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Polymers in a disordered environment

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Abstract. A polymer chain in equilibrium in a disordered environment is studied using a Flory theory and by mapping the problem onto random walks in an environment with traps. The asymptotic behaviour of the size of the polymer, R , as a function of the number of monomers, N , is obtained. If the disorder is weak in comparison with the self-repulsion of the chain, the self-avoiding random walk result is found. The random environment leads to effective attractive forces which, for sufficiently strong disorder, lead to the collapse of the chain. The properties of the collapsed chain depend upon the type of disorder and on the self-repulsion of the chain. If the self-repulsion increases sufficiently fast as the density increases then the collapsed chain has a finite density ($N/R^d \rightarrow \text{constant}$ as $N \rightarrow \infty$); otherwise several other interesting scaling forms are possible.

Despite a decade of study [1-11] the problem of a polymer chain in equilibrium in a quenched random environment remains controversial. Part of the controversy stems from disparate definitions of the problem. For example, the environment may consist of a Gaussian random potential or, alternatively, it may consist of excluded regions. The interaction of the polymer chain may be taken as strict self-avoidance or as a soft repulsion. We shall see that each of these possibilities leads to a qualitatively different result. Part of the controversy has its source in the need for extremely large system sizes in order to uncover some of the scaling forms in numerical studies.

In the present paper we study the size, R , of a single polymer in a disordered environment using a Flory theory. The advantage of this approach is that we can give a unified and relatively simple treatment of several types of disorder and polymer interactions. The Flory arguments are supplemented by exploiting an exact mapping onto the problem of random walks in an environment with random traps. Methods developed previously for the trapping problem support the Flory arguments.

We consider the following description of a polymer chain in a quenched random environment. For the polymer chain we take the Domb and Joyce model [12 and references therein]. At fixed N , each possible chain α is a connected sequence of N steps on a d -dimensional hypercubic lattice of size L^d . The statistical weight, W_α , associated with a chain is given by

$$W_\alpha = \exp\left(-g \sum_i n_\alpha(i)^2\right) \quad (1)$$

where the sum is over the lattice sites, $n_\alpha(i)$ is the number of times the chain α visits the site i and the dimensionless parameter g measures the strength of the interaction. The model goes over to a self-avoiding walk (SAW) in the limit $g \rightarrow \infty$. For any positive g the Domb and Joyce model is in the SAW universality class and its continuum limit

is the Edwards model studied in [6, 8-10] in the context of a random environment. For negative g the chain collapses to a pair of points unless additional repulsive terms are added to the Hamiltonian.

We consider two kinds of quenched random environments. The first consists of site dilution of the lattice. Each site is classified as 'allowed' with probability p or 'forbidden' with probability $1-p$. The chain must exist on the allowed sites. Each configuration of the environment is labelled by a set c of forbidden sites. The statistical weight of the walk α in this configuration is multiplied by an indicator function, $\chi_S(c, \alpha)$, which is zero if the sets c and α intersect and one otherwise:

$$\chi_S(c, \alpha) = \begin{cases} 1 & \alpha \cap c = \emptyset \\ 0 & \alpha \cap c \neq \emptyset \end{cases} \quad (2)$$

The site disorder is uncorrelated so that the probability, P_c , of a configuration of M forbidden sites is given by the binomial distribution

$$P_c = \binom{L^d}{M} (1-p)^M p^{L^d-M}. \quad (3)$$

The second kind of environment involves a random potential in which the lattice interacts with the monomers at site i with a strength $V_c(i)$ so that the statistical weight of each walk in configuration c is multiplied by the factor, $\chi_G(c, \alpha)$:

$$\chi_G(c, \alpha) = \exp\left(-\sum_i V_c(i) n_\alpha(i)\right). \quad (4)$$

The potentials are taken to be independent Gaussian variables with zero mean and variance, v , so that the probability density for a configuration is

$$P_c = \frac{1}{(\sqrt{\pi v})^{L^d}} \exp\left(-\sum_i V_c(i)^2/2v\right). \quad (5)$$

It is straightforward to generalise the random environment to include both forbidden sites with probability $1-p$ and random potentials with variance v by taking the overall statistical weight due to the environment, $\chi(c, \alpha)$, to be a product of factors given in (2) and (4). The probability of a configuration of the random environment is then the product of (3) and (5). It is this combined problem which we shall consider in the following.

The potential model, (4) and (5), is used in the continuum theories while the site dilution model, (2) and (3), more nearly corresponds to the simulations of [7] and to real polymers in porous media.

The quantity which we seek to compute is the root mean squared end-to-end distance, R , of a chain of length N which is in equilibrium in a random environment. We consider the quenched average,

$$R^2 = \sum_c P_c \left[\sum_\alpha r_\alpha^2 \chi(c, \alpha) W_\alpha \left(\sum_\alpha \chi(c, \alpha) W_\alpha \right)^{-1} \right]. \quad (6)$$

The sum over α is over all possible chains of fixed length N with r_α the end-to-end distance of the chain. The limit $L \rightarrow \infty$ is taken after the average over configurations.

Equation (6) can be simplified by appealing to self-averaging. That is, we assert that for almost all c with L sufficiently large, the denominator on the RHS of (6) takes

on a definite value:

$$\sum_{\alpha} \chi(c, \alpha) W_{\alpha} \left(\sum_{\alpha} W_{\alpha} \right)^{-1} \rightarrow \phi \quad \text{as } L \rightarrow \infty \quad (7)$$

where ϕ depends only on the parameters g , p and v . It can be evaluated by averaging over configurations:

$$\begin{aligned} \phi &= \sum_c P_c \left[\sum_{\alpha} \chi(c, \alpha) W_{\alpha} \left(\sum_{\alpha} W_{\alpha} \right)^{-1} \right] \\ &= \sum_{\alpha} \exp \left(-G \sum_i n_{\alpha}(i)^2 - K S_{\alpha} \right) \left[\sum_{\alpha} \exp \left(-g \sum_i n_{\alpha}(i)^2 \right) \right]^{-1} \end{aligned} \quad (8)$$

where S_{α} is the number of distinct sites visited by the random walk,

$$K = -\ln p$$

and

$$G = g - \frac{1}{2}v. \quad (9)$$

Note that the Gaussian random potential leads to a renormalisation of the two-body interaction while site dilution leads to a new interaction which depends on the number of distinct sites visited. For a general random potential with no lower bound both kinds of effective interaction terms will arise, but if the random potential has a lower bound no two-body term appears.

Self-averaging, (7), is justified in the case where N is held fixed as the system size is made infinite. In this limit, the polymer explores many different local environments so that a single very large system may be thought of as an ensemble of large subsystems, each of which is nearly equally likely to be visited. On the other hand, if the system is not sufficiently large for a given N , the chain may be localised in a small number of regions in which the local potential is favourable. This situation leads to an L dependence for R and is discussed in some detail for the free chain case in [11]. In the present work we restrict our attention to the case where first L and then N is taken to infinity.

A more quantitative argument that the polymer is not localised for N finite and $L \rightarrow \infty$ can be made by considering the free energy of the chain. For the case of a Gaussian potential, the deepest expected potential well in a system of size L behaves as $[\ln(L)]^{1/2}$ as $L \rightarrow \infty$. This is the energy which can be gained by localising the chain. On the other hand, the entropy for a delocalised chain behaves asymptotically as $\ln(L)$. Thus the free energy is minimised by having the chain explore the whole system.

Similar arguments can be made for the site dilution case: however, here an additional subtlety arises due to percolation. Given physically reasonable dynamics for the chain, ergodicity is lost at the percolation threshold and the self-averaging property no longer holds. On the other hand, if one considers ensemble rather than time averages, as is done here, the percolation threshold plays no role.

The self-averaging property allows us to replace the polymer in a quenched environment by an interacting random walk on an ordered lattice. Thus (6) becomes

$$R^2 = \sum_{\alpha} r_{\alpha}^2 \exp \left(-G \sum_i n_{\alpha}(i)^2 - K S_{\alpha} \right) \left[\sum_{\alpha} \exp \left(-G \sum_i n_{\alpha}(i)^2 - K S_{\alpha} \right) \right]^{-1}. \quad (10)$$

The random environment leads to compression of the chain since $K \geq 0$ and $g \geq G$. Site dilution leads to a penalty for new sites visited while the Gaussian random potential leads to an effective two-body attraction. For $G = 0$ the effective random walk is the same as the model discussed by Stanley *et al* [13]. If $K = 0$, we recover the Domb and Joyce model with a renormalised interaction strength. A comparison of the K and G interaction can be found in [14].

Our object now is to determine the phase diagram for the walk defined in (10). The point $G = 0$ and $K = 0$ is an ordinary random walk (RW). The limit $G \rightarrow \infty$ is also easily evaluated since complete self-avoidance implies $S_\alpha = N$, so that the K interaction factors out of the expression and we are left with a SAW. Thus, as first pointed out by Harris [5], a SAW is unaffected by a random environment. This leads us to the expectation that, for any K and sufficiently large G , we are in the SAW universality class. We shall confirm this within a Flory theory.

The starting point for a Flory theory is a free energy as a function of the size, r , of the chain. The most likely size, R , is obtained by minimising this free energy. The free energy must be constructed to take into account the energetics associated with the two interaction terms and the entropy associated with the number of conformations of a free chain of size r . We propose the following free energy:

$$F_N(r) = \frac{GN}{\sigma(N/r^d)} + KN\sigma(N/r^d) - S(r^2/N). \tag{11}$$

The quantity $N\sigma(N/r^d)$ is the average number of distinct sites visited for rws of size r . The first term on the RHS of (11) incorporates the effective two-body interaction and arises from approximating $n_\alpha(i)$ by N/S_α and then replacing S_α by its average over walks of size r . The second term is a transcription of the effective interaction due to site dilution. We assume that the average number of distinct sites visited for walks of size r is a regular decreasing function of the monomer density, $\rho = N/r^d$, so that σ has the limiting behaviour:

$$\sigma(\rho) \approx \begin{cases} C_d/\rho & \rho \gg 1 \\ 1 - a\rho + O(\rho^2) & \rho \ll 1 \end{cases} \tag{12}$$

with $C_d r^d$ the volume of a sphere of radius r . These limits ensure that, for extended walks, the number of distinct sites visited approaches the number of steps in the walk, while for compact walks all sites within r are visited. The leading correction term at low density, $a\rho$, yields the usual Flory interaction energy when it is inserted in the first term of (11). Flory theory is conventionally formulated in terms of ρ rather than σ ; however, by using σ we are able to treat the low and high density regimes in a unified way.

The final term in (11) is, apart from an irrelevant constant, the logarithm of the number of random walks of size r . This entropy is a function of the free random walk scaling variable, $x = r^2/N$. It reaches a single maximum of order 1 at $x = 1$ and has the limiting behaviour:

$$S(x) \rightarrow \begin{cases} -dx/2 & x \gg 1 \\ -\gamma_d/2dx & x \ll 1 \end{cases} \tag{13}$$

where γ_d is the smallest eigenvalue of Laplace's equations in a unit sphere with zero boundary conditions. The large- x behaviour of $S(x)$ is the usual Flory 'spring constant' while the small- x behaviour may be obtained by considering the number of surviving walks within a sphere of radius r with absorbing boundaries. In the large- N limit this

quantity is dominated by the smallest eigenfunction of the diffusion equation: thus the factor $\gamma_d/2$.

For a given value of N , the r which minimises the free energy is identified with the equilibrium size, R , of the chain. To obtain the exponent ν ($R \sim N^\nu$) we then take the large- N limit and identify the dominant terms in the free energy. Differentiating (6) with respect to r we obtain the equation for extrema of the free energy:

$$0 = d N^2 R^{-d-1} \sigma'(\rho) (G \sigma(\rho)^{-2} - K) - 2 R S'(x) / N. \quad (14)$$

If G and K vanish we have the RW limit with the minimum occurring at the maximum of the entropy term, $R = N^{1/2}$. If $G - K > 0$ we obtain the Flory result for $1 < d < 4$ in which the large- x behaviour of the entropy balances the low-density behaviour of the interaction term in (14). In this limit $\sigma \rightarrow 1$, $\sigma' \rightarrow a$ and $S' \rightarrow d/2$ so that

$$R = [a(G - K)]^{1/(d+2)} N^{3/(d+2)}. \quad (15)$$

If $G \neq 0$ but $G - K < 0$ there is an additional minimum for which the energy terms dominate the entropy terms. In this case (14) determines the density, ρ_0 , which minimises the energy and

$$R = (N/\rho_0)^{1/d}. \quad (16)$$

It is straightforward to check that with this scaling the entropy term is less than order N . The equilibrium density satisfies the equation

$$\sigma(\rho_0) = (G/K)^{1/2} \quad (17)$$

or, if we approximate σ by its low-density behaviour,

$$\rho_0 \approx C_d (K/G)^{1/2}. \quad (18)$$

We refer to this scaling as the compact walk regime.

There is a transition between the compact and SAW regimes when $K = G$. Along this θ line ($K = G > 0$) the balance between energy and entropy leads to the asymptotic behaviour [15]

$$R = (2a^2 G)^{1/2(d+1)} N^{2/(d+2)} \quad (19)$$

in the range $1 < d < 3$ and RW scaling for $d \geq 3$.

If G vanishes the minimum in the free energy occurs when the K interaction balances the entropy. This balance occurs in the high-density limit, $S \sim -\gamma_d N/2dr^2$ and $\sigma \sim C_d r^d/N$, leading to

$$R = \left(\frac{\gamma_d N}{d^2 C_d K} \right)^{1/(d+1)} \quad (20)$$

We refer to this behaviour as Donsker-Varadhan (DV) scaling because of the close connection to the problem, first studied in [16], of the expected value of $\exp(-KS_\alpha)$.

Finally, if $K = 0$ and G is negative, the free energy is unstable against r vanishing for $d > 2$ while R goes to zero in N for $d < 2$ so, in either case, the Flory theory predicts $R \rightarrow 0$. Taking into account the underlying lattice leads to the conclusion that the chain shrinks to a single pair of points. We refer to this as the localised regime.

The full phase diagram for the Flory theory for $1 < d < 4$ is shown in figure 1 and summarised in table 1. For $d > 3$ the θ line obeys RW scaling and for $d > 4$ the SAW phase is replaced by the RW phase. For $d = 1$ the SAW and compact phases merge and the equilibrium density depends on all three terms in the free energy.

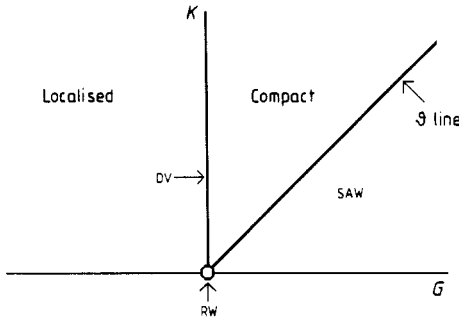


Figure 1. The phase diagram for polymers in a random environment applicable for $1 < d < 4$.

Table 1. The scaling behaviour predicted by the Flory theory for various values of G , K and d .

R	Conditions	Designation
1	$G < 0$	Localised
$N^{1/2}$	$G = K = 0$	RW
$(\gamma_d N / d^2 C_d K)^{1/(d+2)}$	$G = 0, K > 0$	DV
$(N / \rho_0)^{1/d}$	$K > G > 0$	Compact
$(2a^2 G)^{1/2(d+1)} N^{2/(d-1)}$	$G = K > 0$	θ line ($1 < d < 3$)
$[a(G - K)]^{1/(d+2)} N^{3/(d+2)}$	$G > K > 0$	SAW

The localised, DV and RW phases are unphysical in the sense that they are unstable to an arbitrarily weak k -body repulsive interaction for $k > 2$. For example a three-body interaction can be added to the lattice model by modifying the statistical weight, (1), to be

$$W_\alpha = \exp\left(-\sum_i [gn_\alpha(i)^2 + hn_\alpha(i)^3]\right). \tag{21}$$

Within the Flory theory this leads to a new term in F_N of the form hN/σ^2 . With a three-body repulsive interaction, $h > 0$, one finds a compact phase if a value of the density, ρ_0 , can be found which minimises the energy term in F_N and thus satisfies

$$K - G/\sigma(\rho_0)^2 - 2h/\sigma(\rho_0)^3 = 0. \tag{22}$$

A SAW phase exists when (22) has no solution and the LHS of (22) is negative as $\rho \rightarrow 0$, i.e. the net force remains repulsive for extended chains. The θ line occurs when K , G and h are related by (22) with $\sigma = 1$. If $h > 0$ these are the only phases possible—the random walk, Donsker-Varadhan and localised phases cease to exist. The phase diagram for $h > 0$ is shown in figure 2.

There is a close connection between the site dilution problem and the problem of random walks in the presence of randomly distributed traps. By exploiting this connection we can provide additional support for the Flory theory. Note that $\phi = \phi(g, K)$, defined by the first equality of (8) (with $v = 0$) can be interpreted as the number of walks which survive after N steps in an environment where the forbidden sites are replaced by trapping sites.

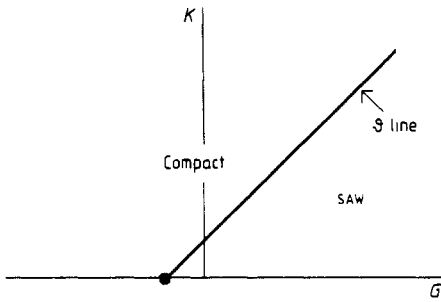


Figure 2. The phase diagram applicable for $1 < d < 4$ if a weak repulsive three-body interaction is added.

There are rigorous results for the survival fraction in the SAW and RW case. The survival fraction for a SAW is trivially evaluated since $S_\alpha = N$ so that

$$\phi(\infty, K) = e^{-KN}. \tag{23}$$

The case of a free random walk is much more difficult but has been rigorously evaluated for asymptotically large N by Donsker and Varadhan [16] with the result,

$$\ln \phi(0, K) \sim -\left(\frac{d+2}{2}\right)(C_d K)^{2/(d+2)}(\gamma_d N/d)^{d/(d+2)}. \tag{24}$$

Within the Flory theory the survival fraction of walks in an environment with random traps is given as

$$-\ln \phi = F_N(R; g, K) - F_N(R; g, 0). \tag{25}$$

For the RW case, $g = 0$, we recover the rigorous Donsker-Varadhan result, (24), while in the SAW regime, $g/K > 1$, we recover the simple exponential decay characteristic of SAW. The agreement between the Flory results and the rigorous results lends weight to the Flory argument. In the compact regime, $0 < g/K < 1$, we find exponential decay with a smaller decay rate:

$$-\ln \phi \approx NK[2(g/K)^{1/2} - g/K]. \tag{26}$$

The Flory theory treatment of ϕ is formally identical to Grassberger and Procaccia's [17] calculation of the survival fraction for free random walkers in an environment with traps. This calculation is based on the hypothesis that the walkers which dominate the survival fraction are to be found in large, approximately spherical, regions which are devoid of traps. The energy term in the Flory calculation corresponds to the logarithm of the probability per site of finding a void of size r while the entropy term corresponds to the survival fraction for long walks within a void, assuming absorbing boundary conditions. The expected survival fraction is obtained within a steepest descents calculation by maximising with respect to r the product of the void probability and survival fraction. Arguments of this type are familiar from discussion of the closely related Lifshitz tail problem.

The identification of large voids as the equilibrium location for a chain in the DV phase allows us to estimate the system size required to observe DV scaling. The optimal void has a size R and a probability of occurrence of roughly $L^d \exp(-KC_d R^d)$. Thus, for a free chain of length N , DV scaling will be observed if $L > L_{\min}$ with

$$L_{\min} \sim \{\exp[(KC_d)^{2/(d+2)}(\gamma_d N/d^2)^{d/(d+2)}]\}^{1/d}. \tag{27}$$

This constraint explains why DV scaling was not observed in recent numerical simulations [7] of a free chain in a random environment where $L = 300$ and $N \leq 150$. For example, if $p = 0.6$ and $N = 100$ we find $L_{\min} \approx 2000$.

We can use methods developed for the trapping problem to directly check the Flory prediction for DV scaling. Notice that R in (6) can be interpreted as the mean squared displacement of surviving walkers in an environment in which the forbidden sites are replaced by trapping sites.

The field theoretic methods developed by Lubensky [18] and Renn [19] for the trapping problem are applicable to this problem. These authors calculate the survival fraction, ϕ , and the fraction returning to the origin, ψ , for random walks in an environment with random traps. In the notation of [18, 19] ϕ is referred to as $[\phi N]$ and ψ as $[\phi_N(0)]$. The results for these quantities are (see (1.5)-(1.8) of [19])

$$\phi \sim N^{\zeta} \exp[k(N)] \quad (28)$$

and

$$\psi = N^{\Delta} \exp[k(N)] \quad (29)$$

where

$$\zeta = \frac{4(\rho - 1) - d}{2(d + 2)} \quad (30)$$

and

$$\Delta = \frac{4(\rho - 1) + d}{2(d + 2)}. \quad (31)$$

$k(N)$ is given by RHS of (24) and ρ is the band tail exponent, the value of which is not needed in the present calculation. According to the usual connection between the size of random walk and the probability of return to the origin we have

$$\psi / \phi \sim 1 / R^d \quad (32)$$

so that

$$\zeta - \Delta = d\nu \quad (33)$$

which agrees with the Flory result, $\nu = 1/(d + 2)$. One can also easily generalise [18] to obtain the product $R\phi$ directly from field theory.

In summary, we have developed a theory of polymer chains in a quenched random environment. The random environment is represented by effective attractive interactions whose form depends on the nature of the randomness. For site dilution, the effective interaction depends on the number of distinct sites visited. For a Gaussian random potential the effective interaction appears as a renormalisation of the two-body interaction.

Within a Flory theory we found that the attractive forces lead to several collapsed phases described in figures 1 and 2 and table 1. With the exception of the finite-density compact phase all of these phases are delicate in the sense that they are destroyed if an arbitrarily weak repulsive three-body interaction is added to the problem. The question of finite N and L crossovers between these phases remains to be fully explored and it is possible that evidence of the delicate phases may appear in physical experiments.

From a mathematical point of view, the most interesting of the collapsed phases is the Donsker-Varadhan phase in which the chain is localised in large regions free of forbidden sites. This phase can be mapped exactly onto the problem of random walks in the presence of random traps and we have appealed to rigorous and field theoretic results for this problem to support our conclusions for the DV phase.

Our results are in agreement with Harris [5] and consistent with several recent calculations [6, 8-11]. However, none of these authors have treated the physically relevant case of a weakly interacting chain in an environment with site dilution. Our main prediction for experiments on polymers in porous media is that the θ point is shifted to higher temperatures and that the polymer density will diverge as the θ temperature is approached from below. On the other hand, the Gaussian random potential considered in the continuum theories leads to a rather different compact phase stabilised by three-body interactions [10], with the result that the density reaches a finite value as the θ temperature is approached from below.

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Note added in proof. A similar Flory theory has been developed independently by J D Honeycutt and D Thirumalai (1989 *J. Chem. Phys.* **90** 4542).

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