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Polymer chain in disordered media

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We study the magnitude of the energy fluctuations of a long polymer chain with excluded-volume interactions placed in a media with a weak random potential. It is shown that there always exists a critical length N^* of a polymer segment or a critical length scale L^* at which the fluctuations of the interaction energy between the polymer segment and the medium are of the order of kT. At larger scales the problem reduces to that of the minimum energy path in a strong random potential. Using an analogy with the directed polymer problem, we suggest that the size of a polymer coil is of order $L^*(N/N^*)^{2/3}$ in three dimensions. In the two-dimensional case, the size of the polymer coil is controlled by excluded-volume effects: $R \sim N^{3/4}$. The magnitudes of the energy barriers between the different, neighboring configurations are $(N/N^*)^{1/3}kT$ and $(N/N^*)^{3/8}kT$ for the cases $d=3$ and 2, respectively. Those energy barriers cause the trapping of a long polymer chain. The coil-to-globe transition in disordered media is also discussed.

INTRODUCTION

There are two different classes of processes that deal with disorder. They are usually called annealed and quenched disorder problems. The averaging over the different realizations of disorder in the first problem can be done simultaneously with a thermodynamical averaging. The polymer chain in a complicated solvent, which contains other chains or monomers, can be considered an example of this type of problem. It is evident that if we first average over all configurations of the inhomogeneities of the solution, this problem reduces to the problem of a chain in a homogeneous medium. But the effective parameters of the excluded-volume interaction can be rather exotic in this case. In quenched disorder problems, the quantities of physical interest must be calculated first (or measured) for a particular configuration of disorder, only after which the average over the disorder can be taken.

We shall be interested here in a problem of configurational statistics of a polymer chain in a medium with a fixed disorder. It can be a problem of polymer chain adsorbed on a rough surface (two-dimensional case), or a problem of a chain in a three-dimensional disordered matrix, such as a gel or a porous medium. This problem was studied using different techniques including computer simulation, the replica method, and the Flory approach (see the recent papers[1-7] and references herein). The results of these investigations for the size of the polymer chain and its statistics are often controversial. The aim of this paper is to point out pecularities of the averaging procedure as one possible source of this controversy. The excluded-volume effects are also very important in this problem.

If the system is large enough, the thermodynamical average over all possible polymer configurations also includes the summation over all possible positions of a polymer in a disordered medium, i.e., over different disorder realizations. Thus, formally, it is equivalent to the problem of a polymer chain with annealed disorder. What we shall show in this paper is that there are serious limitations for this reduction. The reason is that the interaction energy of a chain and a medium differs from site to site. The magnitude of this difference grows with the increase of the length N of a polymer as a power of N. Thus, for long enough polymers, these fluctuations can exceed kT. In this case, the main contribution to the partition function of a chain is given by the rare regions of the disordered media, where the interaction energy is minimal. The volume needed to obtain true "averaged" statistics of a chain grows exponentially with N. The time needed to obtain the "averaged" statistics should also be exponentially large. It could happen that for any reliable observation time, the typical configuration of a long polymer chain will differ from the configuration of a polymer in an averaged environment.

These effects cannot be calculated in the framework of a model of a polymer in an infinitely large system. Thus we shall start with a problem which cannot be deliberately reduced to an annealed disorder case. It is a problem of a polymer in a restricted volume of a disordered medium. This restriction can be realized in different ways: by box limitations (fixing the position of the center of mass of the chain) or by fixing the ends of the chain.

WEAK DISORDER

For the sake of simplicity, we shall consider the problem of a chain with a fixed position of one end placed in a medium with high ($c \sim 1$) concentration of weak impurities of two different kinds with the interaction energy $\pm w$ ($w \ll 1$ in kT units). At first we shall neglect the excluded volume effects by considering the chain as a Gaussian one.

The large-scale structure of the polymer can be represented as a chain of subunits (blobs) of size r, each containing r^2 monomers. Each blob occupies a volume of order r^d. The difference between the number of attractive and repulsive impurities in this volume is of the order $r^{d/2}$, and this provides the coarse-grained random potential for each monomer inside this blob. The total number of monomers in a blob is r^2, so that the interaction energy of the medium and a blob fluctuates as $(\pm w r^{2-d/2})$ from one blob to another. At length scales $r \sim w^{-2/(4-d)}$, the fluctuations of the interaction energy is of order of unity (of order kT).

This qualitative consideration can be carried out more accurately including the excluded volume effects by the use of replica formalism.[8] The trick is to introduce n identical polymer chains in the same random medium and to average over the disorder configurations. Then for an n-chain Hamiltonian, translationally invariant, the renormalization-group procedures can be applied. Finally, n should be put equal to zero. Omitting the technical details, we will briefly describe the results of the above consideration. There are two independent charges in the theory. One is the effective second virial coefficient B_{ii}. It is shifted slightly with respect to its homogeneous value B (Refs. 2, 3, and 5):

$$B_{ii}^{(0)} \Longrightarrow B_{ii}^{(0)} - cw^2 \; . \tag{1}$$

Another charge B_{ij}, describes the specific effect of disorder—the interaction between the polymer chains with different replica indices ij $(i \neq j)$. This attractive interaction $B_{ij} < 0$ has a very simple physical explanation. If one polymer chain is attracted to certain places in a random medium and repulsed from other ones, the same happens with another chain placed in the same medium. In terms of the translationally invariant n-chain Hamiltonian, this mutual correlation in configurations of different polymers can be described as their attraction to each other.

The renormalization-group equations for B_{ii} and B_{ij} are

$$\frac{\partial B_{ii}}{\partial \xi} = \epsilon B_{ii} - 32(B_{ii})^2 \; , \tag{2a}$$

$$\frac{\partial B_{ij}}{\partial \xi} = \epsilon B_{ij} - 16 B_{ij} B_{ii} - 16(B_{ij})^2, \quad i \neq j \; , \tag{2b}$$

where $\xi = In_L$; $\epsilon = 4-d$.

These are the same as the equations first obtained by Nikomarov and Obukhov[9] for the similar problem of the statistics of a probe polymer chain surrounded by other chains. The solution of Eq. (2) is[9]

$$B_{ii} = \left[\frac{L}{a} \right]^{\epsilon} \frac{B_{ii}^{(0)}}{1+32 B_{ii}^{(0)} x} \; , \tag{3a}$$

$$B_{ij} = \left[\frac{L}{a} \right]^{\epsilon} \frac{B_{ij}^{(0)}}{1+16 B_{ij}^{(0)} t} \frac{1}{(1+32 B_{ii} x)^{1/2}} \; , \tag{3b}$$

where

$$x = \epsilon^{-1}[(L/a)^{\epsilon} - 1], \quad t = \frac{1}{16 B_{ii}^{(0)}}[(1+32 B_{ii}^{(0)} x)^{1/2} - 1] \; .$$

For $B_{ij}^{(0)} < 0$, there always exists a critical length scale $L^* = e^{\xi_c}$ at which $B_{ij}^{(0)}$ diverges. If $|B_{ij}^{(0)}| > B_{ii}^{(0)}$, the singularity in B_{ii} occurs at $\xi_c \approx 1/16 B_{ij}^{(0)}$; if $|B_{ij}^{(0)}| < B_{ii}^{(0)}$, at $\xi_c \approx B_{ii}^{(0)}/8(B_{ij}^{(0)})^2$. The divergence of B_{ij} means that at the scale $l^* = e^{\xi_c}$, the magnitude of the energy fluctuations becomes to be of the order of one. At this scale, the chains cannot any longer be considered as free ones. Above, we only considered the divergences caused by the first denominator in the right-hand side of Eq. (3b). If $B_{ii}^{(0)} < B_{ij}^{(0)}$, this singularity can be forestalled by a singularity in B_{ii} [second denominator in the right-hand side of Eq. (3b)]. It manifests the collapse of the polymer chain due to the attractive monomer-monomer interaction. In any realistic polymer model, this collapse would be restricted by high-order excluded-volume interactions, i.e., by repulsive three-body interactions. Nevertheless, the singularity in B_{ii} means that the renormalization can be done only up to the scale $\xi \sim 1/32|B_{ii}|$. Actually, it should be stopped when B_{ii} becomes of the order of unity; thus B_{ij} at this scale is equal to

$$B_{ij} \approx \frac{B_{ij}^{(0)}}{(B_{ii}^{(0)})^{1/2}} \quad \text{if } |B_{ij}^{(0)}| < |B_{ii}^{(0)}| \; . \tag{4}$$

In this case, B_{ij} is less than unity. It means that the renormalized interaction of a polymer and a medium at this scale is weak. Later we shall come back to the case $B_{ii} < 0$.

STRONG DISORDER: LARGE-SCALE CONSIDERATION

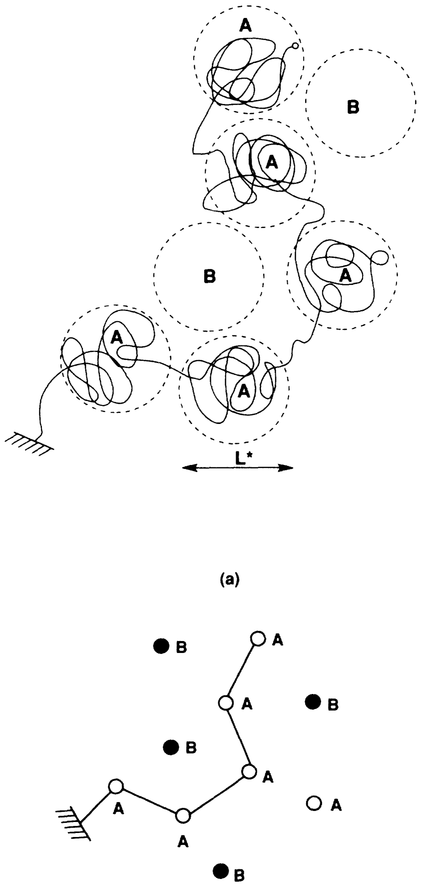
The large-scale problem can be formulated now as a problem of placing a chain in a medium with a strong disorder. The size of new "monomers" is L^*: the same as the scale of disorder fluctuations. Each monomer is a subchain [see Fig. 1(a)] of $N^* \simeq (L^*)^{1/\nu}$ elementary monomers. Here, ν is the exponent controlled by excluded-volume effects: $\nu = \frac{1}{2}$, or $\nu = 3/(d+2)$. The amplitude of disorder fluctuations is of order kT.

In the absence of excluded-volume interactions, the problem is rather simple. In this case we must find the most attractive region in the neighborhood of the point to which one end of a polymer chain is attached. The main part of the chain will be hidden in this region; the rest will connect it with a point of attachment. The detailed analysis of the optimal configuration on the lattice with a Gaussian distribution of the interaction potential was made by Cates and Ball.[1] Below, we shall proceed from the fact that, for real polymers, the excluded-volume effects should be taken into account. We shall assume that at a critical length L^*, the magnitude of the repulsive two-body interaction is large enough to prevent the two monomers from occupying the same place simultaneously. Thus the problem is to find a minimum energy configuration for a chain of fixed length $\tilde{N} = N/N^*$, where each site can be visited only once [see Fig. 1(b)]. The main quantities of interest are (a) the typical size of a polymer chain and (b) the typical energy barrier between two neighboring optimal configurations. We shall give here self-consistent estimates for the two corresponding exponents ν and α, defined through $R \sim \tilde{N}^{\nu}$ and $E \sim \tilde{N}^{\alpha}$, based on Flory-type arguments.

The first relation between these exponents can be obtained if we assume that the free energy associated with the entropy of the polymer coil $R^2/\tilde{N}$ should be of the order of the amplitude of the energy fluctuations $\tilde{N}^{\alpha}$. This gives

$$\alpha=2\nu-1 . \tag{5}$$

Now let us consider a small shift $x \ll R$ of a fixed end of a polymer from its previous position. Only a small part of the optimal configuration will be affected by this shift, and the length of this part is of the order x (see Fig. 2). Since the main part of the polymer remains positioned in the same region as before, only the connection with this region is changed. The difference in the interaction energy of the two "tails" should be of the order of $x^{1/2}$. When x becomes comparable with R, we can expect the whole configuration to be switched to another one. Thus $R^{1/2}$ should be of the order of the energy fluctuations $\tilde{N}^{\alpha}$. This is the second relation between the exponents $\nu/2=\alpha$, and we get $\nu=\frac{2}{3}$ and $\alpha=\frac{1}{3}$ (for any spatial dimension). Similar arguments were used to predict the exponents in the problem of a directed polymer in a random potential.[10] It is clear that both problems are closely related, but in our problem we have additional restrictions connected with the absence of self-intersections. In the case of a directed polymer problem, these exponents are proven to be exact at $d=2$ (exact solution[11,12]) and probably in higher dimensions (numerical results,[10] theoretical arguments[13]). But in the latter case, the situation remains controversial because there are d-dependent numerical results for the same exponents in some modified stochastic growth models.[14–17]



(a)

(b)

FIG. 1. (a) At length scale L^*, the energy fluctuations become of order kT. This means that some regions of the medium (A) become more preferable for the chain, whereas the others (B) do not. (b) The large-scale problem can be formulated now as a problem of placing a chain in a medium with strong disorder.

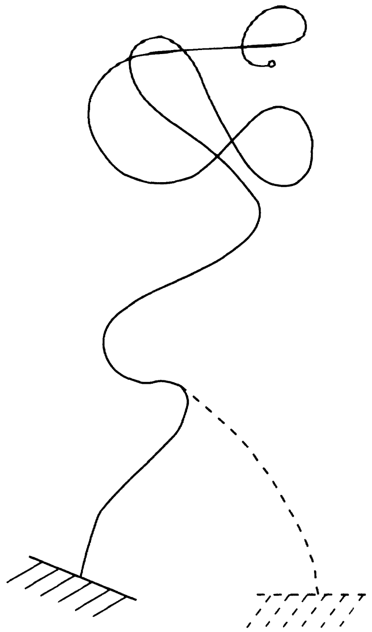


FIG. 2. Consider a small shift $x \ll R$ of a fixed end of a polymer from its previous position. Only a small part of the optimal configuration will be affected by this shift, and the length of this part is of the order x. When x becomes comparable to R, we can expect the whole configuration to be switched to another one.

We took into account the excluded-volume effects when we assumed that at each step a new site was visited. To be sure that those configurations, selected by the above consideration, are as a rule non-self-intersecting, we can estimate the magnitude of the Flory two-body interaction term. It is $\tilde{N}^2/R^d$ or $\tilde{N}^{2-d\nu}$ and must be compared with $R^2/\tilde{N}$ or $\tilde{N}^{\alpha}$ terms. For $d=3$, this term is negligible, and the above consideration is correct.[18] At $d=2$, this interaction term becomes dominant. The exponent ν is determined by comparing $R^2/\tilde{N}$ and $\tilde{N}^2/R^d$ terms to be $\nu=\frac{3}{4}$, and the exponent for energy fluctuations is given by $\alpha=\frac{3}{8}$. The relation Eq. (5) no longer holds.

The above consideration was carried out for a chain with a fixed position of one end. The results we obtained for the size of a polymer chain at $d=3$ are rather unusual. The typical configuration is stretched with respect to the configuration in a homogeneous medium, even if the excluded-volume effects are taken into account. Now we can understand why the averaging over all the configurations of a free polymer chain in an infinite medium gives a different result. It is because the partition function of the latter problem can be written as a sum:

$$Z = \sum_{z} Z'(r) , \tag{6}$$

where $Z'(r)$ is the partition functions of the polymer with an end fixed at the point r. In the strong-coupling problem, the logarithm of $Z(r)$ is simply the interaction energy of a chain and a medium which fluctuates from site to site with the amplitude much larger than kT. Thus site-to-site fluctuations of $Z(r)$ are exponentially large, and the main contribution to the partition function Eq. (6) comes from exponentially rare regions with the minimal interaction energy. The polymer configurations in these regions can be quite different from the typical ones.

If we have a long free polymer chain in a disordered medium, we cannot actually speak about averaging over all possible configurations, because even geometrically closest optimal configurations are separated by the energy barriers with an amplitude of order $(N/N^*)^{\alpha}$. An exponentially large time is needed for the chain to overcome the barrier. And in order to obtain the "averaged" statistics, the chain must pass through an exponentially large number of such barriers.

This is very similar to the situation in spin glasses, where the "true" ground state is unobtainable and measurable quantities depend logarithmically on the observation time.

The dynamics of a polymer chain can be characterized by four different regimes. If the chain is placed in a random medium (with a weak disorder) at time $t=0$, we can expect first a free relaxation of segments of a chain with $L \sim t^{1/4}$ dependence of a scale of relaxation on time.[19] At $t \sim L_c^4$, this regime will be superseded by logarithmically slow relaxation with an $L \sim \ln^2 t$ dependence. It means that there will be $1/f$ noise in all quantities which characterize the polymer chain position. At $t \sim \exp c_1 (N/N^*)^{\alpha}$, we shall obtain another logarithmical regime (also with $1/f$ noise) with transitions of the polymer chain as a whole between different optimal configurations. Here c_1 is some numerical constant. And, asymptotically, at $t > \exp c_2 (N/N^*)^{\alpha}$, where c_2 is another numerical constant, we shall obtain the large-scale classical diffusion of a polymer chain. The average size of a chain will be the same as in a homogeneous medium (but with renormalized, excluded volume interactions). This regime can be obtained only if the concentration of chains in a medium is small enough. It must be less than one chain per volume, which is needed to obtain the averaged behavior.

COIL-TO-GLOBE TRANSITION

Using the Flory approximation, we can write the free energy of polymer chain in large-scale units as follows:

$$F = R^2/\tilde{N} + B\tilde{N}^2/R^d + V\tilde{N}^3/R^{2d} - R^{\alpha} \quad (B \equiv B_{ll}) . \tag{7}$$

Here the third term on the right-hand side represents the repulsive three-body interaction (we shall assume for simplicity that $V=1$). The fourth term represents the stretching effect of the interaction of the chain and the medium. In the globular state, the average size of the polymer chain is determined by minimization of the sum of the second and third terms in Eq. (7):

$$R^d \sim \tilde{N} |B|^{-1} \quad (B < 0) . \tag{8}$$

The energy of particle-particle interactions is of order $-B^2\tilde{N}$. The coil-to-globe transition occurs when this energy becomes of order $\tilde{N}^{\alpha}$:

$$B \sim \tilde{N}^{-(1-\alpha)/2} \sim \tilde{N}^{-1/3} . \tag{9}$$

The size of the globe near the transition point is

$$R \sim \tilde{N}^{4/9}, \quad d=3 , \tag{10a}$$

$$R \sim \tilde{N}^{2/3}, \quad d=2 . \tag{10b}$$

A typical globular configuration is shown in Fig. 3. It can be realized in many different ways using different connections between the same occupied sites. The fluctuations of the interaction energy of the globular chain and the medium near the transition point are of order[18]

$$\Delta E \sim \tilde{N}/R^{d/2} \sim \tilde{N}^{1/3} , \tag{11}$$

i.e., of the same order as above the transition point. If

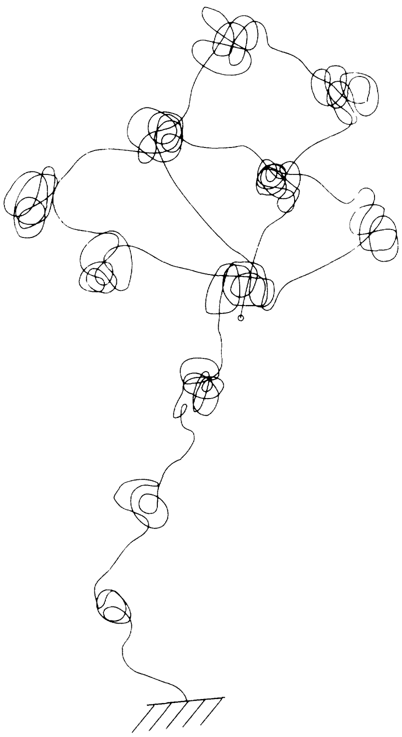


FIG. 3. Typical globular configurations can be realized in many different ways using different connections between the attractive regions. If one end of a polymer chain is fixed at some point, there is a "tail" which connects the globular main body with this point. The length of the "tail" is of the same order of magnitude as the size of the polymer above the transition point.

the position of one end of the polymer chain is fixed, there will be a tail connecting it with the globular main body. The elastic energy needed to stretch this tail should be of the order of the interaction energy in Eq. (11). It means that the length of the tail S is of the same order of magnitude as the size of the polymer above the transition point:

$$S \sim \tilde{N}^{2/3} . \qquad (12)$$

At $|B|=1$, the density correlation length of a globular state becomes of order of one unity (in blob units). It means that the globular state becomes compact, and there are no "holes" between blobs as in Fig. 3. If the density correlation length becomes less than blob size L^*, we return to the weak disorder problem [see Eq. (4)]. We can now use the standard description of the globular state in a homogeneous media for configurational statistics. Nevertheless, the total interaction energy of a globule and a media is of order $\omega|B^0|^{1/2}\tilde{N}^{1/2}$, and this results in a trapping of long chains.

Note added. Copies of two unpublished papers have recently come to my attention. In Ref. 20, by Machta and Kirkpatrick, the properties of the averaged partition junction and its moments are investigated, and the equations similar to (2a) and (2b) are derived independently. In Ref. 21, Honeycutt and Thirumalai develop a Flory-Lifshitz theory for optimal cavities in a random media which reduces disorder.

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[1] M. E. Cates and R. C. Ball. J. Phys. (Paris) **49**, 2009 (1987).

[2] S. F. Edwards and Y. Chen, J. Phys. A **21**, 2963 (1988).

[3] M. Muthukumar, J. Chem. Phys. **90**, 4594 (1989).

[4] J. Machta and R. A. Guyer, J. Phys. A **22**, 2539 (1989).

[5] J. D. Honeycutt and D. Thirumalai, J. Chem. Phys. **90**, 4542 (1989).

[6] T. Nattermann and W. Renz, Phys. Rev. A **40**, 4675 (1989).

[7] A. Baumgartner and M. Muthukumar, J. Chem. Phys. **87**, 3082 (1987).

[8] S. F. Edwards and P. W. Anderson, J. Phys. F **7**, 965 (1975).

[9] E. S. Nikomarov and S. P. Obukhov, Zh. Eksp. Teor. Fiz. **80**, 650 (1981) [Sov. Phys.—JETP **53**, 328 (1981)].

[10] M. Kardar and Y. C. Zhang, Phys. Rev. Lett. **58**, 2087 (1987).

[11] P. Meakin, P. Ramanlal, L. M. Sander, and R. C. Ball, Phys. Rev. A **34**, 5091 (1986).

[12] D. Dhar, Phase Trans. **9**, 51 (1987).

[13] A. J. McKane and M. A. Moore, Phys. Rev. Lett. **60**, 527 (1988).

[14] R. Jullien and P. Meakin, Europhys. Lett. **4**, 1385 (1987).

[15] J. G. Zabolitzky and D. Stauffer, Phys. Rev. A **34**, 1523 (1986); Phys. Rev. Lett. **57**, 1809 (1986).

[16] J. M. Kim and J. M. Kosterlitz, Phys. Rev. Lett. **62**, 2289 (1989).

[17] D. E. Wolf and J. Kertész, Europhys. Lett. **4**, 651 (1987).

[18] The Flory-type arguments used for derivation $\nu=\frac{2}{3}$ are crude enough, but we do not know of any other numerical or analytical results concerning the problem of optimal path in random media. Thus we shall use the $\nu=\frac{2}{3}$ at $d=3$ for the remainder of the paper.

[19] If disorder causes the topological entanglement of the chain, the relaxation will take place only near the ends of the polymer chain due to the mechanism of reptation.

[20] J. Machta and T. R. Kirkpatrick (unpublished).

[21] J. D. Honeycutt abd D. Thirumalai (unpublished).