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Adsorption of polymer chains by disordered traps

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Abstract. We study the adsorption cross-over of ideal polymer chains in an environment of disordered traps. Starting from the assumption of an optimal cluster size of traps (optimal fluctuation method) we derive a general scaling form of the free energy function for arbitrary spatial dimensions. For small concentrations of traps we find a cross-over from localized (adsorbed) behavior to delocalized behavior depending on the chain's length and on the depth of the traps; this is connected with the non-monotonic behavior of the chain's extension. In terms of the free energy of the chain this cross-over resembles a first order transition scenario, the chain gets localized at many traps at once.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 36.20.-r Macromolecules and polymer molecules – 64.70.-p Specific phase transitions

1 Introduction

The behavior of polymer chains in disordered environments has received much attention from the theoretical point of view, see for instance [1–6]. The general result here is the localization or collapse of the chain induced by the disorder which has dramatic consequences also for the dynamic behavior [5]. On the other hand there are many practical examples such as polymers in lamellar structures (lipid layers, block copolymers), polymers adsorbed onto chemically disordered surfaces and polymers embedded in porous media or networks which correspond to one, two and three-dimensional realizations of quenched disordered environments. Moreover, there is a close analogy between polymers in disordered environments and nonlinear growth models of KPZ-type [7] *via* the Cole-Hopf transformation, see [2], as well as the apparent analogy between the d-dimensional polymer and the $d+1$-dimensional directed polymer problem. Finally, it is well known, that the statistics of ideal polymer chains in an external potential has close similarities with the dynamics of a Schrödinger particle. Therefore methods developed for the Schrödinger equation [8–10] can be applied to the polymer problem as well [6,11,12].

Returning to the practical situation of polymer chains in some structured environment we should state that disorder can never be avoided completely. It is only the question of when the disorder becomes *relevant* to the static and dynamical properties of the chain. This point has received considerably less attention in the literature. However, by taking the week disorder limit as the limit of sparse attractive defects (traps) the cross-over from unperturbed to localized chains is an interesting generalization of the adsorption cross-over of polymers at isolated defects such as interfaces, cylinders or spheres. Moreover, increasing the density of traps (having a finite depth) beyond the cross-over point will increase the size of the localized chains again. Thus the static and also the dynamic properties display a pronounced *non-monotonic* behavior around the cross-over region [12,13]. This strongly nonlinear behavior may have interesting applications such as electrophoresis.

The effect of frozen-in structural disorder is a general problem of statistical physics. As has been discussed by Thirumalai [3] the replica variational approach is limited for the problem at hand. Lifshitz [8] has argued long time before that very rare events of connected clusters of defects determine the distribution of the lowest lying energy states in the corresponding quantum system. Thus, because of ground state dominance, these levels control the statistics of polymer chains in the the disordered environment. The ground state dominance (G.S.D.) means here, that a very long chain is trapped by a cluster of radius R, *i.e.* it is localized within the length $L \simeq R \ll lN^{1/2}$, with l being the statistical segment length of the chain. On the other hand the probability of finding a cluster containing $V \sim R^d$ defects is given by $P(n) \simeq p^V$, which is an exponentially small quantity for large values of V. For a given chain length there will be a balance between the gain in free energy $F(V,N,E)$ due to localization at energetically favorable clusters of traps and the probability $p(V)$ to find a cluster of size V. Here E means the interaction energy gain per monomer in the trap. As a result an optimal value emerges for the cluster size and hence for the localization length L of the trapped chain. This argument is well known and was recently applied again to the problem of directed polymers by Nieuwenhuizen [14].

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Usually it is assumed that the ground state of the polymer is simply given by the complete confinement of the chain (or quantum state) within the volume V. Here the depth of the traps E is a constant which can be omitted in the minimization procedure. However, depending on E, the chain will also extend into the outer space with a finite probability, resulting in a deviation of the chain's free energy function from the simple confinement behavior. By taking account of the full solution for the ground state in a spherical potential well of radius R, we predict a cross-over value $R^{\times} \sim 1/\sqrt{E}$, below which localization of chains in optimal clusters is no more favored compared with extended states in between the traps. For small values of E, $R^{\times}$ can be large and the cross-over from the free chain behavior to the trapped state is reminiscent to a first order transition scenario, assuming $R(E,N,p)$ (the optimal cluster size) as an order parameter. Moreover, using the exact ground state solution within the Lifshitz argument we naturally arrive at a dimensionless scaling expression for the free energy of the chain, yielding in particular $\widetilde{g} \sim \ln(1/p)/(NE^{1+d/2})$ as the universal control parameter for the localization cross-over. We illustrate our results by numerical solutions for the three cases $d = 1, 2, 3$.

2 Scaling form of the free energy for a single chain in a field of disordered traps

We assume the most simple two component discrete model of the disordered environment providing all the basic features but stripped from unnecessary details. This corresponds basically to the model of saturated disorder as introduced in reference [2]. Here a unit in space of size ξ is either "white" or "black", where the black sites correspond to traps. If a monomer is located there it gains an energy E. The probability for a trap is given by p. In the following we will be interested in clusters of connected traps. Here for $d > 1$ very different "lattice animals" appear with irregular shapes. However, for simplicity we assume a spherical shape for $V \gg 1$ only, *i.e.* $V \sim R^d$, see [4,10]. Note that within this model the depth of a cluster is given by the depth of the traps.

The key quantity of interest is the free energy of an ideal chain in disordered media. Generally, one would have to calculate the partition function $Z(N, E, \{\mathbf{r}_k\})$ for a given set of traps located at random positions $\mathbf{r}_k$ in order to obtain the free energy $F = -\ln Z$ in the limit of infinite volume with fixed density of defects p. Here and in the following we consider all energies in units of kT. Since the free energy is a self-averaging quantity, an *a posteriori* average over the disorder can be applied which in turn might be approached by the replica formalism [1,3,4].

However, there is a much more intuitive picture given by the optimal fluctuation method as introduced by Lifshitz [8] which we will apply here. The idea is that the chain prefers regions in space containing many closely connected traps forming a cluster of size $V \sim R^d$. The free energy is then controlled by the ground state of the cluster-chain interaction for sufficiently long chains of length N (number of segments)[1]. We denote this ground state solution by $N\lambda(R,E)$, where the chain length appears naturally as a prefactor, λ is the ground state free energy per monomer. According to this idea the free energy per monomer is given by:

$$f = \frac{F}{N} = \lambda(E,R) + V\frac{\ln(1/p)}{N} = \lambda(E,R) + R^d g, \qquad (1)$$

where we have introduced the parameter g as:

$$g = \frac{\ln(1/p)}{N} V(1), \qquad (2)$$

with $V(1)$ as the volume of the unit sphere in the given spatial units. The basic assumption is that the chain is localized by single clusters of radius R. Note that R is not equivalent to the localization or adsorption length of the chain L which corresponds to the extension of the wave function in the original Lifshitz argument. As we will see below, there is a unique relation between L and R, so that we keep R as the characteristic parameter. The second term of equation (1) is the logarithm of the probability of finding a cluster of size V, $p(V) \sim p^V$. Its appearance in the free energy can also be understood from the following argument: The free energy of the chain trapped by the cluster must be compared to the free energy of translation between the clusters $F_{\mathrm{tr}} = -\ln \overline{V}$, where $\overline{V}$ is the average free volume per cluster given by $1/p(V)$. Hence, equation (1) displays simply the balance between the translational free energy of the free chain and the free energy of trapping. Note the interesting correspondence between the picture of one cluster (defect) and many chains, *i.e.* a finite density c [15] and the situation at hand. We now minimize the free energy with respect to R which yields the optimal localized state dominating the free energy:

$$\frac{\partial f}{\partial R} = 0 \to R^{*}. \qquad (3)$$

Within the approach of spherical clusters of traps we can use the *exact* ground state solution of the polymer chain. This can be written as:

$$\lambda(E,R) = -E\widetilde{k}^2(RE^{1/2}), \qquad (4)$$

with

$$\widetilde{k} = k/\sqrt{E}. \qquad (5)$$

The ground state solution in equation (4) corresponds completely the solution of the time independent Schrödinger equation in a potential well [16]. The scaling form of equation (4) is a direct consequence of the *structure* of the Schrödinger equation. For convenience we provided the derivation in Appendix A. The symbol k corresponds to the inverse localization length L of the chain

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[1] For $d > 2$ a minimum value of E for a given cluster size must exist as will be discussed later.

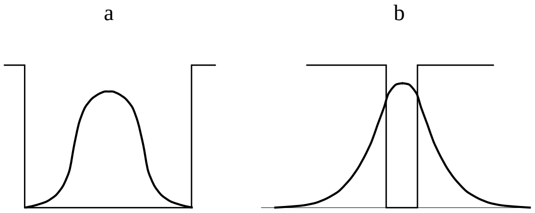

Fig. 1. Depending on the width of the cluster of traps two cases can be distinguished: (a) confinement of the chains and (b) localization by forming large loops outside the trap.

bounded by the cluster: $k \sim 1/L$. Inserting the formal solution (4) into the free energy function of equation (1) we get:

$$f = -E\widetilde{k}^2(\widetilde{R}) + R^d g, \qquad (6)$$

where we have also introduced $\widetilde{R}$ according to:

$$\widetilde{R} = \sqrt{E}R. \qquad (7)$$

Using further

$$\widetilde{f} = f/E \qquad (8)$$

$$\widetilde{g} = g/E^{1+\frac{d}{2}} \qquad (9)$$

we obtain finally:

$$\widetilde{f} = -\widetilde{k}^2(\widetilde{R}) + \widetilde{R}^d \widetilde{g}. \qquad (10)$$

This is the general scaling form of the Lifshitz free energy, where the three parameters E, g and R are expressed by only two scaling variables: $\widetilde{g}$ and $\widetilde{R}$.

In the most simple approach one considers the chain to be completely confined in the cluster, see for instance [2,14], *i.e.* one neglects any overflow into the outer space. Then we have $L = R$, as sketched in Figure 1a and the corresponding *confinement* solution for λ is given by:

$$\lambda_{\text{conf}} = \alpha\frac{1}{R^2} - E \qquad \text{with:}\;\; l^2 = 2d. \qquad (11)$$

The numerical constant α depends on d and on the form of the cluster. To avoid unnecessary prefactors we consider $l/\sqrt{2d}$ as the unit length. Notice that the depth of the cluster E appears only as a constant. We will see below that this solution cannot describe the interesting crossover scenario for small values of p but corresponds to the limiting case of large cluster sizes.

We now consider the properties of $\widetilde{f}$ using the solution $\widetilde{k}(\widetilde{R})$ for $d =$ 1, 2 and 3. For $d > 2$ there is no solution for $\widetilde{R} < \widetilde{R}_{\text{c}}(d)$. In the particular case of $d = 3$ we obtain $\widetilde{R}_{\text{c}}(3) = \pi/2$. To generalize the discussion one can set $\widetilde{R}_{\text{c}}(1) = \widetilde{R}_{\text{c}}(2) = 0$. In Figure 2 the numerical solution of $\widetilde{k}(\widetilde{R})$ is plotted. The function $\widetilde{k}(\widetilde{R})$ increases monotonous and we can distinguish two different regions of behavior: For small values of $\widetilde{R}$ the localized chains extend mostly into the outer space, see Figure 1b. The behavior of $\widetilde{k}$ near the edge $\Delta = \widetilde{R} - \widetilde{R}_{\text{c}} \ll 1$ is usually given by a power law [17]. Both for $d = 1$ and for $d = 3$ we obtain a simple linear relation: $\widetilde{k} = \Delta$. The case $d = 2$ is marginal. The critical value $\widetilde{R}_{\text{c}}(2)$ is still zero but $\widetilde{k}$ becomes exponentially small in the limit $\Delta \to 0$. Instead of a power law we get: $\widetilde{k} = 1/\Delta \exp\{-2/\Delta^2\}$. On the other hand, for large values of $\widetilde{R}$ the chain is confined, see Figure 1a, and equation (11) holds true. The free energy per monomer is bounded by the depth of the traps: $\widetilde{k}$ saturates at unity. The saturation can be quantified by $\kappa = \sqrt{1 - \widetilde{k}^2}$. One gets $\kappa = \sqrt{\alpha}/\widetilde{R}$ with: $\sqrt{\alpha}$ given by $\pi/2, 2.404...$ (first zero of $J_0(x)$) and π for $d = 1, 2$ and 3 respectively.

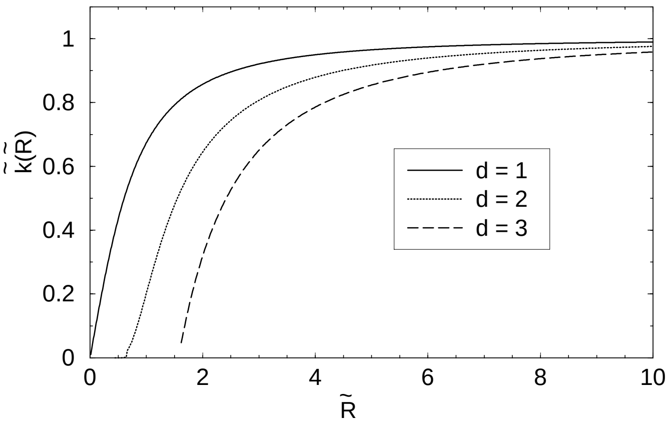

Fig. 2. Full solution of the Schrödinger equation as given by equation (A.11) is displayed.

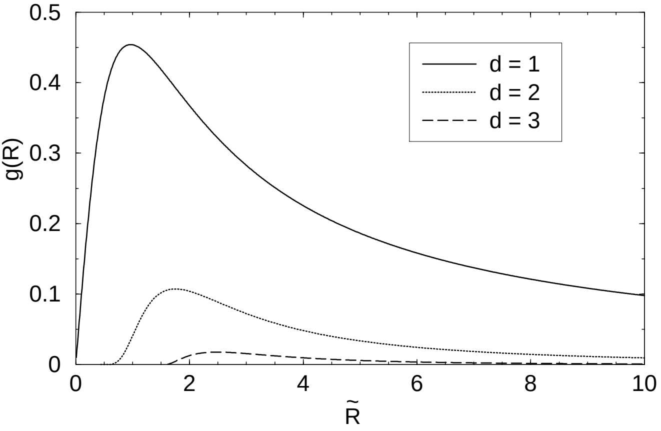

Fig. 3. The control parameter $\widetilde{g}$ as a function of the cluster radius is plotted for the condition $f = 0$.

As a consequence of this behavior we consider a small value value of g. The second term in equation (10) dominates for large enough R, since $\widetilde{k}$ saturates. The effective free energy therefore turns up for large values of R. For small values of R, on the other hand, the first term of equation (10) dominates, hence $\widetilde{f}$ becomes negative, provided g is small enough. As a consequence $\widetilde{f}$ has at least one zero point. Decreasing R further, also $\widetilde{k}$ is decreasing and $\widetilde{f}$ approaches zero again.

The zero points of $\widetilde{f}$ can now be represented as a functional dependence $\widetilde{g}(\widetilde{R})$:

$$\widetilde{g} = \widetilde{k}^2(\widetilde{R})/\widetilde{R}^d. \tag{12}$$

The result is plotted in Figure 3. For $d \leq 2$ and sufficiently low values of $\widetilde{g}$ there exist always two solutions of $\widetilde{f} = 0$. For the case $d = 3$ and above $\widetilde{R}_c$ the picture is similar to the lower dimensional cases. Both solution enclose a negative part of the free energy, which must be a minimum and corresponds to the optimal localization value of $\widetilde{R}^*$. Formally, we can define the optimal localization as a stationary point for the Lifshitz free energy:

$$\frac{\partial}{\partial \widetilde{R}} \widetilde{f} = 0 \tag{13}$$

$$\frac{\partial^2}{\partial \widetilde{R}^2} \widetilde{f} > 0. \tag{14}$$

However, equation (14) is not sufficient for a globally stable solution. A freely moving chain corresponds to $f = 0$ in our representation. This means, that a local minimum according to equations (13, 14) might be only *meta-stable*. Thus, the stationary point of $\widetilde{f}$ represents the stable solution only, if $f(R^*) < 0$. Hence we have to replace equation (14) by:

$$\widetilde{f} \leq 0, \tag{15}$$

which means, that the optimal solution according to equation (13) must be located between the two solutions of equation (12) or, in the case of a missing lower solution ($d = 3$), below the maximum of $\widetilde{g}$, given by equation (12). Considering Figure 3, this means that a stable localized situations can only appear *below* the graph $\widetilde{g}(\widetilde{R})$. An important consequence can be read off directly from Figure 3: there exists a maximum value $g^{\times}$ (connected with the *finite* diameter of the cluster $R^{\times}$) above which the localized solution in not stable. Decreasing g from above, localization sets in with a finite size of the cluster, *i.e.* for several traps at once. Depending on E, this number can be large. While for $d = 1$ this behavior is most pronounced it is generally similar for higher dimensions.

To conclude this section the scaled free energy at the threshold value $\widetilde{f}(\widetilde{R}, \widetilde{g}^{\times})$ is displayed in Figure 4 for $d = 1, 2$ and 3.

3 The cross-over scenario

As becomes obvious from the above results the Lifshitz free energy of polymers in a field of disordered traps shows properties which are characteristic for a *first order transition* scenario. We illustrate this for the case $d = 1$ in Figure 5. Here the scaled free energy $\widetilde{f}$ is again plotted against $\widetilde{R}$ for three different values of $\widetilde{g}$. For simplicity we introduce the distance from the "transition point":

$$\Delta_g = (\widetilde{g} - \widetilde{g}^{\times})/\widetilde{g}^{\times}. \tag{16}$$

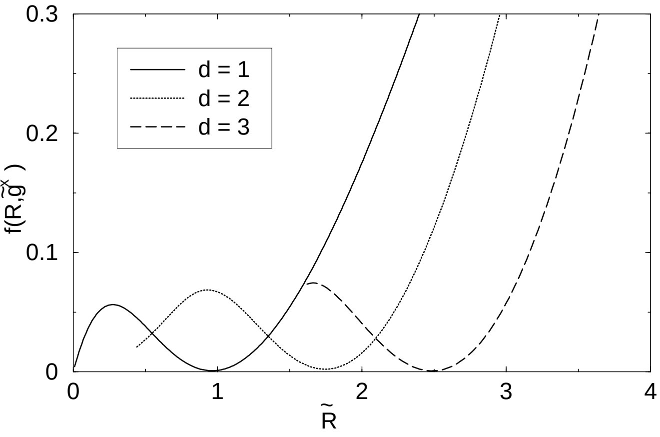

Fig. 4. The free energy *vs.* cluster radius (scaled units) is plotted at the threshold value of the control parameter $g^{\times}$.

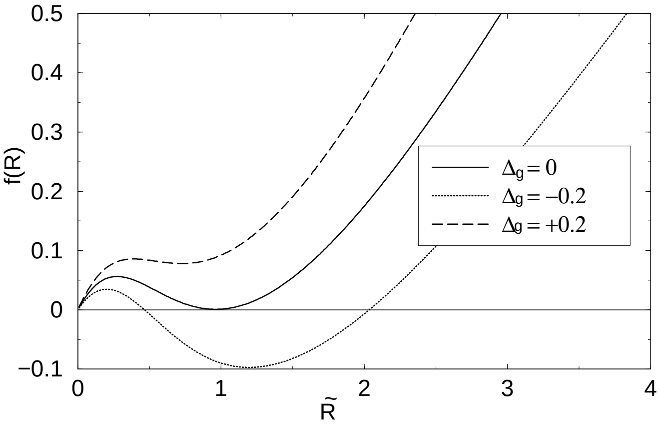

Fig. 5. The free energy *vs.* cluster radius (scaled units) for $d = 1$ is displayed for three values of the control parameter at, below and above threshold value $g^{\times}$. The symbol Δ_g is defined in equation (16).

The upper curve corresponds to $\Delta_g = 0.2$. This exemplifies the meta-stable solution for the optimal localization problem. Note that at this point the confinement solution according to equation (11) would still yield a localized behavior of the chain. For the middle curve, $\Delta_g = 0$, the minimum of f is just at $f = 0$, *i.e.* the localized states are thermodynamically comparable to the free states. Eventually, for $\Delta_g = -0.2$ the minimum is well below the free energy level of the free chain, the chain is localized. To use the picture of a phase transition scenario, we indicate the optimal value $\widetilde{R}^*$ as an *order parameter*. The process described above by lowering the control parameter $\widetilde{g}$ is therefore reminiscent to a first order transition where the order parameter jumps at the transition point. However, we should keep in mind that a real phase transition is a thermodynamic property, *i.e.* is defined only in the limit of infinite systems. The parameter g contains the chain length N, see equation (2), hence a finite size is defined *a priori*. Nevertheless, at least theoretically one can define the limiting case of $N \to \infty$ and $p \to 0$ by keeping g finite.

From the above discussion it follows, that for finite chains a cross-over from an almost free to a localized behavior takes place around $\widetilde{g}^{\times}$ which is defined by equation (13) and the condition $f = 0$. These two conditions fix the two independent variables $\widetilde{g}$ and $\widetilde{R}$, or, geometrically speaking there is a unique maximum of the function $\widetilde{g}(\widetilde{R})$ according to equation (12) and Figure 3. Returning to the original variables we get:

$$R^{\times} = c_R(d)/\sqrt{E}, \tag{17}$$

where the only d-dependence is contained in the constant c_R, which is of order unity, see Figure 4. The behavior $R^{\times} \sim E^{-1/2}$ is therefore universal. For g we get by virtue of the same argument using equation (9):

$$g^{\times} = c_g(d)E^{1+\frac{d}{2}}. \tag{18}$$

Here the constant c_g depends rather strongly on d, as can be read off from Figure 3. Consider E and N as given parameters, we further obtain using equation (2):

$$p^{\times} = \exp\{-c_g' N E^{1+\frac{d}{2}}\}, \tag{19}$$

with $c_g' = c_g/V(1)$. Because of the exponential behavior we can clearly distinguish two regions in the parameter space (N, E) for a fixed value p. For $NE^{1+\frac{d}{2}} > 1/c_g'$, $p^{\times}$ is exponentially small, so that for $p > p^{\times} \simeq 0$ the chain is localized. On the other hand for $NE^{1+\frac{d}{2}} < 1/c_g'$, $p^{\times}$ approaches unity so that for a given $p < p^{\times} \simeq 1$ delocalization takes place. Thus

$$y = NE^{1+\frac{d}{2}} \tag{20}$$

becomes a scaling variable controlling the localization cross-over for a given value of p.

It is interesting to compare these results with the situation where the traps form a *regular array*, see references [11,18]. If p denotes again the density of traps, we get for $d = 1$ the scaling variable $y = NE^2$ [11]. Comparing this with our result of equation (20) for $d = 1$, *i.e.* $y = NE^{3/2}$, we can draw the following conclusion: For in a given density p of defects with the attraction E the chains are easier adsorbed (in terms of the necessary chain length) in a random environment than in a regular array; disorder in the positions of the traps increases the tendency for chain adsorption.

We consider now the extension of the chains as a function of p. For $p \ll p^{\times}$ no localized solution for f exist. Therefore, the polymer is basically free and its extension is comparable to $R_0 = N^{1/2}$. Approaching $p^{\times}$ the chain gets trapped for longer times (meta-stability), so that the average extension decreases rapidly if p is increased. At $p^{\times}$ the extension is given by $R^{\times}$ depending only from the energy per trap E, see equation (17). Eventually, for p well above $p^{\times}$ the confinement approach (11) holds, R^* (which represents the optimal extension of the chain in the confined state) increases according to:

$$R^* \sim \ln(1/p)^{-1/(2+d)}. \tag{21}$$

As a consequence, the chain's extension passes through a minimum at the cross-over point $p^{\times}$.

4 Discussion

We have presented a Lifshitz approach to polymer localization in quenched disordered media described in terms of randomly distributed energetic traps. Using the approach of spherical clusters of radius R we have discussed the full ground state solution for the free energy per monomer $\lambda(E, R)$. For small values of R, which correspond to low densities of traps, the confinement solution is no more appropriate, instead of this the chains are localized around the traps by forming large loops. We have shown that this regime yields an unstable behavior of the free energy in the Lifshitz approach. The full solution shows a first order transition scenario, where the optimal value of the localization length becomes thermodynamically favored only beyond a value $R^{\times} \sim E^{-1/2}$. One can reconsider this result using a simple hand waving argument: The optimal Lifshitz free energy per monomer for the confinement solution according to equation (1) and using equation (11) can be written as:

$$f = -E + \alpha'/(R^*)^2 = -E + \alpha'' g^{+\frac{2}{d+2}}, \tag{22}$$

where α' and α'' are numerical constants. This solution is thermodynamically stable only if $f < 0$. Therefore, we obtain again: $R^{\times} \sim 1/\sqrt{E}$ and $g^{\times} = E^{1+d/2}$, but now as a limitation of the confinement solution.

Generally, we have shown that the free energy can be written as a homogeneous function with respect to E, *i.e.* it has a general scaling form for all values of the parameters, see equations (7, 8, 9, 10). Of course, this is only true within the Lifshitz approach, *i.e.* the idea of considering the localized states only at single clusters of connected traps. This means that the *a posteriori* average of the self-averaging free energy is obtained by sampling over a very particular subspace of the high dimensional random parameter space. These rather improbable clusters (for small p) give still the leading contribution to the free energy provided there is enough time left for the system to explore these regions. For a thorough discussion of the dynamical problems in the one-dimensional case, see [14].

We have explicitly considered the solutions for $d = 1$, 2 and 3. In the three-dimensional case, there exist no localized state below a threshold value of $R_c\sqrt{E} = \pi/2$. However, within the Lifshitz method, this concerns the region which is unstable from the thermodynamical point of view, see Figure 4. Note that also for lower dimensions $d = 1, 2$ a *finite* cluster size $R^{\times}$ is required to localize the polymer chain.

Crossing the threshold value by changing the parameter p, we predict a non-monotonic behavior of the chain's extension, having a minimum around $p^{\times}$. For finite chain lengths, this minimum should be shifted to somewhat larger values of p, since there is always a finite probability for the chain to escape from the optimal states, thus enlarging the average extension. This behavior was already predicted and simulated by the author for the special case of $d = 1$ [12,19]. The present work shows that this is also expected for higher dimensions. We note, that the constant c_g controlling the cross-over to the localized state is rapidly decreasing when d increases, see Figure 3, so that for higher dimensions larger chains are necessary to display the predicted behavior. This might be crucial if non-spherical clusters are present either due to statistical fluctuations of the shape itself or as a result of correlated "crack-like" disorder. In this case the chains should prefer the more anisotropic defect regions resulting in a tendency to lower the effective dimension of the disorder. Therefore corrections due to the non-spherical form of the clusters should enhance the effects near the localization cross-over.

Finally the threshold value $p^{\times}$ should also influence dynamical quantities such as the diffusivity. In fact Slater and Wu [13] as well as the present author [19] found a pronounced minimum for the diffusivity for small values of p. This might be of interest for electrophoresis of polymers in disordered media.

Appendix A: Exact ground state solution

We have to find the ground state solution of the time independent Schrödinger equation in a d-dimension spherical potential well of depth E, which describes a single cluster of traps. In the given units we can write this as follows:

$$D_r^2\phi(r) + (\lambda - U(r))\phi(r) = 0, \tag{A.1}$$

where ϕ is the ground state solution as a function of r, *i.e.* the distance to the center of the well. The potential is given by:

$$U(r) = \begin{cases} -E & \text{if } 0 \le r < R, \\ 0 & \text{if } r \ge R. \end{cases} \tag{A.2}$$

The operator D_r^2 denotes the r-dependent contribution from the Laplace operator in d spatial dimensions. Since we are looking for the ground state solution we can generally neglect the angle dependent part. It is most important for the general results below, that we can introduce scaled variables as follows:

$$\widetilde{r} = \sqrt{E}r \tag{A.3}$$

$$\widetilde{\lambda} = -\widetilde{k}^2 = \lambda/E \tag{A.4}$$

$$\widetilde{k} = k/\sqrt{E}. \tag{A.5}$$

Using this definitions, we can write the inner and the outer solution as follows:

$$D_{\widetilde{r}}^2\phi_{\mathrm{i}} + (1-\widetilde{k}^2)\phi_{\mathrm{i}} = 0 \quad \text{if } 0 \le r < R \tag{A.6}$$

$$D_{\widetilde{r}}^2\phi_{\mathrm{o}} - \widetilde{k}^2\phi_{\mathrm{o}} = 0 \quad \text{if } r > R. \tag{A.7}$$

Using the necessary conditions: $\lim_{x\to 0}\phi_{\mathrm{i}}(x) = \text{const} < \infty$ and $\lim_{x\to\infty}\phi_{\mathrm{o}}(x) = 0$ the only solutions in both regions are given by:

$$\phi_{\mathrm{i}}(x) = c_{\mathrm{i}}\mathcal{C}(x) \tag{A.8}$$

$$\phi_{\mathrm{o}}(x) = c_{\mathrm{o}}\mathcal{E}(x). \tag{A.9}$$

Table 1. Solutions of the Schrödinger equation as defined in equations (A.8, A.9) for various spatial dimensions. The symbols J_0 and K_0 denote the Bessel function of first and third kind (Basset function) respectively.

d	$\mathcal{C}(x)$	$\mathcal{E}(x)$
1	$\cos(x)$	$\exp(-x)$
2	$J_0(x)$	$K_0(x)$
3	$\sin(x)/x$	$\exp(-x)/x$

The letters $\mathcal{C}$ and $\mathcal{E}$ shall remind to the cosine-like and exponential-like solutions in the inner and the outer region respectively. Their realizations in one, two and three dimensions are shown in Table 1. As well known the state function ϕ must obey the usual continuity conditions at the interface between both regions, which results in the following equation:

$$\frac{\mathrm{d}}{\mathrm{d}\widetilde{R}}\ln\mathcal{C}\left((1-\widetilde{k}^2)^{1/2}\widetilde{R}\right) = \frac{\mathrm{d}}{\mathrm{d}\widetilde{R}}\ln\mathcal{E}(\widetilde{k}\widetilde{R}) \tag{A.10}$$

with the unique solution:

$$\widetilde{k} = \widetilde{k}(\widetilde{R}). \tag{A.11}$$

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