

Polymers with self-avoiding interaction in random medium: a localization-delocalization transition

Y.Y. Goldschmidt^{1,a} and Y. Shiferaw^{1,2}

¹ Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh PA 15260, USA

² Physics Department, Northeastern University, Boston, MA 02115, USA

Received 13 November 2002

Published online 14 March 2003 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2003

Abstract. In this paper we investigate the problem of a long self-avoiding polymer chain immersed in a random medium. We find that in the limit of a very long chain and when the self-avoiding interaction is weak, the conformation of the chain consists of many “blobs” with connecting segments. The blobs are sections of the molecule curled up in regions of low potential in the case of a Gaussian distributed random potential or in regions of relatively low density of obstacles in the case of randomly distributed hard obstacles. We find that as the strength of the self-avoiding interaction is increased the chain undergoes a delocalization transition in the sense that the appropriate free energy per monomer is no longer negative. The chain is then no longer bound to a particular location in the medium but can easily wander around under the influence of a small perturbation. For a localized chain we estimate quantitatively the expected number of monomers in the “blobs” and in the connecting segments.

PACS. 36.20.Ey Conformation (statistics and dynamics) – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 75.10.Nr Spin-glass and other random models – 64.60.Cn Order-disorder transformations; statistical mechanics of model systems

1 Introduction

The properties of polymer molecules trapped in a random environment like a gel network [1] or inside porous materials or membranes [2–4] is of considerable interest. On the theoretical side many papers were written on the subject in an effort to understand the basic properties of the model, like the radius of gyration (or end-to-end distance) of a single molecule immersed in the random medium [5–14]. In several papers an ideal (Gaussian) chain has been used, which corresponds approximately to the experimental situation at the so called Θ -temperature when the solvent effectively screens the self-avoiding interaction of the chain. Even in that case the properties of a single molecule in a random potential are not simple. First, the properties depend on the type of randomness introduced—like a Gaussian random potential *versus* a sea of hard obstacles. Second, it may depend on whether the random potential is annealed or quenched, *i.e.* if the impurities are free to move or fixed. Additionally, different results apply if the chain is anchored or free to move. It turns out that for quenched randomness and a chain that is free to move, the size of the total volume of the medium is important for determining the chain size. For example, in the case of a random potential with a Gaussian distribution, the chain size saturates as a function of its

length L (number of monomers) for a very long chain, in contrast to a dependence like $R_g = aL^{1/2}$ (where R_g is the radius of gyration and a is the monomer size) in the absence of a random potential. A logarithmic dependence of the chain size on the volume of the medium was argued in reference [7] using qualitative arguments. An analytic derivation of the logarithmic dependence was derived in reference [12] using the replica method and the variational approximation, with a replica-symmetry-breaking solution. In reference [13] the result was justified from a mapping of the polymer problem to the problem of the localization of a quantum particle in a random potential. In reference [14] results were obtained for a polymer immersed in a sea of random obstacles, and various behaviors were identified as a function of the system size. Again the use of localization theory [15] and extreme value statistics were instrumental to the derivation.

In some of the papers [5,8,9] there was an attempt to include the effects of the self-avoiding interaction of the polymer. These attempts were far from complete. For example in reference [8] it was assumed that the conformation of the polymer consists of one spherical blob and it was argued that a quenched random potential is irrelevant for a very long chain. In reference [9] analytical results were obtained for annealed disorder, and simulations were performed for strictly self-avoiding walks. Reference [5] presents numerical evidence for a size transition

^a e-mail: yadin@pitt.edu

of the polymer as a function of the relative strength of the disorder and the self-avoiding interaction. The simulations were carried out for a random distribution of hard obstacles with a concentration exceeding the percolation threshold. It is the aim of the present paper to shed more light on this important problem. We will make use mainly of Flory-type arguments, and consider both the case of a Gaussian random potential and the case of randomly placed obstacles. A polymer with self avoiding interaction can not be mapped into a quantum particle at a finite temperature in a simple manner, because for a quantum particle there no impediment to return at a later time (or Trotter time) to a position it visited previously.

An important point to keep in mind is the strength of the excluded volume interaction. If one consider a strictly self-avoiding walk on a lattice (SAW) corresponding to a non-self-intersecting chain, then the strength of the Edwards parameter v [16] is fixed at $O(1) \times a^3$ where a is the step size (or monomer size) and depends only on the type of lattice. On the other hand one can consider a Domb-Joyce model [17] where there is a finite penalty for self overlapping of polymer segments, and then the strength of v can be varied substantially and reduced continuously to zero. The interplay between the strength of the self avoiding interaction and the strength of the disorder can then be investigated to a larger extent. Experimentally the Edwards parameter is given approximately [18] by $v = a^3(1-2\chi)$, where χ is the Flory interaction parameter, which depends on the chemical properties of the polymer and the solvent, and on the temperature (and pressure). It takes the value 1/2 at the Θ -point. The case $\chi = 0$ corresponds to a solvent that is very similar to the monomer. In general good solvents have low χ whereas poor solvents have high χ resulting in v being negative. In the following we will restrict ourselves to the case of positive v , which leads to the more interesting and non-trivial results.

Before we proceed to investigate the effects of the self-avoiding interaction, let us summarize in more detail the known results for a free Gaussian chain in a quenched random potential with a Gaussian distribution with variance g , and for a free Gaussian chain in a sea of fixed random obstacles with average concentration x per site.

For an uncorrelated Gaussian random potential, it was argued using qualitative arguments in references [7,8] that a very long Gaussian chain, that is free to move in the medium, will typically curl up in some small region of low average potential. The polymer chain is said to be localized, and for long chains the end-to-end distance (R_F) becomes independent of chain length L (number of monomers) and scales like

$$R_F \propto (g \ln \mathcal{V})^{-1/(4-d)}, \quad (1)$$

where \mathcal{V} is the volume of the system, d is the number of spatial dimensions, and the random potential satisfies $\langle U(\mathbf{x})U(\mathbf{x}') \rangle = g\delta(\mathbf{x} - \mathbf{x}')$. The binding energy per monomer of the chain is given approximatel by

$$U_{bind}/L \sim (g \ln \mathcal{V})^{2/(4-d)}. \quad (2)$$

These results were also obtained by the replica method in reference [12], and rederived using a mapping to a quantum particle's localization in reference [13]. For very short chains the end-to-end distance scales diffusively ($R_F^2 \sim L$), and it saturates at the R_F value quoted above for large L . Notice, that in the infinite volume limit, the chain completely collapses. This results from the fact that the depth of the potential is unbounded from below, and the chain is always able to find with reasonable probability a deep enough narrow potential well to occupy, overcoming its tendency to swell due to the entropy of confinement. The collapse of the chain in the infinite volume limit agrees with the results for a chain in an annealed potential, since the ability of a free chain to scan all space for a favorable environment is equivalent to the random potential adapting itself to the chain configuration.

In contrast, a tethered chain that is anchored at one end behaves very differently. Such a chain has a tadpole structure. The end of its tail is anchored and its head is a curled coil situated at a deep potential well. Such a chain has an end-to-end distance of order

$$R_T \sim \frac{g^{1/(4-d)}L}{(\ln L)^{1-1/(4-d)}}, \quad (3)$$

which is ballistic in three dimensions, since the chain has to look far to find a low potential. Here there is no dependence on the system's volume and the quenched and annealed cases are very different from each other even in the infinite volume limit.

In reference [14] we considered the effect of randomly distributed obstacles on the behavior of a free Gaussian chain. We have shown that in the presence of infinitely strong obstacles, that totally exclude the chain from visiting sites occupied by obstacles, with average concentration x per site, there are three possible behaviors of the end-to-end distance depending on the system's volume \mathcal{V} . For $2 < d < 4$, if the volume of the system is smaller than $\mathcal{V}_1 \simeq \exp(c_1 x^{-(d-2)/2})$, then the polymer is localized, as in the case of a Gaussian random potential, and $R_I \sim (x \ln \mathcal{V})^{-1/(4-d)}$. For $\mathcal{V}_1 < \mathcal{V} < \mathcal{V}_2$, where $\mathcal{V}_2 \simeq \exp(c_2 x^{2/(d+2)} L^{d/(d+2)})$, the polymer size is given by $R_{II} \sim (x/\ln \mathcal{V})^{-1/d}$ (c_1 and c_2 are constants of order unity). Finally, for $\mathcal{V} > \mathcal{V}_2$, the polymer behaves the same way as for an annealed potential, and $R_{III} \sim (L/x)^{1/(d+2)}$. Results are given to leading order in x for small x . These results are valid only when the average volume fraction of the obstacles (x) is smaller than the percolation threshold. When x is bigger than the percolation threshold we expect that the system breaks into independent domains whose volume is independent of, and generally much smaller than the total volume of the system.

We end the introduction by revisiting the meaning of localization for polymers in a random medium. Although some authors connect the compact size of the chain when $L \rightarrow \infty$ with the notion of localization, this is actually not so. The compact size should be viewed as a separate feature from the notion of localization. It is rather the binding energy of a chain U_{bind} that has to exceed the

translational entropy $\ln \mathcal{V}$. From equation (2) this amounts to the condition

$$\ln \mathcal{V} < L(g \ln \mathcal{V})^{2/(4-d)}, \quad (4)$$

which holds for any $2 \leq d < 4$ when L is large enough (for $2 < d < 4$ and any fixed L , the condition can be satisfied for large enough \mathcal{V}). This condition assures that the polymer will stay confined at a given location and will not, under a some small perturbation move to a different location. Thus repeating an experiment or a simulation with the same fixed realization of the disorder, but with different initial conditions, will result in finding the polymer situated at the same region of the sample as in a previous experiment, provided of course one waits enough time (which can be enormous) for the system to reach equilibrium. We observe that this condition is satisfied for large enough L provided the binding energy per monomer is positive. Another interpretation of the inequality given above in the context of equilibrium statistical mechanics is that the partition sum is dominated by the term involving the ground state as opposed to the contribution of the multitude of positive energy extended states. The contribution of these states is proportional to the volume of the system and thus the inequality above results from the condition

$$\exp(-LE_0) > \mathcal{V}. \quad (5)$$

What we will see in the following sections is that in the presence of a self-avoiding interaction, a localization-delocalization transition occurs when varying the strength of the self-avoiding interaction for a fixed amount of disorder or alternatively upon varying the strength of the disorder for a fixed value of the self-avoiding interaction. For a chain with self-avoiding interaction it is argued below that the chain is never compact, *i.e.* its radius of gyration grows like a power of L . However we find that for weak self-avoiding interaction the chain is still localized in the more restrictive sense explained above.

2 Chains with self-avoiding interaction – the case of a Gaussian random potential

We now study the case of a self-avoiding chain. In this section we consider the case of a random potential with a Gaussian distribution, and postpone to the next section the investigation of the case of a random distribution of hard obstacles. For simplicity, the discussion in the rest of the paper will be limited to three spatial dimensions ($d = 3$).

We start with a quenched random potential with a Gaussian distribution with variance g at each lattice site. The lattice constant, being equal to the monomer size, is a and we will measure all lengths in units of a . We will also measure all energies in units of kT which is equivalent to setting $kT = 1$. We first recall the beautiful argument given by Cates and Ball [7] for an ideal chain with no self-avoiding interaction. If we coarse-grain the system and divide it into regions of volume $\sim R^3$, the (average) potential

in such a region has a Gaussian distribution with variance g/R^3 . Thus the distribution of the potential strength V for such coarse-grained volumes is given by

$$P(V) \sim \exp\left(\frac{-R^3 V^2}{g}\right). \quad (6)$$

Here and in what follows we omit constants of order unity. If the volume of the system is \mathcal{V} ($\gg R^3$), the lowest (negative) value U of the coarse-grained potential that is likely to be found in such a volume is given by

$$\int_{-\infty}^U P(V) dV = R^3/\mathcal{V}, \quad (7)$$

which yields the estimate

$$R^3 U^2/g \sim \log(\mathcal{V}), \quad (8)$$

or

$$U = -\sqrt{\frac{g \log(\mathcal{V})}{R^3}}. \quad (9)$$

This is the energy per each monomer which resides in this low potential region. Thus if our ideal polymer chain is assumed to have a spherical shape of diameter $\sim R$, it will curl itself in the region of the lowest potential given by equation (9) above. To determine the volume R^3 occupied by the chain we recall that we have to pay in confinement entropy for compacting the chain below its natural size. Thus we have to balance the confining entropy *versus* the gain in potential energy from the random potential. Thus the free energy is given by

$$F \approx \frac{L}{R^2} - L \sqrt{\frac{g \log(\mathcal{V})}{R^3}}. \quad (10)$$

Notice that an unimportant constant, resulting from the entropy of a free chain, has been dropped ($S_0 = L \log(z)$ on a lattice with z the number of nearest neighbors, which contributes $-S_0$ to the free energy. This term does not depend on R and does not contribute to the binding energy). The optimal size R_m is found by minimizing F and is found to be

$$R_m \sim \frac{1}{g \log(\mathcal{V})} \equiv \frac{1}{G(\mathcal{V})}. \quad (11)$$

where we defined the volume dependent disorder strength by $G(\mathcal{V}) = g \log(\mathcal{V})$. Substituting this result in F we obtain

$$F_m = -\frac{L}{3R_m^2} \approx -G(\mathcal{V})^2 L. \quad (12)$$

We see that $-F_m/L$ is the binding energy per monomer, and it is strictly positive, so the polymer is localized [19]. In what follows we will assume that g is small enough so that $G \ll 1$ for the given system volume, hence $R_m \gg 1$, and the chain is not totally collapsed unless $\mathcal{V} \rightarrow \infty$.

We now add a self avoiding interaction and assume first that it is small, *i.e.* $v \ll g$, or at least $v < g$. If the

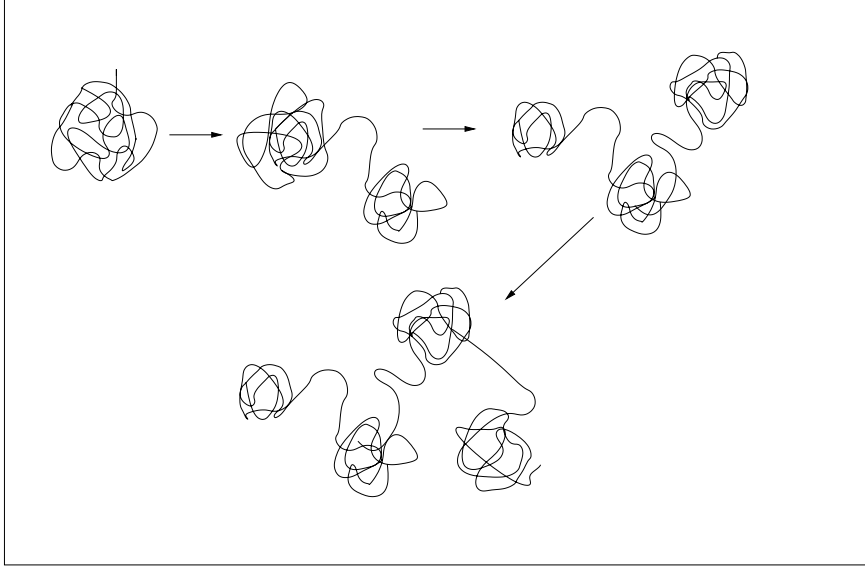


Fig. 1. Illustration of how the low free energy conformations evolve with increasing chain length. The chain length increases with the direction of the arrows.

chain is still localized in the same well, which we will see momentarily not to hold when L is large, then

$$F = \frac{L}{R_m^2} - L\sqrt{\frac{g \log(\mathcal{V})}{R_m^3}} + \frac{vL^2}{R_m^3} \approx -G(\mathcal{V})^2 L + vG(\mathcal{V})^3 L^2. \quad (13)$$

Here, beside assuming that v is small we assume for the moment that L is not too big so the last term in the free energy, resulting from the self-avoiding interaction, is small enough so one does not have to take into account the change in R_m due to the presence of v . If we plot F vs. L , we see that it is lowest when

$$L = L_m = \frac{1}{2vG(\mathcal{V})}. \quad (14)$$

Thus if $vg \ll 1$, we have $L_m \gg 1$, and

$$F_m = -\frac{G(\mathcal{V})}{4v}. \quad (15)$$

For $L = 2L_m$ the free energy vanishes and for larger L it eventually increases fast like L^2 . We can now verify that if L does not exceed L_m then the approximation used above, assuming that R_m does not change appreciably from its ideal chain value, is justified. If we differentiate the above F in equation (13) with respect to R_m we find

$$R_m \sim \frac{1}{G(\mathcal{V})} \left(1 + \frac{vL}{R_m}\right)^2 \approx \frac{1}{G(\mathcal{V})} (1 + vG(\mathcal{V})L)^2, \quad (16)$$

again omitting constants of order unity. Thus the correction vGL evaluated at $L = L_m$ is of order unity, and we can still use the value $R_m \sim 1/G$.

For larger L the approximation seems to break down, but fortunately what happens is that since the free energy

increases when L exceeds L_m , it is energetically favorable for part of the chain to jump into a distant well. Even though there is a cost for the polymer segment between the wells one still gains in the overall free energy from the binding energy in the wells. Thus the picture that emerges is that as L increases, the chain divides itself into separate blobs with connecting segments. In each blob the number of monomer does not exceed L_m , which is the optimal value for that well. The idea is depicted in Figure 1.

To be more specific we will now construct a model for the free energy of the chain. The first blob will be located in the deepest minimum in the total volume, whose depth is roughly given by $-G(\mathcal{V})^2$ per monomer, where \mathcal{V} is the total volume of the system. Subsequent blobs will reside in the most favorable well within a range Y , which has to be taken self-consistently as the length of the jump. Thus within a range Y the chain is likely to find a potential minimum of depth $-G(Y^3)^2$. The farther you jump, the deeper well you are likely to find. Thus assuming for simplicity that the jumps are roughly of equal size, and there are K blobs in addition to the initial blob, the free energy of the chain will be given roughly by

$$F(w, m, Y; L) \approx -\frac{G(\mathcal{V})}{4v} + K \left(\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - wG(Y^3)^2 + vw^2G(Y^3)^3 \right), \quad (17)$$

with

$$K = \frac{L - L_0}{w + m}, \quad L_0 = \frac{1}{2vG(\mathcal{V})}, \quad G(Y^3) = 3g \ln(Y). \quad (18)$$

We defined w to be the number of monomers in each blob, and m to be the number of monomers in each connecting segment. The term Y^2/m results from the ‘‘stretching’’

Table 1. Parameters and free energy for the case $g = 0.05$.

v	Y	m	w	f
0.00001	2206	2413	16178	-0.835249
0.0001	346	534	2580	-0.421023
0.001	60	148	461	-0.164673
0.01	13.7	66	97	-0.0370883
0.02	11.1	69.2	60.8	-0.0156444
0.03	12.8	105.5	41.9	-0.0056033
0.04	22	302.6	26.8	-0.0009992
0.045	35.6	720.1	20.7	-0.0001776
0.0478	69.4	2342.4	16.5	0
0.048	77	2800	16	0.00000725

entropy of the segment and m/Y^2 from the confinement entropy. The term vm^2/Y^3 represents the self-avoiding interaction for the connecting segments. L_0 is the number of monomers in the initial blob whose free energy was taken care of separately. It is evident that when L is very large we can neglect the free energy of the first blob and also take $K \approx L/(w+m)$. Thus we find for the free energy per monomer

$$f(w, m, Y) \equiv \frac{F(w, m, Y; L)}{L} \approx \frac{1}{w+m} \times \left(\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - wG(Y^3)^2 + vw^2G(Y^3)^3 \right). \quad (19)$$

This function has to be minimized with respect to w , m and Y to find the parameters giving rise to its lowest value. For the connecting pieces of the chain we did not include a contribution from the random potential since it is expected to average out to zero for these parts. To gain some feeling into the behavior of this function and the values of the parameters which minimize it, we display in Table 1 the value of the parameters and free energy per monomer for $g = 0.05$ and various values of v , as obtained from a minimization procedure. The delocalization transition is the point where f changes sign from negative to positive, as discussed earlier. Actually, to be more precise, the delocalization transition occurs when $f = -(\ln \mathcal{V})/L$ for finite L , when the translational entropy starts to exceed the binding energy. In the limit of large L we can say that the transition is at $f = 0$. We observe that the delocalization transition occurs at $v = 0.0478$ which is close to the value of g . We also observe that $m \ll w$ for $v \ll g$ and $m \gg w$ near the transition. Also for small v , $m \sim Y$, whereas near the transition $m \sim Y^2$. If we compare the value of w from Table 1 with the value of $L_m = 1/(2vG(Y^3))$ we find that w is smaller than L_m in the entire range. The ratio w/L_m varies from ~ 0.4 to 1 as v changes from 10^{-5} to 0.048. Thus the assumption we have made previously concerning this ratio is justified *a posteriori*.

Luckily it was possible to solve the minimization equations analytically almost entirely in both the limits $v \ll g$, and near the transition when $f \approx 0$. Details of the solutions are given in the Appendix. Here we only display the results:

A. The case $v \ll g$.

The parameters are given by

$$Y = \frac{2}{v}(\ln Y - 1)^{-1/2}(\ln Y + 3)^{-3/2}, \quad (20)$$

$$m = \frac{2}{3vg \ln Y}(\ln Y - 1)^{-1}(\ln Y + 3)^{-1}, \quad (21)$$

$$w = \frac{2}{3vg \ln Y}(\ln Y + 3)^{-1}, \quad (22)$$

$$f = -9g^2(\ln Y)^2(\ln Y - 1)(\ln Y + 3)^{-1}. \quad (23)$$

The first equation can be easily solved numerically for Y for a given value of v and the result substituted in the other equations. Very good agreement is achieved with Table 1 for small values of v .

B. Solution near the delocalization transition.

Let us define the parameter

$$\kappa = \frac{4v}{3g}. \quad (24)$$

In terms of this parameter we have

$$Y = \frac{1}{v\kappa} \left(\frac{1 + \sqrt{1 + \kappa^2}}{\kappa} \right)^2, \quad (25)$$

$$m = \frac{1}{v^2\kappa^2} \left(\frac{1 + \sqrt{1 + \kappa^2}}{\kappa} \right)^3, \quad (26)$$

$$w = \frac{\kappa}{8v^2 \ln Y} = \frac{1}{2vG(Y^3)}. \quad (27)$$

The transition point is obtained by solving the equation

$$\frac{1 + \sqrt{1 + \kappa^2}}{\kappa} + \frac{\kappa}{1 + \sqrt{1 + \kappa^2}} + \frac{1}{\kappa} \left(1 - 2 \ln \left(\frac{2(1 + \sqrt{1 + \kappa^2})}{\sqrt{3g\kappa^2}} \right) \right) = 0. \quad (28)$$

Once the solution κ_c is determined for a given g , then the transition point v_c is determined from $v_c = 3g\kappa_c/4$. For g in the range 0.01–0.2 we find that κ_c is a number of order unity (varies from 1.7 to 0.96 as g changes in that range). This means that v_c is quite close to g . Once v_c is known, all the parameters Y , m and w at the transition are determined by the solution above. For $g = 0.05$ we get $\kappa_c = 1.2744$, and thus $v_c = 0.0478$ in excellent agreement with the minimization results from Table 1.

For $v > v_c$ the chain is delocalized. The above expression for the free energy may no longer be accurate, but the general picture is clear. There will be very few monomers in the low regions of the potential, and the chain will behave very much like an ordinary chain with a self-avoiding interaction in the absence of a random potential. Any little perturbation can cause the chain to move to a different location in the medium (see Fig. 2).

For small values of v when the chain is localized, we still expect its size to grow like that of a self-avoiding walk. Thus we expect roughly

$$R_g \sim YK^{0.6}, \quad (29)$$

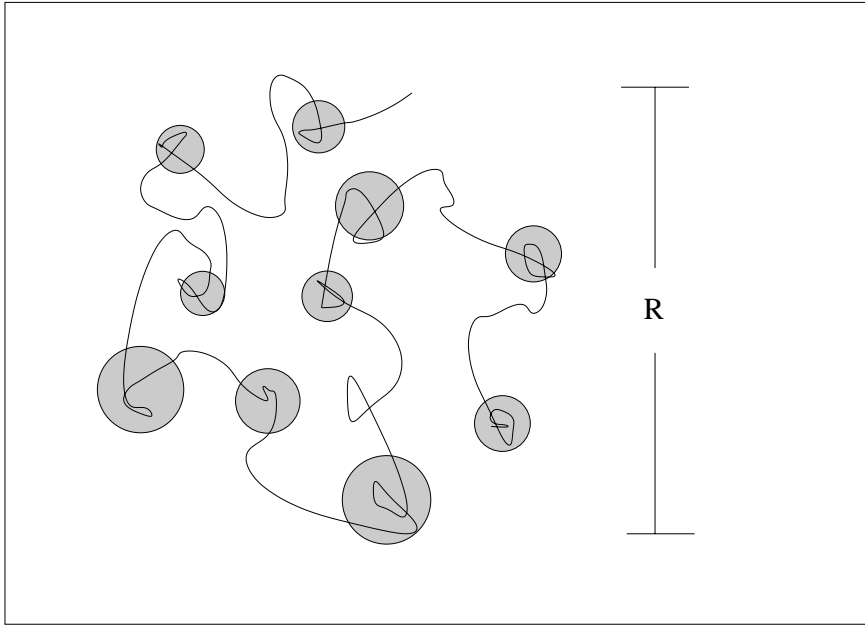


Fig. 2. A typical chain conformation when $v \gg g$. The dark regions are regions of low average potential. Only short segments of the chain are situated in these regions.

since Y is the step size, and K is the number of steps. But since $K \approx L/(m+w)$ for large L , we find

$$R_g \sim \frac{Y}{(m+w)^{0.6}} L^{0.6}. \quad (30)$$

Thus the chain behaves as a self avoiding walk with an effective step size per monomer given by

$$\frac{a_{eff}}{a} = \frac{Y}{(m+w)^{0.6}}. \quad (31)$$

From Table 1 it becomes clear that the effective monomer size changes from a value of 6 for $v = 0.00001$ to a value of ~ 0.66 at the transition. The reason for the large value of the effective monomer size at very small v is that the chains makes long jumps to take advantage of deep wells of the random potential, very much like anchored chains in a random potential that make sub-ballistic jumps [7]. This is also the reason why the number of monomers w in each well is somewhat less than L_m , since a sufficient number of monomers need to be used for the connecting segments. For $v \gg v_c$ in the delocalized phase we expect the effective monomer size to be about 1, since the chain behaves almost like an ordinary self-avoiding chain with the random potential not playing any significant role. Thus the chain is expected to have its smallest size in the vicinity of the transition.

It is important to notice that the discussion above is in the limit for very large L . If $L \lesssim 1/(2vG(\mathcal{V}))$, then in the localized phase when $v \ll v_c$ the polymer will be confined to a single well and will appear compact, even though it will not remain so for large L . This may explain why in simulations that were done typically with $L \leq 320$ [5] the delocalization transition appeared as a transition from a compact to a non-compact state of the polymer.

We should also note that for an annealed random potential there is a transition from a collapsed state into an ordinary self-avoiding chain as v increases through the point $v = g$ [8]. This is because the annealed free energy reads

$$F(R) = \frac{L}{R^2} - \frac{gL^2}{R^3} + \frac{vL^2}{R^3} + \frac{R^2}{L}. \quad (32)$$

For $v < g$ the fourth term is negligible and the free energy is lowest when $R \rightarrow 0$ (when L is large). For $v > g$ the first term is negligible, and the radius of gyration grows like

$$R \sim (v - g)^{1/3} L^{3/5}. \quad (33)$$

3 The case of hard obstacles

The case of hard obstacles was investigated recently by us in reference [14]. As already discussed in the introduction, three different behaviors were identified as a function of the system's volume. Region I is defined when the system's volume $\mathcal{V} < \mathcal{V}_1 \sim \exp(c_1/\sqrt{x})$, where c_1 is a constant of order unity. Here $0 < x < 1$ is the average concentration of obstacles per site (total number of obstacles divided by total number of sites). We also assume that x is less than the percolation threshold ($x_c = 0.3116$ for a cubic lattice), so sites occupied by obstacles don't percolate. In Region I we recall [14] that in the absence of a self-avoiding interaction, the free energy per site for a chain situated in a spherical region of volume R^3 in three dimensions is given by

$$F_I/L = -\ln(z) + 1/R^2 + \hat{x} \quad (34)$$

where \hat{x} is the actual concentration of obstacles in that region, whose minimal expected value in a system of total volume \mathcal{V} is

$$\hat{x}_m \simeq x - \sqrt{\frac{x \ln \mathcal{V}}{R^3}}. \quad (35)$$

The binding energy per monomer inside the blob resulting from the lower concentration of obstacles in this region is given by $x - \hat{x}$, since it is equal the entropy gain from a lower concentration as compared to the average (background) concentration x . The chain is “sucked” towards regions with low concentration of obstacles since it can maximize its entropy there, and these regions of space act like the negative potential regions of the Gaussian random potential. Thus in order for the free energy per monomer to reflect correctly the binding energy of the chain inside the blob, both the constant x of the background and the constant term $-\ln(z)$, which is always there regardless of the chain’s position, have to be subtracted. The relevant free energy per monomer situated in the blob (which is equal to minus the binding energy) is given by

$$f_I = \frac{1}{R^2} - \sqrt{\frac{x \ln \mathcal{V}}{R^3}}. \quad (36)$$

This result coincides with equation (10) upon the substitution $g \rightarrow x$. Thus all the results of the previous section carry on to Region I with this simple substitution.

Therefore we are going to discuss the situation when the system’s volume is greater than \mathcal{V}_1 (Region II). In this case the many blob picture still holds, where the blobs are now situated in regions free of obstacles (with $\hat{x} = 0$) whose size is determined again by the distance Y of the jump which is also assumed to satisfy $Y^3 \gtrsim \mathcal{V}_1$ (an assumption which will be justified *a posteriori*). In this case the farther the jump, it is more likely for the chain to find a larger space empty of obstacles, which will reduce further its confinement entropy w/R^2 and also the self-avoiding energy (but there is a cost resulting from the connecting segments and the constraint of the total length being fixed). The blob size is given by $R_{mII} = 1/G_o$ (the largest expected empty region in a volume Y^3) with [14]

$$G_o(Y^3) \approx \left(\frac{x}{3 \ln Y}\right)^{1/3}. \quad (37)$$

Thus the free energy per monomer of a chain consisting of a number of blobs with connecting parts, each of length Y , is given by

$$f(w, m, Y) \approx \frac{1}{w + m} \left(\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - w(x - G_o(Y^3)^2) + vw^2 G_o(Y^3)^3 \right), \quad (38)$$

where again the constant x , which is independent of m , w and Y , has been subtracted. This assures that the delocalization transition again occurs at $f = 0$ and not at $f = x$. The results of a numerical minimization of this free energy is displayed in Table 2 for the case of $x = 0.1$.

Table 2. Free energy and parameters for a polymer in a sea of blockers when $\mathcal{V} > \mathcal{V}_1$.

v	Y	m	w	f
0.00001	552	2206	72092	-0.062
0.0001	127	565	9135	-0.051
0.001	38	206	1241	-0.034
0.01	23	230	207	-0.0077
0.02	32	536	137	-0.0019
0.03	59	1737	120	-0.00035
0.04	194	13915	131	-0.0000099
0.041	248	21327	134	-0.0000023
0.042	357	39310	144	0.0000024

The transition occurs between $v = 0.041$ and 0.042 . Again we could find analytically almost the entire solution both for $v \ll x$ and at the transition. The solution is given in the Appendix. There we show that the transition occurs at $v = 0.04142$. We observe that as for the case of a Gaussian random potential the ratio w/m changes from $\gg 1$ to $\ll 1$ as v approaches the transition from below. The values of Y are seen to be consistent with the assumption $Y^3 \gtrsim \mathcal{V}_1$. We also checked that the free energy from Table 2 is lower than what one would obtain by constraining Y to be in Region I, *i.e.* $Y^3 < \mathcal{V}_1$.

Finally for $\mathcal{V} > \mathcal{V}_2$, where $\mathcal{V}_2 \simeq \exp(x^{2/(d+2)} L^{d/(d+2)})$ (Region III), we expect the behavior of the chain to stay the same. This is because for jumps within a volume \mathcal{V}_2 the situation reverts to the previously discussed scenario, since the effective volume of interest which determines the statistics of the free spaces is of order Y^3 and we don’t expect Y to be that large.

An important point to note is that if one performs a simulation with strict self-avoiding-walks on a diluted lattice (with $x < 1$), one has $v \sim 1$, and hence one will always be in the delocalized phase and will not see any localization effects [20].

A few words are in order about the case of an annealed potential. This case has been already investigated in the literature [9], and we will review it briefly. The free energy in the annealed case reads (for $d = 3$)

$$F(R) \approx \frac{L}{R^2} + xR^3 + \frac{vL^2}{R^3}. \quad (39)$$

The second term represents the entropy cost of a fluctuation in the density of obstacles that creates an appropriate spherical region of diameter $\sim R$. It was assumed that the chain occupies a spherical volume, or at least deviations from a spherical shape are not large [9]. In the case $v = 0$ one obtains by minimizing the free energy that $R \sim (L/x)^{1/5}$, a well known result. For $v > 0$ the first term is irrelevant (and so is the “stretching term” of the form R^2/L) and one finds that $R \sim (v/x)^{1/3} L^{1/3}$. In d dimension, the size scales like $L^{1/d}$ when $v > 0$, which is larger than the $L^{1/(d+2)}$ dependence in the $v = 0$ case. There is no indication for a phase transition in these arguments, although some authors [9] speculate that it breaks down for large v and a transition to a Flory $L^{3/(d+2)}$ dependence takes place.

4 Conclusions

In this paper we have considered the case of a long molecule subject to a combination of a random environment and a self-avoiding interaction. We have found that in the limit of a very long chain and when the self-avoiding interaction is weak, the conformation of the chain consists of many blobs with connecting segments. The blobs are situated in regions of low potential for a Gaussian random potential or in regions of low density of obstacles in the random obstacles case. We have found that as the strength of the self-avoiding interaction is increased the chain undergoes a localization-delocalization transition since the binding energy per monomer is no longer positive. The chain is then no longer attached to a particular location in the medium but can easily wander around due to any perturbation. For a localized chain we have estimated quantitatively the expected number of monomers in the blobs and in the connecting segments. It has been argued that in the “localized phase” the chain size still grows with its length (see Eq. (30)), but the localization follows from the more restrictive definition given in the introduction.

YYG acknowledges support of the US Department of Energy (DOE), grant No. DE-FG02-98ER45686.

Appendix

In this Appendix we solve the minimization conditions for the free energy, both for $v \ll g$ and at or just below the transition. The equations obtained by minimizing f from equation (19) with respect to Y, w and m are in that order

$$\frac{2Y}{m} - \frac{2m}{Y^3} - \frac{3vm^2}{Y^4} - \frac{6gwG}{Y} + \frac{9vgw^2G^2}{Y} = 0, \quad (40)$$

$$-G^2 + 2wvG^3 = f, \quad (41)$$

$$-\frac{Y^2}{m^2} + \frac{1}{Y^2} + \frac{2vm}{Y^3} = f, \quad (42)$$

where we used

$$G \equiv G(Y^3) = 3g \ln Y, \quad (43)$$

and

$$f = \frac{1}{w+m} \left(\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - wG^2 + vw^2G^3 \right). \quad (44)$$

First, in the case $v \ll g$, some terms are very small and can be neglected (compare with Tab. 1). The equations become

$$\frac{2Y}{m} - \frac{6gwG}{Y} + \frac{9vgw^2G^2}{Y} = 0, \quad (45)$$

$$-G^2 + 2wvG^3 = f, \quad (46)$$

$$-\frac{Y^2}{m^2} = f, \quad (47)$$

$$f = \frac{1}{w+m} \left(\frac{Y^2}{m} - wG^2 + vw^2G^3 \right). \quad (48)$$

These equations can now be solved analytically with the result given in equations (20, 21, 22, 23).

At or very near the transition we put $f = 0$ on the rhs of equations (42, 41). Equation (41) yields

$$w = \frac{1}{2vG}.$$

The other two equations become

$$-\frac{2m}{Y} \left(-\frac{Y^2}{m^2} + \frac{1}{Y^2} + \frac{2vm}{Y^3} \right) + \frac{vm^2}{Y^4} - \frac{3g}{4vY} = 0, \quad (49)$$

$$-\frac{Y^2}{m^2} + \frac{1}{Y^2} + \frac{2vm}{Y^3} = 0. \quad (50)$$

Thus using the second of these equations to eliminate the first term in the first, the first equation becomes

$$Y^3 = \kappa vm^2 \equiv \kappa x^6 / v^3, \quad (51)$$

where we defined $\kappa = 4v/(3g)$ and $x^3 = v^2m$. The second equation becomes

$$\kappa^{5/3} x^2 - 2x - \kappa^{1/3} = 0, \quad (52)$$

which has the solution

$$x = \frac{1 + \sqrt{1 + \kappa^2}}{\kappa^{5/3}}. \quad (53)$$

The values of m and Y follows from the relations $m = x^3/v^2$ and $Y = \kappa^{1/3}x^2/v$, which coincide with equations (25, 26, 27). Equation (28) just follows from equation (44) and the condition $f = 0$.

For the case of random obstacles and $\mathcal{V} \gtrsim \exp(1/\sqrt{x})$ we could also solve the minimization equations of the free energy both for $v \ll x$ and at the transition. In the first case the equation reads

$$\frac{2Y}{m} - \frac{2wG_o^2}{3Y \ln Y} - \frac{vw^2G_o^3}{Y \ln Y} = 0, \quad (54)$$

$$-x + G_o^2 + 2wvG_o^3 = f, \quad (55)$$

$$-\frac{Y^2}{m^2} = f, \quad (56)$$

$$f = \frac{1}{w+m} \left(\frac{Y^2}{m} - xw + wG_o^2 + vw^2Go^3 \right) \quad (57)$$

where

$$G_o = \left(\frac{x}{3 \ln Y} \right)^{1/3}. \quad (58)$$

We display the solution in the form valid when v is small enough so that $\ln Y \gg 1$. It reads

$$y = \frac{1}{v} \frac{2G_o}{9(\ln Y)^2} \frac{1}{\sqrt{x - G_o^2}}, \quad (59)$$

$$m = \frac{1}{v} \frac{2G_o}{9(\ln Y)^2} \frac{1}{x - G_o^2}, \quad (60)$$

$$w = \frac{1}{v} \frac{2}{3G_o \ln Y}, \quad (61)$$

$$f = -x + G_o^2. \quad (62)$$

Since G_o still contains $\ln Y$, the first equation has to be solved numerically for Y and then the rest of the solution follows.

At the transition the minimization equations read

$$\frac{2y}{m} - \frac{2m}{Y^3} - \frac{3vm^2}{Y^4} + 2wG_o \frac{d}{dy}G_o + 3vw^2G_o^2 \frac{d}{dy}G_o = 0, \quad (63)$$

$$-\frac{Y^2}{m^2} + \frac{1}{Y^2} + \frac{2vm}{Y^3} = 0, \quad (64)$$

$$-x + G_o^2 + 2wvG_o^3 = 0, \quad (65)$$

with

$$\frac{d}{dy}G_o = -\frac{G_o^4}{xY}. \quad (66)$$

Defining

$$\sigma = \frac{4xv}{(3x + G_o^2)(x - G_o^2)}, \quad (67)$$

the solution reads

$$Y = \frac{1}{v\sigma} \left(\frac{1 + \sqrt{1 + \sigma^2}}{\sigma} \right)^2, \quad (68)$$

$$m = \frac{1}{v^2\sigma^2} \left(\frac{1 + \sqrt{1 + \sigma^2}}{\sigma} \right)^3, \quad (69)$$

$$w = \frac{x - G_o^2}{2vG_o^3}. \quad (70)$$

The transition point (v_c) is determined from the equation

$$\frac{Y^2}{m} + \frac{m}{Y^2} + \frac{vm^2}{Y^3} - w(x - G_o^2) + vw^2G_o^3 = 0, \quad (71)$$

which becomes

$$\frac{1 + \sqrt{1 + \sigma^2}}{\sigma} + \frac{\sigma}{1 + \sqrt{1 + \sigma^2}} + \frac{1}{\sigma} - \frac{(x - G_o^2)^2}{4vG_o^3} = 0. \quad (72)$$

Actually since G_o and σ still depend on $\ln Y$ one has to solve numerically two coupled nonlinear equations.

The solution gives $v_c = 0.04142$, $y = 302.8$, $m = 30145$, $w = 140$.

References

1. L. Liu, P. Li, S.A. Asher, *Nature (London)* **397**, 141 (1999); L. Liu, P. Li, S.A. Asher, *J. Am. Chem. Soc.* **121**, 4040 (1999)
2. D.S. Cannell, F. Rondelez, *Macromolecules* **13**, 1599 (1980)
3. G. Guillot, L. Leger, F. Rondelez, *Macromolecules* **18**, 2531 (1985)
4. M.T. Bishop, K.H. Langley, F. Karasz, *Phys. Rev. Lett.* **57**, 1741 (1986)
5. A. Baumgartner, M. Muthukumar, *J. Chem. Phys.* **87**, 3082 (1987); see also review chapter by these authors in *Advances in Chemical Physics* (Vol. XCIV) *Polymeric Systems*, edited by I. Prigogine, S.A. Rice (John Wiley & Sons, Inc., New York, 1996) and references therein
6. S.F. Edwards, M. Muthukumar, *J. Chem. Phys.* **89**, 2435 (1988)
7. M.E. Cates, R.C. Ball, *J. Phys. France* **49**, 2009 (1988)
8. T. Nattermann, W. Renz, *Phys. Rev. A* **40**, 4675 (1989)
9. J.D. Huneycutt, D. Thirumalai, *J. Chem. Phys.* **90**, 4542 (1989)
10. K. Leung, D. Chandler, *J. Chem. Phys.* **102**, 1405 (1995); D. Wu, K. Hui, D. Chandler, *J. Chem. Phys.* **96**, 835 (1992)
11. J. Dayantis, M.J.M. Abadie, M.R.L. Abadie, *Comput. Theoret. Polymer Sci.* **8**, 273 (1998)
12. Y.Y. Goldschmidt, *Phys. Rev. E* **61**, 1729 (2000)
13. Y. Shiferaw, Y.Y. Goldschmidt, *Phys. Rev. E* **63**, 051803 (2001)
14. Y.Y. Goldschmidt, Y. Shiferaw, *Eur. Phys. J. B* **25**, 351 (2002)
15. I.M. Lifshits, S.A. Gredeskul, L.A. Patur, *Introduction to the Theory of Disordered Systems* (Wiley, NY, 1988); I.M. Lifshits, *Adv. Phys.* **13**, 483 (1964)
16. M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986)
17. C. Domb, G.S. Joyce, *J. Phys. C* **5**, 956 (1972)
18. P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979)
19. For a more complete discussion on the connection with localization theory of a quantum particle see reference [13], equations (7.15–7.20) and reference [14], equations (3–6). There we comment on the derivation of the results from extreme value statistics and give more details of the distributions
20. K. Barat, B.K. Chakrabarti, *Phys. Rep.* **258**, 377 (1995)