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## A note on the convergence of perturbation theory in polymer problems

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**Abstract.** It is shown that the Fixman perturbation expansion for the number of configurations of a self-interacting polymer molecule (from which the entropy, end-to-end distance etc can be calculated) is not convergent for any strength of interaction, but is asymptotic.

### 1. Introduction

A basic quantity in the theory of polymer statistics is the number of configurations  $G_n(r, r')$  which a polymer of  $n$  links has when its end points are at  $r$  and  $r'$ . The full structure of  $G_n$  requires a detailed knowledge of the forces between monomers, but as  $n$  increases the fine structure of the force plays a smaller and smaller role, so that for large  $n$ ,  $G$  can be developed in a series in the interaction which has the form:

$$G_n(r, r') \rightarrow G_n^{(0)}(r, r') + zG_n^{(1)}(r, r') + z^2G_n^{(2)}(r, r') + \dots \quad (1)$$

where

$$z = \left( \frac{3}{2\pi b^2} \right)^{3/2} \beta n^{1/2} \quad (2)$$

and  $\beta$  is the binary cluster integral,  $b$  the mean square length of a segment. The series is developed in detail by Yamakawa (1971).

The variable  $z$  is a measure of the effective interaction between points of the chain. From this series the mean end-to-end distance is readily calculated:

$$\langle R^2 \rangle = \frac{\int (r-r')^2 G_n d^3(r-r')}{\int G_n d^3(r-r')} \quad (3)$$

and the entropy of the system is just  $\kappa \ln G$ .

In this note it will be shown that  $G_n$  can be represented by an integral over a set of variables  $\phi_k$  such that

$$G = \int \mathcal{G}(rr'; \phi_1, \phi_2, \dots) \exp \left( - \sum_k |\phi_k|^2 \right) \pi d\psi_k. \quad (4)$$

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This form suggests an application of Watson's lemma, which states that a power series expansion of

$$g(z) = \int f(x, z) e^{-x^2} dx \quad (5)$$

converges if and only if the power series of

$$f(x, z) = \sum z^m f_m \quad (6)$$

converges absolutely for all  $z$ . A good account of the lemma is given in the chapter on asymptotic series in Jeffreys and Jeffreys (1956). It can be shown in the present case that  $\mathcal{G}$  does not so converge so that the series for  $G$  diverges.

## 2. The representation of $G$

The simplest weighting of configurations appears in the Boltzmann interaction with a potential  $W(\mathbf{r}-\mathbf{r}')$ . If the polymer is considered to be a necklace of points  $\mathbf{R}_n$  a configuration will have a weight factor:

$$\exp\left(-\sum_{\substack{l,m \\ l \neq m}} W(\mathbf{R}_l - \mathbf{R}_m)/uT\right). \quad (7)$$

If this is considered as a power series in  $W$ , the terms of some order  $q$ , ie in  $(W)^q$  will involve terms where all the  $\mathbf{R}_m$  are different, then two are the same, and so on down to a term  $\Sigma(W(\mathbf{R}_l - \mathbf{R}_m))^q$ . Consider for the moment all the terms in  $W(\mathbf{R}_1 - \mathbf{R}_2)$ . When added up these constitute a complete solution of the number of configurations involving just  $\mathbf{R}_1$  and  $\mathbf{R}_2$ . Taking this set alone, there will be some pseudopotential  $w(\mathbf{R}_1 - \mathbf{R}_2)$  which, when treated as a perturbation, exactly reproduces the interaction of 1 and 2 in its first-order term. Thus  $w$  is in fact  $uT\beta \delta(\mathbf{R}_1 - \mathbf{R}_2)$  where  $\beta$  is the binary collision integral. For very long chains, and small  $\beta$ , the whole behaviour of the polymer will be accurately treated by replacing  $W$  by  $w$ , ie  $(\kappa T)\beta$  and in the sum

$$\exp\left(-\sum_{l,m} \beta \delta(\mathbf{R}_l - \mathbf{R}_m)\right) \quad (8)$$

treating  $\beta$  as a pseudopotential, ie ignoring terms involving powers of the terms of any pair  $l, m$ . This is done analytically by considering the set of points  $\mathbf{R}_1, \mathbf{R}_2 \dots$  tending to a continuum  $\mathbf{R}(s)$  and using

$$\sum_{n,m} \beta \delta(\mathbf{R}_n - \mathbf{R}_m) \rightarrow \beta \int \int ds_1 ds_2 \delta(\mathbf{R}(s_1) - \mathbf{R}(s_2)). \quad (9)$$

This representation automatically discards things like  $(W(\mathbf{R}_1 - \mathbf{R}_2))^q$  and reproduces the Fixman perturbation series for any property of the polymer, provided that the single-loop term which would be divergent for the simple  $\delta$  function representation is made finite. It is an uninteresting constant. Now several statements have been made in the above paragraph which would require some space to be fully proved. However, it is not the purpose of this note to consider the status of the binary collision approximation and

this will simply be assumed. What we wish to do is study the convergence of the expansion, and this is accomplished by a parametric representation based on the identity

$$\int e^{ax-x^2/2} dx = e^{+a^2/2} \int e^{-x^2/2} dx. \tag{10}$$

The double integral can be written in Fourier transform

$$\begin{aligned} \int ds_1 \int ds_2 W(\mathbf{R}(s_1) - \mathbf{R}(s_2)) &= (2\pi)^{-3} \int d^3k U(\mathbf{k}) \int ds_1 \int ds_2 \exp[i\mathbf{k} \cdot (\mathbf{R}_1 - \mathbf{R}_2)] \\ &= \frac{1}{(2\pi)^3} \int d^3k U(\mathbf{k}) [ds_1 \exp(i\mathbf{k} \cdot \mathbf{R}_1)] \int [ds_2 \exp(-i\mathbf{k} \cdot \mathbf{R}_2)] \end{aligned} \tag{11}$$

where  $U(\mathbf{k})$  is the Fourier transform of  $W(\mathbf{r})$ . If  $W$  is represented inside a box, the  $\int d^3k$  is replaced by  $\sum_{\mathbf{k}}$  as in Fourier series. Using the  $\sum_{\mathbf{k}}$  for the moment

$$\begin{aligned} \int \dots \int \exp\left\{i \left[ U(\mathbf{k})^{1/2} \sum_{\mathbf{k}} \left( \int ds_1 e^{i\mathbf{k} \cdot \mathbf{R}} \right) \phi_{\mathbf{k}} \gamma_{\mathbf{k}}^{1/2} - \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{\mathbf{k}}^* \gamma_{\mathbf{k}} \right] \right\} \prod \left[ d\phi_{\mathbf{k}} \left( \frac{2\pi}{\gamma_{\mathbf{k}}} \right)^{1/2} \right] \\ = \exp\left( - \sum_{\mathbf{k}} ds_2 ds_1 e^{i\mathbf{k} \cdot \mathbf{R}_1} e^{-i\mathbf{k} \cdot \mathbf{R}_2} U(\mathbf{k}) \right) \end{aligned} \tag{12}$$

is an identity for any set of labels  $\mathbf{k}$ . Using the identity, trivially extended to complex variables

$$\iint e^{az-zz^*/2} dx dy = e^{-aa^*/2} \iint e^{-zz^*} dx dy \tag{13}$$

where  $z = x + iy$ ,  $z^* = x - iy$ , one can define

$$\phi(\mathbf{r}) = \int e^{i\mathbf{k} \cdot \mathbf{r}} \phi_{\mathbf{k}} d^3k = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \phi_{\mathbf{k}} \quad \text{in a box.}$$

$$\left( \sum_{\mathbf{k}} \equiv \frac{(2\pi)^3}{V} \sum_{n_1, n_2, n_3} (n_1 n_2 n_3) \quad k_1 = \frac{2\pi n_1}{V^{1/3}} \text{ etc.} \right)$$

If for example one uses

$$U(\mathbf{k}) = \beta / (2\pi)^3 \tag{14}$$

then one needs to take the weight factor

$$\exp\left[ i \left( \frac{\beta}{(2\pi)^3} \right)^{1/2} \int \phi \mathbf{R}(s) ds \right] \tag{15}$$

and average with a weight factor

$$\begin{aligned} \prod_{\mathbf{k}} \left( \frac{\gamma_{\mathbf{k}}}{2\pi} \right)^{1/2} d\phi_{\mathbf{k}} \exp\left( - \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{\mathbf{k}}^* \gamma_{\mathbf{k}} \right) \\ = \exp\left[ - \int \phi(\mathbf{r}) d^3r d^3r' \gamma(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \prod_{\mathbf{k}} \left( \frac{\gamma_{\mathbf{k}}}{2\pi} \right)^{1/2} d\phi_{\mathbf{k}} \right]. \end{aligned} \tag{16}$$

Note that the sum over  $k$ , rather than the integral, is brought about by putting the system in a box, which is physically uninteresting, and the number of  $k$  values being infinite is required to build up the precise shape of the pseudopotential  $\delta(\mathbf{r}-\mathbf{r}')$ . The choice of a finite number of  $k$  values will lead to a potential which is periodic of period  $1/M$  where  $M$  values of  $k$  are used. Such a periodicity will not affect our system physically since the distance over which the periodicity occurs can be made larger than the box if  $M$  is large enough. The shape of  $W$  is affected, but as has been already argued, that is of no consequence physically. Alternatively it is to be noted that the function  $\delta_{\mathbf{k}}$  appearing in the parametrization is arbitrary, and can be chosen to permit the use of theorems which allow a rigorous use of an infinite set of  $k$  values to be used, in particular one can choose  $\gamma_{\mathbf{k}}$  so that

$$\int \gamma_{\mathbf{k}}^{-1} d^3k \quad (17)$$

is finite (I am indebted to Dr Dwight Freund for pointing this out to me). This paper is not, however, intended to give a rigorous mathematical proof of a standard acceptable to pure mathematicians and will content itself to show that the parametrization (12) leads to a multiple use of Watson's lemma to show that the partition function diverges. There is no need to confine oneself to the  $\delta$  function; any function  $w(\mathbf{R}(s_1) - \mathbf{R}(s_2))$  will do, but if the Fourier transform of  $w$ ,  $U(\mathbf{k})$ , has both positive and negative components, these must be given different parametric representations. In fact I believe the theorems quoted here can be extended to cover these cases, but it would involve extending, rather than just quoting, the literature. For convenience  $\gamma_{\mathbf{k}}$  will be put equal to unity, but in all that follows can be given any form required for theorem proving.

Consistent with the transition to the integral representation is the use of the diffusion equation to describe the free polymer. This equation defines  $G_0$ :

$$\left( \frac{\partial}{\partial s} - \frac{b}{6} \nabla^2 \right) G_0(\mathbf{r}, \mathbf{r}'; s, s') = \delta(\mathbf{r}-\mathbf{r}')\delta(s-s') \quad (18)$$

$$G_0 = \exp\left(-\frac{3}{2b} \frac{(\mathbf{r}-\mathbf{r}')^2}{(s-s')^2}\right) \left(\frac{3(s-s')}{2b\pi}\right)^{3/2} \quad (19)$$

The addition of the weight factor (15) changes the problem to one of evaluating

$$\left[ \frac{\partial}{\partial s} - \frac{b}{6} \nabla^2 + i \left( \frac{\beta}{(2\pi)^3} \phi(\mathbf{r}) \right)^{1/2} \right] G([\phi], \mathbf{r}, \mathbf{r}'; s, s') = \delta(\mathbf{r}-\mathbf{r}')\delta(s-s') \quad (20)$$

$$G = \int \exp\left(-\sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{\mathbf{k}}^*\right) G([\phi]) \prod d\phi_j \left[ \int \exp\left(-\sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{\mathbf{k}}^*\right) \prod d\phi_j \right]^{-1} \quad (21)$$

Equation (20) amounts to saying that over a distance  $ds$  one can treat the statistics of the free chain, which gives  $\frac{1}{6}b\nabla^2$ , and the interactions, which give  $i[\beta/(2\pi)^3\phi(\mathbf{r})]^{1/2}$  as independent, ie there is no cross term. This is indeed the case, and the mathematical background is fully developed by Freed (1972).

The integral (21) can be manipulated into a form where Watson's lemma can be applied.

### 3. The application of Watson's lemma

The differential equation (20) may be cast as a Fredholm integral equation by using

$$G(\mathbf{n} \mathbf{r}' ; s, s'[\phi]) = G_0(\mathbf{r} - \mathbf{r}', s - s') - i \left( \frac{\beta}{(2\pi)^3} \right)^{1/2} \int \left( G_0(\mathbf{r} - \mathbf{r}_1, s - s') \phi(\mathbf{r}_1) d^3 r ds_1 G([\phi], \mathbf{r}_1, \mathbf{r}' ; s, s') \right). \tag{22}$$

This may be Fourier (or Laplace) transformed on  $s$ , whereupon  $s$  ceases to be an active variable. Also Fourier transform on  $\mathbf{r}$ , introducing

$$\mathcal{G}(\mathbf{k}_1, \mathbf{k}_2 ; p) = \int \exp[ip(s - s')] \exp(i\mathbf{k}_1 \cdot \mathbf{r} + i\mathbf{k}_2 \cdot \mathbf{r}') G(\mathbf{r}, \mathbf{r}' ; s, s'[\phi]) \tag{23}$$

$$\mathcal{G}_0(\mathbf{k}_1, \mathbf{k}_2 ; p) = \frac{1}{ip + \frac{1}{2}bk_1^2} \delta(\mathbf{k}_1 + \mathbf{k}_2) \tag{24}$$

$$\mathcal{G}(\mathbf{k}_1, \mathbf{k}_2 ; p) = \mathcal{G}_0(\mathbf{k}_1, \mathbf{k}_2 ; p) - i \left( \frac{\beta}{(2\pi)^3} \right)^{1/2} \int (\mathcal{G}_0(\mathbf{k}_1, \mathbf{k}_3 ; p) \phi(\mathbf{k}_3 - \mathbf{k}_4) \mathcal{G}(\mathbf{k}_4, \mathbf{k}_2 ; p) d^3 k_3 d^3 k_4). \tag{25}$$

But in the end one wants the average of  $G[\phi]$  which will be a function of  $\mathbf{r} - \mathbf{r}'$  and hence the average over  $\phi$  of  $G$  will contain a term in  $\delta(\mathbf{k}_1 + \mathbf{k}_2)$ . Thus in (25) it suffices to consider the integral over  $\mathbf{k}_2$  which, with

$$g(\mathbf{k}) = \int \mathcal{G}(\mathbf{k}, \mathbf{k}_2 ; p) d^3 k_2 \tag{26}$$

$$g_0(\mathbf{k}) = \int \mathcal{G}_0(\mathbf{k}, \mathbf{k}_2 ; p) d^3 k_2 = \frac{1}{ip - k^2} \tag{27}$$

$$g(\mathbf{k}) = g_0(\mathbf{k}) - i \left( \frac{\beta}{(2\pi)^3} \right)^{1/2} \int g_0(\mathbf{k}) \phi_{\mathbf{k}, \mathbf{j}} g(\mathbf{j}) d^3 j \tag{28}$$

which has the classical Fredholm form

$$g(\mathbf{k}) + \int K(\mathbf{k}, \mathbf{j}) g(\mathbf{j}) d^3 j = g_0(\mathbf{k}). \tag{29}$$

Note that using the Fourier series for  $\phi$ , the term in  $\phi_0$  merely represents the uniform average of  $\phi$  over the box and can be taken zero without loss of generalities. Also recall that we can expect some trouble from the simple  $\delta$  function interaction at very short distances, ie in the evaluation of the average the term representing infinitesimally tight loops will need  $U(\mathbf{k}) \neq 1$  to be convergent. Within these comments (29) may be directly evaluated by a perturbation series which can be represented by writing  $g_0$  as a full line, and  $\phi$  as a dotted line, when

$$g = \text{---} + \text{---} \begin{matrix} \vdots \\ \vdots \\ \vdots \end{matrix} + \text{---} \begin{matrix} \vdots \\ \vdots \\ \vdots \end{matrix} + \text{---} \begin{matrix} \vdots \\ \vdots \\ \vdots \end{matrix} + \dots \tag{30}$$

The integration over  $\phi$  joins up the dotted lines in all ways and writes a  $U(\mathbf{k})$  there, or

(apart from the simple loop which requires  $U(k)$  to show its structure to be convergent) just gives the contact points, ie

$$\int \left( \begin{array}{c} \vdots \\ \vdots \\ \vdots \end{array} \right) \exp \left( - \sum_k |\phi_k|^2 \right) \rightarrow \begin{array}{c} U(k) \\ \text{---} \circ \text{---} \end{array} \rightarrow \begin{array}{c} \text{---} \circ \text{---} \end{array} \quad (31)$$

$$g = \left. \begin{array}{l} \text{---} + \begin{array}{c} \circ \\ \times \end{array} + \begin{array}{c} \circ \\ \times \end{array} + \begin{array}{c} \circ \\ \times \end{array} \\ + \begin{array}{c} \circ \\ \times \\ \circ \\ \times \end{array} \\ + \begin{array}{c} \circ \\ \times \end{array} \end{array} \right\} + \dots \quad (32)$$

Thus the physical contacts of the chain are directly represented by the series in  $\beta$  and the series thus obtained is that appropriate when binary encounters alone are significant (as indeed they are under small- $\beta$  large- $L$  conditions).

But this series is the expansion of the Fredholm integral which is solved as the ratio of two absolutely convergent series, the Fredholm resolvent and the Fredholm determinant. Watson's lemma tells one that the average of  $g$  will only possess a convergent series if and only if the series for  $g$  is absolutely convergent for all  $\phi_k$ . This is not the case since the Fredholm determinant will have roots and its inverse will not be expandable as an absolutely convergent series. To put it in more general terms, it is not enough to argue  $\beta$  is small, or anyway repulsive. Roughly speaking, if the Fixman series for  $G$  diverges for any  $\beta$ , it will diverge for all  $\beta$ . This is clearly recognized as being asymptotic. It does, however, cast a shadow on doing enormous amounts of work to push the series further along.

The reason for the divergence is clear once one studies the topology of the series. There is a combinatorial explosion, and at order  $\beta^n$  there are  $n!$  terms.

If one now considers derived quantities like

$$\langle R^2 \rangle = \frac{\int \langle r^2 G \rangle}{\int \langle G \rangle} = \frac{[\partial^2 g / \partial k^2]_{k=0}}{g(0)} \quad (33)$$

It is given by the ratio of two quantities both of which are asymptotic if expanded in  $\beta$ . Their ratio will likewise be asymptotic unless some miraculous cancellation takes place, ie there is a relationship such that the many terms in the  $n$ th order cancel. However, I can offer no proof.

**Acknowledgments**

This note was prepared at the request of Professor M Gordon and I thank him for his suggestion that it is of interest to polymer scientists. It is largely a reworking of a much

earlier proof by the author (Edwards 1953) of the divergence of quantum field theory. I should also like to thank Dr Dwight Freund for the help noted in the text.

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