

$$F_{rep} = c_2 N^2/R^d. \quad (2)$$

Here  $c_1$  and  $c_2$  are inessential numerical constants. Minimisation of the sum of (1)

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and (2) with respect to  $R$  leads to the equilibrium radius  $R$

$$R \sim N^\nu \quad \text{with } \nu = 3/(2+d) \quad (d \leq 4). \quad (3)$$

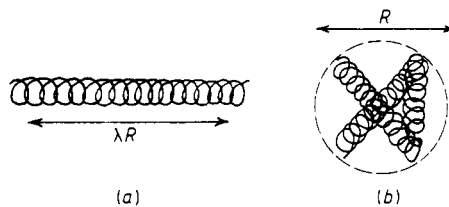
Although obtained in a very crude approximation, this formula gives successful estimations at  $d = 3$  and  $d = 2$ , with an accuracy exceeding 1.5% and 0.3%, respectively (see Majid *et al* 1983). At  $d = 4$  and  $d = 1$ , this formula is exact, but below  $d_c = 4$  it disagrees with the rigorous result of  $4 - \varepsilon$  expansion:  $\nu = \frac{1}{2} - \frac{1}{16}\varepsilon$  (de Gennes 1972), and near the marginal dimension  $d = 1$  it disagrees with the result of  $1 + \varepsilon$  expansion  $\nu = 1 - \frac{1}{3}\varepsilon$  (see a review by Stanley *et al* 1982, and references therein).

Regarding the accuracy of (3), one often refers to the paper by de Gennes (1976). He considered that terms (1) and (2) are overestimated by factors of  $N^{2\nu-1}$  and  $N^{\gamma-1}$  and the effectiveness of the Flory formula follows from the proximity of the critical exponents  $2\nu$  and  $\gamma$ . However, this explanation is not satisfactory because these exponents are connected by the relation  $(2 - \eta)\nu = \gamma$  and the exponent  $\eta$  is known not to be small at low dimension  $d$ . Moreover, near upper critical dimension  $d_c = 4$ , where the difference  $2\nu - \gamma$  is really small and of the order of  $\varepsilon^2$  ( $\varepsilon = 4 - d$ ), formula (3) disagrees with the exact result of  $\varepsilon$  expansion in first order of  $\varepsilon$ .

Now we shall construct the analogue of the Flory approximation in terms of perturbation theory, from which its accuracy can be estimated. The elastic energy of the  $N$ -monomer chain on a lattice can be written as follows

$$F_{el} = -\ln \mathcal{N}(R), \quad (4)$$

where  $a$  is a lattice unit and  $\mathcal{N}(R)$  is a total number of all possible configurations, including self-intersected ones of size  $R$ . It should be pointed out here that the term 'stretched configuration' is ill defined: the simplest stretched configuration is shown in figure 1(a), but it has the size  $R$  only in the direction of strain. Its probability is of the order of  $\exp(-R^2/R_0^2)$ . The 'typical' stretched configuration which is useful to keep in mind can be thought of as a stretched polymer coil of figure 1(a), but with a few zigzags added as in figure 1(b), so that in each direction the size of the configuration



**Figure 1.** (a) Polymer coil stretched in one direction, the probability of such kind of configuration  $\sim \exp(-\lambda^2 R^2/R_0^2)$ . (b) Stretched polymer coil with zigzags, so that in each direction the size of configuration is  $\approx R$ .

is of the order of  $R$ . The probability of such a configuration is  $\exp(-\lambda^2(R^2/R_0^2))$ , where  $\lambda$  is the number of zigzags, so coefficient  $c_1$  is equal to  $\lambda^2$  in this picture. Any other configuration of size  $R \gg R_0$  which differs strongly from that of figure 1(b) (with one more zigzag, for example) needs the longer initial polymer coil of figure 1(a) and is exponentially rare compared to the configuration of figure 1(b). In this picture the coil is stretched only on large scales, remaining Gaussian on small scales. Below we introduce the self-similar picture where the coil is stretched on all scales.

From all configurations  $\mathcal{N}(R)$  we must choose only configurations without self intersection and the probability of such configurations can be written as

$$W(R) = \left\langle \prod_x \left( 1 - \frac{1}{2} \sum_{k \neq l} \rho_k(x) \rho_l(x) \right) \right\rangle_R$$

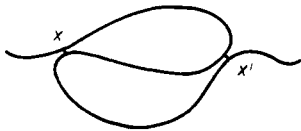
$$= \exp \left( - \sum_x \langle \rho^2(x) \rangle_R + 2 \sum_x \rho(x) + \frac{1}{2} \sum_{x, x'} \langle \langle \rho^2(x) \rho^2(x') \rangle \rangle_R - \dots \right). \quad (5)$$

Here  $\rho_k(x)$  is the density of the  $k$ th segment of a chain at point  $x$ ,  $\rho(x) = \sum_k \rho_k(x)$ ,  $\langle \dots \rangle_R$  denotes the average over all configurations of size  $R$ , and  $\langle \langle \dots \rangle \rangle_R$  denotes the irreducible average. The term  $\sum_x \rho(x)$  in (5) is linear in  $N$  and can be omitted. The product  $\mathcal{N}(R)W(R)$  defines the most probable size of the configurations without self intersections. It takes its maximal value when the sum of arguments in (5) and in  $\mathcal{N}(R) \sim \exp(-c_1 R^2/N)$ .

$$c_1 R^2/N + \sum_x \langle \rho^2(x) \rangle_R - \frac{1}{2} \sum_{x, x'} \langle \langle \rho^2(x) \rho^2(x') \rangle \rangle_R + \dots \quad (6)$$

is minimal. The first two terms in (6) reproduce the Flory free energy (sum of (1) and (2)). Now the impact of additional terms in (6) must be estimated. The difference between series (6) and the usual perturbation theory expansion comes from distinct averaging procedures. In the usual perturbation theory, each term is averaged over all unperturbed configurations, dominated by the size  $R_0$ . For an unperturbed set of configurations, the consecutive terms in (6) diverge at large scales at  $d < 4$  and are, by a factor of the order of  $R_0^{4-d}$ , larger than the previous ones, so one encounters the problem of the summation of the whole divergent series.

In (6), each term is rather averaged over the set of *stretched* configurations of size  $R$ . The large scales cannot be essential in this case. Consider the diagrammatic representation of the last term in (6) (figure 2): the path from  $x$  to  $x'$  is duplicated three times and cannot be of order of  $R$  because in this case the full length of the stretched coil is larger than that for the typical stretched configuration, and this over-stretched configuration is exponentially rare compared to the typical stretched one.



**Figure 2** Diagram representation of the last term in (6); the distance  $x - x'$  cannot be large because in this case the path from  $x$  to  $x'$  is duplicated three times and the full length of stretched polymer coil (see figure 1(a)) is larger than that for the typical one. This overstretched configuration is exponentially rare with respect to the typical ones.

Hence, there must exist a maximal scale  $R' \ll R$  at which the high-order terms are important, so that for the scales  $R' < r < R$  only binary interaction is relevant. The implication is, that instead of introducing monomers, we introduce new integrated units of size  $R'$  containing  $N'$  monomers, the application of the Flory approximation for free energy of the chain of such blobs

$$F = c_1 (R/R')^2 / (N/N') + c_2 (N/N')^2 / (R/R')^d \quad (7)$$

will be correct.

In order to determine the number  $M$  of such blobs it should be noted that from the zigzag picture, figure 1(b),

$$M \equiv N/N' = \lambda R/R'. \quad (8)$$

Then it is reasonable to assume that the structure of the blob is similar to the structure of the entire coil. From this similarity, it follows that  $R = cN^\nu$  and  $R' = c(N/M)^\nu$ . Combining this with (8) we get

$$M = \lambda^{1/1-\nu} \gg 1. \quad (9)$$

Considering the structure of a blob of radius  $R'$ , we can pick out the smaller blobs of radius  $R''$  from which this blob is constructed etc.

Thus, for a long  $N \rightarrow \infty$  polymer chain there is a sequence of scales  $R, R', R'', \dots$ , such that at each interval  $R > r > R', R' > r > R'' \dots$  the Flory approximation can be applied.

The free energy of the whole coil, which is simply the sum of free energies at all scales, is now proportional to  $N$  instead of  $N^{2\nu-1}$  in the original Flory formulation.

The fact that  $M$  is a large, but finite, constant restricts the accuracy of the Flory method. From (9) it can easily be seen that the minimum of free energy is not very sharp when the number of blobs is finite. As the zigzag picture suggests that  $c_1$  in (7) is  $\lambda^2$ , one readily finds the width of the distribution of most probable  $R$  and, by virtue of

$$\delta R/R' \approx M^{\nu+\delta\nu} M^\nu, \quad (10)$$

we obtain

$$\frac{\delta\nu}{\nu} \approx \frac{2^{1/2}}{(d+3)^{1/2}} \frac{1}{\nu M^{1/2} \ln M}. \quad (11)$$

The minimal number of zigzags in  $d$ -dimensional space is  $d$ . Then combining (3), (10) and (11) we get

$$\delta\nu/\nu \approx 10^{-1} - 10^{-2} \quad \text{for } 1 \leq d < 4 \quad (12)$$

so this rather rough evaluation gives results which are consistent with experimental data about the accuracy of the Flory method mentioned above†.

The results of this letter can be summarised as follows.

(1) The Flory approximation can be applied with rather high accuracy to the systems with short-range repulsive interaction. The repulsive interaction is necessary because it provides the averaging procedure over the stretched configurations, which reduces the input of high-order terms. The short-range character of the interaction is also necessary, because in the case of long-range forces, the stretching does not crucially reduce the value of high-order terms.

(2) The Flory approximation cannot also be used for non-diluted solutions of polymers while the interaction between different polymers in a solution causes an effective long-range self interaction, but it can be used successfully in disordered system problems because of the replica trick which removes all vacuum contributions in the diagrams.

I gratefully acknowledge the kind hospitality of the staff of Nordita during the work on this paper.

† I want to thank L. Peliti for a discussion and critical remarks about the accuracy of this evaluation.

## References

- de Gennes P G 1972 *Phys. Lett.* **38A** 339  
— 1976 *Macromolecules* **9** 587  
Fisher M 1969 *J. Phys. Soc. Japan (suppl.)* **26** 44  
Flory P J 1971 *Principles of Polymer Chemistry* (Ithaca, New York: Cornell University Press)  
Isaacson J and Lubesky T C 1980 *J. Physique* **41** L469  
Kolb M 1984 *Preprint*  
Majid I, Jan N, Coniglio A and Stanley H E 1984 *Preprint*  
Majid I, Djordjevic Z V and Stanley H E 1984 *Phys. Rev. Lett.* **52** 1257  
Muthukumar M 1983 *Phys. Rev. Lett.* **50** 839  
Obukhov S P 1984 *Sov. Phys.-JETP* in press  
Pandey R B 1984 *J. Phys. A: Math. Gen.* **17** L579  
Pietronero L 1983 *Phys. Rev. B* **27** 5887  
Redner S and Coniglio A 1982 *J. Phys. A: Math. Gen.* **15** L273  
Stanley H E, Reynolds P J, Redner S and Family F 1982 in *Real-space renormalization* ed T W Burkhardt and J M J van Leeuwen (Heidelberg: Springer)