

Home Search Collections Journals About Contact us My IOPscience

Configurational statistics of a disordered polymer chain

This article has been downloaded from IOPscience. Please scroll down to see the full text article. 1986 J. Phys. A: Math. Gen. 19 3655 (http://iopscience.iop.org/0305-4470/19/17/028)

View the table of contents for this issue, or go to the journal homepage for more

Download details: IP Address: 129.252.86.83 The article was downloaded on 31/05/2010 at 12:56

Please note that terms and conditions apply.

## Configurational statistics of a disordered polymer chain

S P Obukhov

L D Landau Institute for Theoretical Physics, USSR Academy of Sciences, Moscow, USSR

Received 3 December 1985

Abstract. A problem of the configurational properties of a long flexible polymer chain with a guenched disorder is considered. The chain is assumed to be randomly constructed from monomers of two different kinds with different constants for the two-body interaction. Near the theta point, i.e. when the average interaction of monomers is small, the spatial correlation of the repulsive and attractive monomers of different kinds leads to an increase of effects of the disorder on large scales. There is also the competing effect of the repulsive three-body interaction which tends to screen the effects of disorder on large scales. For both effects the upper critical dimension is  $d_c = 3$ . A solution of the renormalisation group equation indicates that there always exists a critical scale at which the relative dispersion of sizes of polymers with different random sequences of monomers becomes of the order of unity. The magnitude of this critical scale depends strongly on the relation between the constant which characterises the dispersion of the two-body interaction  $\vec{B}_0$  and the constant of the repulsive three-body interaction  $\tilde{V}_0$ . If  $\tilde{B}_0 < \frac{3}{32}\tilde{V}_0$  at each physically attainable scale the effects of screening are prevalent and the dispersion of sizes of polymers with different sequences of monomers is small near the theta point. If the reverse inequality holds, the dispersion of sizes becomes of the order of unity near the theta point.

The overwhelming majority of all polymer molecules in nature—DNA molecules and nuclei molecules—are non-homogeneous. This causes the variety of their unique physical and chemical properties. Recent investigations have shown no evidence for any special regularity in the sequences of monomers along the DNA or nuclei molecules, so that from a statistical point of view these sequences can be considered as random ones.

Even if, in principle, the configurational properties of a chain with a certain fixed sequence of monomers can be calculated, one still encounters the problem of how to average these quantities over a set of polymers with different sequences. The technical difficulty is how to average the logarithm of the partition function of a random chain and its various derivatives over the randomness.

This problem is reminiscent of the averaging procedure problem in solid state disordered systems (spin glasses). But, while in solid state systems randomness is fixed on a lattice, in the case of polymers randomness is fixed on the flexible chain which can move freely with two- and three-body interactions in physical space.

We start with the simple Flory mean-field theory in order to evaluate the effect of randomness in linear polymers. Later, we shall calculate the first-order corrections to the dispersion of the two-body interaction due to the space correlations of repulsive and attractive elements. It turns out that near the theta point, corrections are logarithmic at  $d_c = 3$ . Then we shall present a functional integral formalism which allows one to

use renormalisation group techniques to take into account, near the theta point, both the effects of randomness and repulsive three-body interaction, and to calculate the critical scale at which the effects of randomness become of the order of unity. We shall then briefly discuss the coil-to-globe transition of disordered linear polymers.

For the sake of simplicity, we consider a set of polymer chains of fixed length N which are randomly constructed from only two different kinds of monomers of unit length which only differ in their interactions. In the general case these elements can differ in their length too. But this only leads to small fluctuations of the total length of different polymers and can easily be taken into account. As to the interaction constants, it will be clear from further consideration why only the randomness in two-body interaction constant is relevant. For two types of monomers there are three different two-body interaction constants:  $g_{11}, g_{12}, g_{22}$ . They can be written in the form

$$g_{ij} = g + u(\varepsilon_i + \varepsilon_j) + w\varepsilon_i\varepsilon_j \tag{1}$$

where

 $\varepsilon_i = \begin{cases} 1/2\rho_1 & \text{if the ith monomer is of the first kind} \\ 1/2\rho_2 & \text{if the ith monomer is of the second kind.} \end{cases}$ 

Here  $\rho_1$  and  $\rho_2$  are the relative densities of each kind of monomer  $(\rho_1 + \rho_2 = 1)$ , so the average  $\langle \varepsilon_i \rangle_{av}$  over all polymers vanishes. Below, we shall suppose that  $\rho_1 = \rho_2 = \frac{1}{2}$  and  $\varepsilon_i = \pm 1$ . We can now estimate the dispersion of sizes of polymers of length N with different compositions. Following Flory (1971) the free energy of a polymer coil of size R can be written as a sum of an 'elastic' term and terms which describe the two-and three-body interactions:

$$F = \frac{R^2}{N} + \bar{g}\frac{N^2}{R^d} + V\frac{N^3}{R^{2d}}$$
(2*a*)

where the 'mean' two-body interaction constant  $\bar{g}$  can be written as

$$\bar{g} = g + uO(1/N^{1/2}) + wO(1/N).$$
 (2b)

The minimisation of (2a) with respect to R, subject to condition (2b), allows one to estimate the typical variation of sizes of different polymers. At the theta point

$$\frac{\delta R}{R} \sim u N^{(3-d)/2} \qquad d \ge 3$$

$$\frac{\delta R}{R} \sim u V^{-(2+d)/(2+2d)} N^{(d-3)/(2+2d)} \qquad d < 3$$
(3)

and far from the theta point

$$\frac{\delta R}{R} \sim \frac{u}{g} \frac{1}{N^{1/2}} \qquad d \le 4 \tag{4}$$

where R is the mean-field size of the polymer

$$R \sim N^{1/2} \qquad d \ge 3 R \sim V^{-1/(2+2d)} N^{2/(1+d)} \qquad d < 3$$
(5)

at the theta point and

$$R \sim g^{1/(d+2)} N^{(3/(d+2)} \qquad \text{if } g > N^{(d-4)/2}$$

$$R \sim \left(\frac{V}{g}\right)^{1/(2+2d)} N^{2/(1+d)} \qquad \text{if } g < -V N^{(2-d)/2} \qquad (6)$$

far from the theta point.

From (2b) it follows that the effect of randomness is always small, except maybe the theta point case at d = 3.

In spite of its simplicity, the Flory approximation appears to give accurate estimates of exponents of power dependences for polymer problems (de Gennes 1976, Isaacson and Lubensky 1980). However, it usually fails in the vicinity of the upper critical dimension ( $d \le d_c$ ) of the examined problem (Obukhov 1984). In this case a rigorous RG consideration is necessary. For the problem of the random chain the upper critical dimension is  $d_c = 3$ , which can be seen from the average magnitude of the two-body interaction term in (2a) and (2b) in the theta region. It is of the order of  $uN^{3/2}/R^d$ , i.e.  $uN^{(3-d)/2}$  for an unperturbed polymer coil with  $R \sim N^{1/2}$ . For d > 3 this term is negligible in equation (2a) for large polymer length, but for  $d \le d_c = 3$  it becomes relevant.

From the point of view of the Flory theory there are two apparently different problems: (i) there is the problem of fixed length polymers which are constructed randomly from two kinds of monomers and (ii) there is also the problem of polymers with fixed numbers of monomers of each kind, but with different ordering of thesemonomers. In this case the above consideration would not predict any variation of sizes of different polymers. This, however, is incorrect. Indeed, the repulsive and attractive monomers situated in the middle of a chain and near its endpoint have different environments, and the total effect cannot be expressed only through their mean interaction, which is zero. Later on we shall consider this case in more detail.

Now we shall consider the effect of spatial fluctuations in the non-homogeneous polymer. The first-order correction to the bare coupling constant  $g_{ij}$  is given by figure 1(a).



**Figure 1.** (a) The first-order correction to  $g_{ij}$ . The broken lines are the interactions  $g_{ij}$  and  $g_{kl}$ . Because  $\langle g_{kl} \rangle_{av} = 0$ , the average value of this correction vanishes. (b) The correction to  $g_{ij}^2$ . Here the independent integrations over p and p' must be carried out. The average  $\langle g_{kl}g_{kT} \rangle_{av}$  is non-vanishing only if some of the indices k, l, k', l' coincide.

It can be written as

$$\delta g_{ij} = g_{ij} \sum_{k,l} g_{kl} \int G_{il}(x) G_{jk}(x) d^d x = g_{ij} \sum_{k,l} g_{kl} \int G_{il}(p) G_{jk}(p) \frac{d^d p}{(2\pi)^d}$$
(7)

where  $G_{il}(x)$  is a Gaussian correlator of a random walk of length |i-l|. For future purposes it is more convenient to use its momentum representation  $G_{il}(p) = \exp(-\frac{1}{2}p^2|i-l|)$ . It is evident that at the theta point (g=0) the correction of figure 1(a) averaged over all possible polymer sequences vanishes as  $\langle g_{kl} \rangle_{av} = 0$ . But for each particular polymer, the correction of figure 1(a) has its own particular value, and the dispersion of interaction between monomers *i* and *j* increases due to this correction. This can be considered as an effective increase of the *u* term in the interaction  $g_{ij}$  (see figure 1(b)):

$$2\delta u^{2} = \langle (\delta g_{ij})^{2} \rangle_{av} = \left\langle g_{ij}^{2} \sum_{klk'l'} g_{kl} g_{k'l'} \int \exp[-\frac{1}{2}p^{2}(|j-k|+|i-l|)] \frac{d^{d}p}{(2\pi)^{d}} \right\rangle$$

$$\times \int \exp[-\frac{1}{2}(p')^{2}(|j-k'|+|i-l'|)] \frac{d^{d}p'}{(2\pi)^{d}} \rangle_{av}$$

$$= \text{constant} \times g_{ij}^{2} \sum_{klk'l'} \langle g_{kl} g_{k'l'} \rangle \frac{1}{(|j-k|+|i-l|)^{d/2}} \frac{1}{(|j-k'|+|i-l'|)^{d/2}}.$$
(8)

From (1) it follows that (g = 0)

$$\langle g_{kl}g_{k'l'}\rangle_{av} = u^2(\delta_{kk'} + \delta_{kl'} + \delta_{lk'} + \delta_{ll'}) + w^2(\delta_{kk'}\delta_{ll'} + \delta_{kl'}\delta_{lk'}).$$

Thus as  $d \leq 3$  there is a divergent term in (8):

$$\delta u^{2} \sim \begin{cases} (u^{2})^{2} \ln N & d = 3\\ (u^{2})^{2} N^{3-d} & d < 3. \end{cases}$$
(9)

At  $d \leq 2$  the divergent corrections from the w terms also appear.

It is well known for a homogeneous polymer chain that near the theta point the three-body interaction must be taken into account, and for this problem  $d_c = 3$ . Hence the effects of randomness must be consisdered simultaneously with the effects of three-body interactions. We shall do this using a conformal space functional integral method proposed by Edwards (1966) (see also Kholodenko and Freed 1983, Freed and Kholodenko 1983).

The generating functional for the non-homogeneous polymer chain problem can be written in the form

$$Z = \int_{r(0)=0} Dr \exp(-H\{r\})$$
(10)

where

$$H\{r\} = \frac{1}{2} \int_{0}^{N} d\tau \left(\frac{\partial r(\tau)}{\partial \tau}\right)^{2} + \frac{1}{2!} \int_{0}^{N} \int_{0}^{N} d\tau d\tau' g_{\tau\tau'} \delta(r(\tau) - r(\tau')) + \frac{V}{3!} \int_{0}^{N} \int_{0}^{N} \int_{0}^{N} d\tau d\tau' d\tau'' \delta(r(\tau) - r(\tau')) \delta(r(\tau) - r(\tau'')) - \int dR h(R) \delta(r(N) - R).$$
(11)

We introduce here the continuous variables  $\tau$ ,  $\tau'$ ..., instead of the discrete *i*, *j*,..., ones.

One end of a polymer chain is assumed to be fixed at the origin of the coordinates and the location of the other one is controlled by the field h(R). The correlation function of a polymer chain is

$$G(R) = \frac{\partial \ln Z}{\partial h(R)} \bigg|_{h=0}.$$
 (12)

The mean square distance between the endpoints of a polymer can be written as<sup>†</sup>

$$\langle R^2 \rangle = -\frac{\partial^2 G(p)}{\partial p^2} \Big|_{p=0}$$
(13)

where p is the Fourier variable conjugate to R. We are interested in quantities which are averaged over all possible sequences of monomers. This problem of averaging  $\ln Z$  over the randomness can be reduced to the problem of averaging the partition function using the replica trick:

$$\langle \ln Z \rangle_{\rm av} = (1/n) \lim_{n \to 0} \ln \langle Z^n \rangle_{\rm av}.$$

Here  $Z^n$  can be understood as the partition function of *n* identical polymer chains with one fixed sequence of monomers. The averaging of  $Z^n$  can be done in a straightforward way:

$$\langle Z^n \rangle_{av} = \int_{r_\alpha(0)=0} \exp(-H\{r_\alpha\}) \prod_{\alpha=1}^n Dr_\alpha$$
(14)

with  $H\{r_{\alpha}\}$  as a 'homogeneous' *n*-chain Hamiltonian:

$$H = \frac{1}{2} \sum_{\alpha} \int_{0}^{N} d\tau \left(\frac{\partial r_{\alpha}(\tau)}{\partial \tau}\right)^{2} + \frac{g}{2!} \sum_{\alpha} \int_{0}^{N} \int_{0}^{N} d\tau d\tau' \, \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau'))$$

$$- B_{0} \sum_{\alpha \neq \beta} \int_{0}^{N} \int_{0}^{N} \int_{0}^{N} d\tau d\tau' d\tau'' \, \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau')) \delta(r_{\beta}(\tau) - r_{\beta}(\tau''))$$

$$+ \frac{V_{0}'}{3!} \sum_{\alpha} \int_{0}^{N} \int_{0}^{N} \int_{0}^{N} d\tau d\tau' d\tau'' \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau')) \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau''))$$

$$- \sum_{\alpha} \int dR_{\alpha} h(R_{\alpha}) \delta(r_{\alpha}(N) - R_{\alpha}). \qquad (15)$$

Here  $B_0 = \frac{1}{2}u^2$ ,  $V'_0 = V - 6B_0$ . It should be noted here that the structure of the  $B_0$  and  $V'_0$  terms is quite similar and differs only in replica indices.

A calculation of arbitrary configurational and thermodynamical properties of an individual polymer, averaged over all polymers, can be expressed in terms of the averaged correlation function

$$\langle G(R) \rangle_{\mathrm{av}} = \frac{\partial \ln \langle Z^n \rangle_{\mathrm{av}}}{\partial h(R_\alpha)} \bigg|_{\substack{h=0\\n=0}}$$

where  $\alpha$  is an arbitrary replica index.

 $\uparrow\langle\cdots\rangle$  means the average over all configurations of one polymer (thermal average) and  $\langle\cdots\rangle_{av}$  the average over all polymers.

All these properties are the same as for a homogeneous polymer chain with the Hamiltonian

$$H\{r_{\alpha}\} = \frac{1}{2} \int_{0}^{N} d\tau \left(\frac{\partial r_{\alpha}}{\partial \tau}(\tau)\right)^{2} + \left(\frac{g}{2!} - 2B_{0} \left\langle\!\!\left\langle\sum_{\beta \neq \alpha_{0}} \int_{0}^{N} d\tau'' \,\delta(r_{\beta}(0) - r_{\beta}(\tau'')\right)\!\!\right\rangle\!\!\right\rangle_{av}\!\right) \\ \times \int_{0}^{N} \int_{0}^{N} d\tau \,d\tau' \,\delta(r_{\alpha}(\tau) - r_{\alpha}(\tau')) + \frac{V_{0}'}{3!} \int_{0}^{N} \int_{0}^{N} \int_{0}^{N} d\tau \,d\tau' \,d\tau'' \\ \times \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau')) \delta(r_{\alpha}(\tau) - r_{\alpha}(\tau'')) \\ - \int dR_{\alpha}h(R_{\alpha})\delta(r_{\alpha}(N) - R_{\alpha}).$$
(16)

The average

$$\left\langle \left\langle \sum_{\beta \neq \alpha_0} \int_0^N \mathrm{d}\tau'' \, \delta(r_\beta(0) - r_\beta(\tau'')) \right\rangle \right\rangle_{\mathrm{av}}$$

on the RHS of (16) is equal to  $-\int_0^N \langle G_\tau(0) \rangle_{av} d\tau$  (in the limit of n = 0) where  $G_\tau(R)$  is a correlation function of part of a chain of length  $\tau$ . The main contribution to this integral comes from the region of small  $\tau$ , i.e. it is determined by the microscopical properties of the model. Summarising this consideration, we conclude that for mean values of physical quantities (not their dispersion) the disorder in a polymer chain amounts to a certain shift of the mean two- and three-body interactions to the repulsion and attraction domain, respectively. All the dispersions in thermal averages are closely connected with the non-diagonality of the Hamiltonian (15) in replica indices. Of utmost importance for physical applications is a calculation of the dispersion of thermally averaged sizes of polymers with different sequences. This can be written as

$$D(\langle R^2 \rangle) = \langle\!\langle R^2 \rangle^2 \rangle_{\rm av} - \langle\!\langle R^2 \rangle\!\rangle_{\rm av}^2 = \int \int R_\alpha^2 R_\beta^2 \frac{\partial^2 \ln\langle Z^n \rangle_{\rm av}}{\partial h(R_\alpha) \partial h(R_\beta)} \, \mathrm{d}R_\alpha \, \mathrm{d}R_\beta.$$
(17)

The first-order diagram contributing to  $D(\langle R^2 \rangle)$  is shown in figure 2. The momentum presentation is used. The  $B_0$  term is indicated on figure 2 by two vertices in  $p_{\alpha}$  and  $p_{\beta}$  physical spaces. In each vertex the momentum conservation rule holds. The wavy lines present the  $-\partial^2/\partial p^2$  operators. The integration should be carried over  $\tau$ ,  $\tau'$ ,  $\tau''$  and  $p_{\alpha}$ ,  $p_{\beta}$ . After a simple calculation we get

$$D(\langle R^2 \rangle) = N^2(\pi + 4) I_1^2 B_0 \qquad I_1 = 1/8\pi^{3/2}.$$
 (18)

The main contribution in (18) comes from the large scale region where  $p_{\alpha}$ ,  $p_{\beta} \sim N^{-1}$ . Thus the first-order correction to  $B_0$ , (9), and other higher-order corrections must be taken into account. We can do this using the renormalisation method described in detail by Kholodenko and Freed (1983) for the problem of a homogeneous polymer. It consists of introducing the arbitrary length scale  $L \gg 1$  instead of a microscopic one, and in calculating the renormalised coupling constants which characterise the observed macroscopic quantities on the length scale L. The renormalisation group equation can be obtained by expanding the partition function (14) up to the second order in powers of  $B_0$ ,  $V'_0$  which are dominant interactions in the theta region. Then the diagrams contributing to the renormalised coupling constants must be calculated. One of them is the same as in figure 1(b) (here the notation must be changed from *i*, *j*, *k*,..., to  $\tau$ ,  $\tau'$ ,  $\tau''$ , ...). The combinatorial factors in the diagrams are obtained by considering



**Figure 2.** The first-order term in  $D(\langle R^2 \rangle)$ . ( $\alpha$ ) and ( $\beta$ ) correspond to two different replica spaces. The momentum representation is used and the wavy line is the second derivative over the momentum,  $\partial^2/\partial p^2$ .

all possible orderings of  $\tau, \tau', \tau'', \ldots$ . The RG equations for renormalised constants B, V' are (d = 3):

$$dB/d\xi = 64I_2B^2 - 16I_3BV'$$

$$dV'/d\xi = -22I_3(V')^2$$
(19)

where

$$I_2 = 1/8 \pi^3$$
  $I_3 = 1/16 \pi^2$   $\xi = \ln L$ 

The solution of equation (15) is

$$\tilde{V} = \frac{\tilde{V}_0}{1 + 22 \tilde{V}_0 \xi}$$

$$\tilde{B} = \frac{\tilde{B}_0}{(1 + 22 \tilde{V}_0 \xi)^{8/11}} \left( 1 - \frac{32}{3} \frac{\tilde{B}_0}{\tilde{V}_0} \left[ (1 + 22 \tilde{V}_0 \xi)^{3/11} - 1 \right] \right)^{-1}$$

$$= \frac{3}{32} \frac{\tilde{V}_0}{1 + 22 \tilde{V}_0 \xi} \left[ \left( \frac{1 + 22 \tilde{V}_0 \xi_c}{1 + 22 \tilde{V}_0 \xi} \right)^{3/11} - 1 \right]^{-1}$$
(20)

where

$$\xi_{c} = \frac{1}{22 \, \tilde{V}_{0}} \left[ \left( 1 + \frac{3}{32} \, \frac{\tilde{V}_{0}}{\tilde{B}_{0}} \right)^{11/3} - 1 \right] \tag{21}$$

and

$$\tilde{V} = I_3 V' \qquad \tilde{B} = I_2 B.$$

This solution can be understood as follows. There always exists the critical scale  $L \sim e^{\xi_c}$  at which the charge  $\tilde{B}$  diverges, but the value of this critical scale depends strongly on the relationship between the initial values of  $\tilde{V}$  and  $\tilde{B}$ , as follows.

(a) If  $\tilde{B}_0 > \frac{3}{32} \tilde{V}_0$ , the effect of screening of randomness due to the repulsive threebody interaction is negligible and the divergence of  $\tilde{B}$  can be seen, in principle, for a long enough polymer.

(b) If a reverse inequality holds, the critical scale becomes astronomically large, and at each physically reliable scale the effects of screening are prevalent:

$$\tilde{B} = \tilde{B}_0 (1 + 22 \, \tilde{V}_0 \xi)^{-8/11}.$$
(22)

If we take into account the higher-order corrections to B and to  $\langle R^2 \rangle$ , equation (18) can be rewritten in the form<sup>†</sup>

$$\frac{D(\langle R^2 \rangle)}{\langle \langle R^2 \rangle \rangle_{av}^2} = (\pi + 4) I_1^2 B(\xi).$$
(23)

So far we have only considered the case where the effects of a two-body interaction are negligible:  $g \ll N^{-1/2}$ . If the opposite inequality holds, the renormalisation can be made only up to the scale  $R^* \sim (N^*)^{1/2} \sim 1/g$ . On the larger scale, the two-body interaction is dominant and the mean-field considerations (4) and (6) can be applied in terms of renormalised units of size  $R^*$  containing  $N^*$  monomers with a renormalised randomness B and a renormalised three-body interaction constant. This consideration can be carried out only when the scale  $R^*$  is less than the critical one:  $R^* < L_c \sim e^{\xi_c}$ . The qualitative description in the case where  $R^* > L_c$  can be based on the assumption that  $L_c$  remains a characteristic scale where the effects of correlations of attractive and repulsive units are important, and due to this assumption, on scales larger than  $L_c$  the chains of blobs of size  $L_c$  can be considered within the framework of the mean-field approximation. From (3)-(6) we obtain (d = 3):

$$\frac{\delta R}{R} \sim \frac{u^R(\xi)}{gN^{1/2}}$$
 if  $|g| > N^{-1/2}$  (24)

and

$$\frac{\delta R}{R} \sim u^{R}(\xi) \qquad \text{if } |g| > N^{-1/2} \tag{25}$$

where

$$u^{R}(\xi) = \begin{cases} B^{1/2}(\xi) & \xi < \xi_{c} \\ 1 & \text{otherwise.} \end{cases}$$

If the number of monomers of each kind is fixed (case ii) the additional constraint  $\sum_{i=1}^{N} \varepsilon_i = 0$  or  $\int_0^N \varepsilon(\tau) d\tau = 0$  must be satisfied throughout the calculations. In this case it is more convenient to calculate the dispersion (17) first using the unaveraged partition function  $Z^n$ :

$$\langle \langle \mathbf{R}^2 \rangle^2 \rangle_{\rm av} - \langle \langle \mathbf{R}^2 \rangle \rangle_{\rm av}^2 = I_1^2 \left( \int_0^N \varepsilon(\tau) [\tau^{1/2} + (N - \tau)^{1/2}] \,\mathrm{d}\tau \right)^2.$$
 (26)

The average of (26) with  $\varepsilon(\tau)$  as a random variable with  $\langle \varepsilon(\tau)\varepsilon(\tau')\rangle_{av} = \delta(\tau-\tau')$  reproduces equation (18). The constraint  $\int_0^N \varepsilon(\tau) d\tau = 0$  can be taken into account by substituting  $\varepsilon(\tau)$  by  $\varepsilon'(\tau) - (1/N)_0 \int_0^N \varepsilon'(\tau') d\tau'$  in (26), with  $\langle \varepsilon'(\tau)\varepsilon'(\tau')\rangle_{av} = \delta(\tau-\tau')$ . Then we obtain instead of (18):

$$D(\langle R^2 \rangle) = N^2(\pi - \frac{28}{9})I_1^2 B_0.$$
<sup>(27)</sup>

<sup>†</sup> There are also terms containing higher orders of B which contribute to  $D(\langle R^2 \rangle)$ . They do not change the point of singularity  $\xi_c$  of  $D(\langle R^2 \rangle)$ .

This is more than two orders of magnitude less than in case (i). The above constraint only refers to the polymer chain as a whole, whereas on any scale which is smaller than the maximal one the chain can be considered as a random one and the RG equations remain the same. In this case the analogue of equation (23), with multiplier  $\pi - \frac{28}{9}$  instead of  $\pi + 4$ , can be written. If the polymer is long enough, so that *B* diverges at a certain critical length, the qualitative description (24) and (25) is valid.

These results for the coil to the globe transition region are shown schematically in figure 3. Figure 3(a) presents the mean-field prediction of dependence of  $\langle R^2 \rangle$  against mean interaction g. The dispersion of  $\langle R^2 \rangle$  in case (i) is shown by a broken curve. If the number of monomers of different kinds is fixed (case ii) and the polymers are distinguished only by ordering of these monomers, by virtue of the Flory theory there is no dispersion at all (full curve).

The RG results are shown in figures 3(b) and (c). If disorder is weak,  $\tilde{B}_0 < \frac{3}{32}\tilde{V}_0$ , the effects of randomness are screened by repulsive three-body interactions for any physically attainable length of a polymer (figure 3(b)). If the opposite inequality holds, the dispersion of sizes for long polymer  $(N > L_c^2)$  chains becomes of the order of one



Figure 3. (a) The Flory theory prediction for  $\langle R^2 \rangle$  against g (full curve) and its dispersion (the area in between the broken curves). If the number of monomers of different kind is fixed, the mean is as above, whereas the dispersion vanishes by virtue of the mean-field theory. (b, c) RG theory predictions: (b) if  $\frac{3}{32}\tilde{V}_0 > \tilde{B}_0$ , the effects of disorder are screened by repulsive three-body interactions (equation (22)); (c) if  $\frac{3}{32}\tilde{V}_0 < \tilde{B}_0$  the dispersion of sizes for long enough polymer chains  $(N > L_c^2)$  becomes of the order of one near the theta point  $(|g| < N^{-1/2})$ .

near the theta point (figure 3(c)). The same pattern is retained if the number of monomers of different kinds is fixed, the only difference being that in this case the dispersion on figure 3(b) is smaller due to the numerical factor in (27). Remarkably, the mean values for a set of polymers are the same as that for a certain homogeneous polymer chain, and that could hold despite the divergence of dispersions in the former case.

## Acknowledgments

I wish to thank A Grossberg and E Shakhovitch for the discussion which initiated this work, and D Amit and S Alexander for stimulating discussions concerning the irrelevance of high-order charges in this problem. I gratefully acknowledge the kind hospitality of the staff of Nordita during the work on this paper.

## References

de Gennes P G 1976 Macromol. 9 587 Edwards S F 1966 Proc. Phys. Soc. 88 266-80 Flory P J 1971 Principles of Polymer Chemistry (Ithaca, NY: Cornell University Press) Freed K F and Kholodenko A L 1983 J. Stat. Phys. 30 437-47 Isaacson J and Lubensky T C 1980 J. Physique 41 L469 Kholodenko A L and Freed K F 1983 J. Chem. Phys. 78 7390-411 Obukhov S P 1984 J. Phys. A: Math. Gen. 17 L965-9