Density fluctuations of polymers in disordered media

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Density fluctuations of polymers in disordered media

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We study self avoiding random walks in an environment where sites are excluded randomly, in two and three dimensions. For a single polymer chain, we study the statistics of the time averaged monomer density and show that these are well described by multifractal statistics. This is true even far from the percolation transition of the disordered medium. We investigate solutions of chains in a disordered environment and show that the statistics cease to be multifractal beyond the screening length of the solution.

I. INTRODUCTION

In many experimental situations, linear polymers are present in a disordered medium. For example, a free polymer chain inside an elastomeric network, or a DNA molecule in an agarose gel. The properties of single chains in such situations have been the subject of numerous theoretical and numerical work [1–9]. From a theoretical perspective, the problem is of great interest in part because of its strong connection to the phenomenon of quantum mechanical localization [10]. The greens function for a single ideal polymer chain in a potential is mathematically identical to that of an electron in the same potential, but in imaginary time [11]. Therefore a polymer chain is expected to collapse to a small region in space. However the presence of excluded volume of the chain prevents this from occurring. The statistics of a chain in this case was the subject much controversy. This was settled by the work of Cates and Ball [1] who showed that the statistics of a chain on an infinite lattice with frozen disorder, that is the quenched case, was identical to that of a chain with mobile defects, that is the annealed case. They showed this by dividing up the infinite lattice into large finite regions with frozen disorder. The average properties of a chain are obtained by averaging over all these large finite regions. This is equivalent to performing an annealed average. It is easy to perform the annealed average over uncorrelated random disorder and show that this has no effect of chain statistics. Simulations [4] away from the percolation threshold bear out this prediction. Work on off-lattice models of spherical obstacles show more complicated behavior, because the correlations in the disorder are no longer point-like, so this influences the conformation of a chain. For low obstacle volume fraction, these correlations induce an effective attraction causing a decrease in chain size. As the volume fraction gets close to the percolation threshold [8, 9], the exclusion of phase space for finite lattice sizes leads to an increase in the average chain size.

Although chain statistics in the above situation are not affected by frozen disorder, there is another important physical quantity that does change. Consider the density of monomers for a given background of disorder. If this is averaged over time, one expects that the density will fluctuate because of the fluctuations in the random potential. This problem was studied numerically by Gersappe et al [7] in two dimensions [7] where it was shown this time averaged monomer density (TAMD) obeyed multifractal statistics [12–14] over the parameter range studied. The spectrum of multifractal dimensions was computed numerically and gave strong evidence for multifractal scaling.

More recently [15], the properties of a polymer chain on the backbone of a percolating cluster were examined numerically at the percolation transition. They found that it exhibited multifractal properties in agreement with the theoretical work of Janssen and Stenull [6]. A measure of bond density for an ensemble of chains of varying lengths that connect two points separated by a distance R was calculated numerically. That measure was analyzed and shown to have a spectrum of multifractal exponents.

The earlier work of Gersappe et al [7] in two dimensions claimed that multifractal statistics were true even far from the percolation transition where the disorder is dilute. In other words, the multifractal nature of polymers in disordered systems is much more general and in fact, a simpler more experimentally accessible quantity, namely the time averaged monomer density, can be used as a measure.

Multifractal distributions are characterized by very large fluctuations, so in this case, we expect that the TAMD $\rho(\mathbf{r})$ will have a probability distribution that becomes increasingly broad as the system size in increased. We also expect multifractal statistics to be present for scales less than the average radius of gyration, R_g, of the chain. On larger scales, the density fluctuations should saturate so that the distribution P of ρ should obey [13, 14]

$$P(\log\rho) \propto \exp(\log(R_g) f(\log(\rho)/\log(R_g))). \qquad (1)$$

In this paper, we study this problem in two dimensions for different amounts of disorder and show that multifractality is seen in all cases. The original work of Gersappe et al only presented results for one value of disorder. Next we study this system in three dimensions and show that multifractal statistics persist for this case

as well. Next we consider many chains at finite concentrations and demonstrate how this smooths out density fluctuations so that the statistics are no longer multifractal.

In section II we describe the model that we will apply to study this problem. In section III we study the TAMD in two dimensions. The results are similar to what was found earlier [7] but with much improved data providing more solid evidence for multifractality of a range of obstacle densities. Section IV considers the same problem in three dimensions. Although box sizes are smaller, this work provides solid support for the case the TAMD is also a multifractal measure in this case as well. In section V this problem is analyzed for a solution of chains at finite concentration where it is clear that the system ceases to be multifractal over the scale of the radius of gyration of a chain. An interesting bimodal distribution for the distribution of the TAMD is found.

II. THE MODEL

We consider a cubic lattice in $d = 2$ and 3 dimensions, with m self avoiding walks of unit step length of N monomers. The monomers move in a cubic box of width L. Skew boundary conditions are employed [16]. Obstacles are randomly placed on sites which are excluded from occupation by polymer chains. We denote the average fraction of excluded sites as n_o.

The chains are moved using "reptation dynamics" [17]. Briefly, the head or chain of a chain is picked at random and an attempt is made to move it to the other end. The attempt fails if the site is occupied by a chain or an obstacle, otherwise it succeeds. After equilibrating, statistical properties of the chains are measured, such as the radius of gyration and the time averaged monomer density.

To test this method, we checked that the internal chain statistics of a single chain with random disorder were identical within statistical error to that of a self avoiding walk with no disorder.

Next we considered density fluctuations. Moments of the normalized time averaged monomer density ρ_r can be calculated by summing moments of the density over all lattice sites and inferring how this depends on lattice size

$$\langle \sum_r^{L^d} \rho_r^q \rangle \sim L^{-\tau(q)} \tag{2}$$

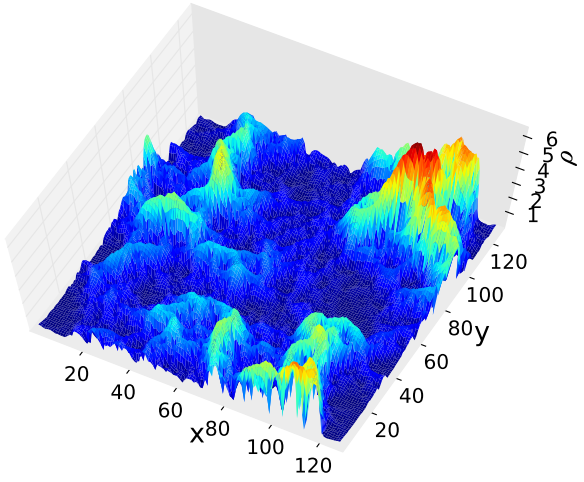
The average is over different realizations of the disorder. However, it is more accurate to obtain the exponents $\tau(q)$ by coarse graining, making use of the self-similar nature of multifractals. If we coarse grain over boxes of width l, and define $\tilde{\rho}_r$ as the density measure coarse grained over that length scale, then it is straightforward to show that

$$T_q(l) \equiv \langle \sum_r^{(L/l)^d} \tilde{\rho}_r^q \rangle \sim l^{\tau(q)-dq}. \tag{3}$$

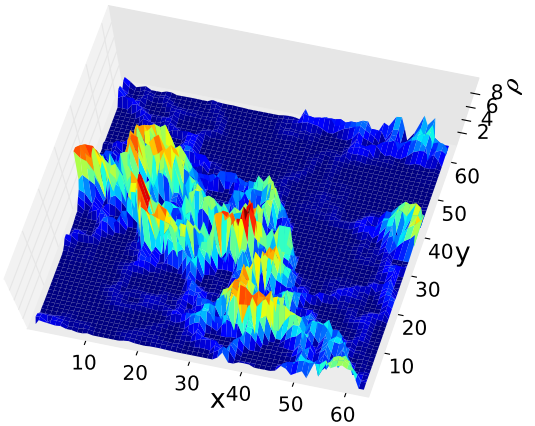
By analyzing how this sum depends on l, $\tau(q)$ can then be determined.

III. SINGLE CHAINS IN TWO DIMENSIONS

The above model was studied for a single chain in two dimensions for different values of the disorder and chain lengths. The TAMD ρ_r is plotted in Figure 1. Figure 1(a) shows a chain of length $N = 512$ in a box of length $L = 128$ with an obstacle density of $n_o = .1$. The self similar nature of the measure is apparent. Figure 1(b) shows the TAMD for $N = 256$ and $L = 64$, with $n_o = 0.3$.



(a)



(b)

FIG. 1. (Color Online) The time averaged monomer density ρ for a self avoiding random walk in two dimensions, (a) $N = 512$, $L = 128$, and $n_o = 0.1$; (b) $N = 256$, $L = 64$, and $n_o = 0.3$. The horizontal axes are labeled x and y.

The density shows a self similar structure with different regions appearing statistically quite similar but differing by an overall multiplicative constant as expected for a multifractal measure. For distances larger than the radius of gyration, one expects multifractal scaling to no longer hold. Similarly, for distances smaller than some cut-off distance l_0, related to the density of obstacles, the density should become smooth so that multifractal scaling no longer applies. But over intermediate scales, as can be seen, the density appears self similar. This will be now quantified below.

Coarse graining of ρ is done by recursive decimation of the original lattice into 2×2 blocks. This implies that the coarse graining length is a power of 2, $l = 2^m$ where m is the number of times the lattice is decimated. Good fits to power laws were obtained between the lower and upper cutoffs for Eq. 3 as shown in Fig. 2. This plots the left hand side of Eq. 3 as a function of coarse graining $m = \log_2 l$. Fig. 2 shows the case $N = 512$, $L = 128$, and $n_o = 0.2$ for $q = -1, 0, 1, 2$. The results were averaged over 200 different realizations of the random obstacles, and each simulation was run for a total of 8×10^9 steps. This is strong evidence of self similar multifractal behavior *far away* from the percolation threshold in two dimensions.

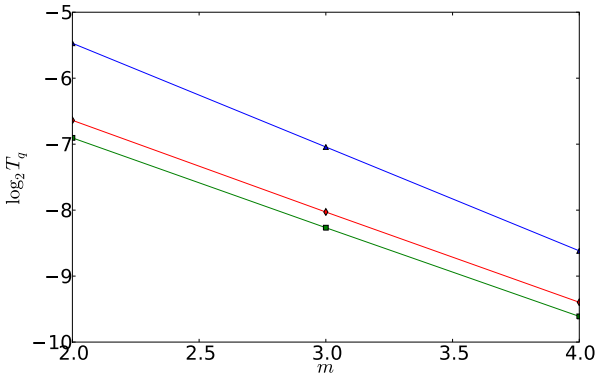


FIG. 2. (Color Online) The scaling of moments of the coarse grained density T_q as defined in Eq. 3 as a function of the amount of coarse graining m in two dimensions. The top line is data for $q = -1$, the middle, $q = 2$, and the bottom is for $q = 1$.

Using these fits, $\tau(q)$ defined in Eq. 3 was calculated. The results are shown in Fig. 3. For clarity we plot the difference in τ defined as $\Delta\tau(q) \equiv \tau(q) - \tau(q - 1/2)$. This is shown for three different sets of parameters, $n_0 = 0.1$, 0.2, and 0.3.

The data give strong evidence for multifractal behavior for a range of different obstacle densities.

IV. SINGLE CHAINS IN THREE DIMENSIONS

The simulation was run in three dimensions and analyzed for the possibility of multifractal scaling, following

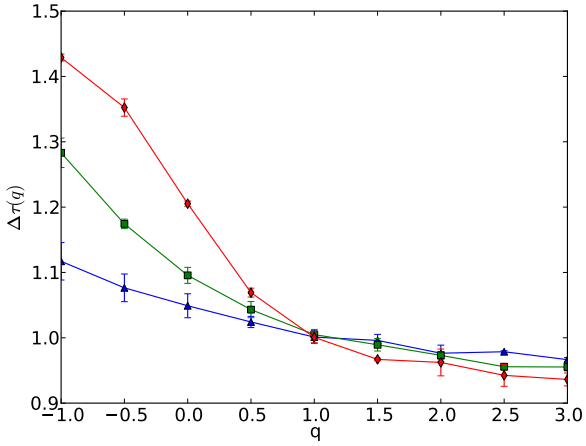


FIG. 3. (Color Online) The results of simulations to determine the multifractal dimensions for for different obstacle densities $n_0 = 0.1$ (triangles), 0.2 (squares), and 0.3 (diamonds) in two dimensions.

the same procedure as in two dimensions. We first plot $\langle\tilde{\rho}^q\rangle$ as a function of the coarse grained length scale l, as is defined in relation to Eq. 3. Fig. 4 shows the case $N = 128$, $L = 32$, and $n_o = 0.3$. Because the box size and the chain length are smaller than in two dimensions, power law scaling can only be seen over a more limited range, however, it does support the hypothesis that the TAMD is multifractal. For $q = 2$ a slight curvature can be seen in the log-log plot which is to be expected from finite size effects. Overall the fits to power laws over this range is very good. Similarly good fits are also seen for $n_0 = 0.2$. In Fig. 5, we display fits for $\Delta\tau$ as a function of q for $n_0 = 0.1$, 0.2, and 0.3.

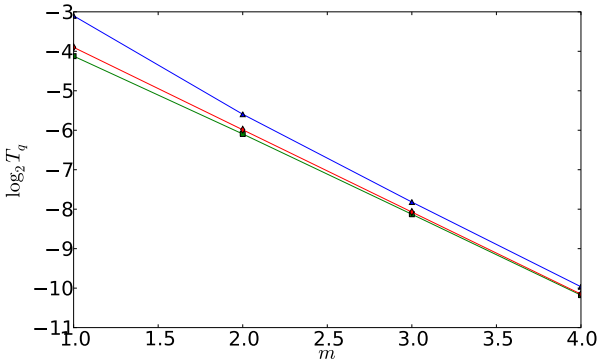


FIG. 4. (Color Online) The scaling of moments of the coarse grained density T_q as defined in Eq. 3 as a function of the amount of coarse graining m in three dimensions for $n_0 = 0.3$. The top line is data for $q = -1$, the middle, $q = 2$, and the bottom is for $q = 1$.

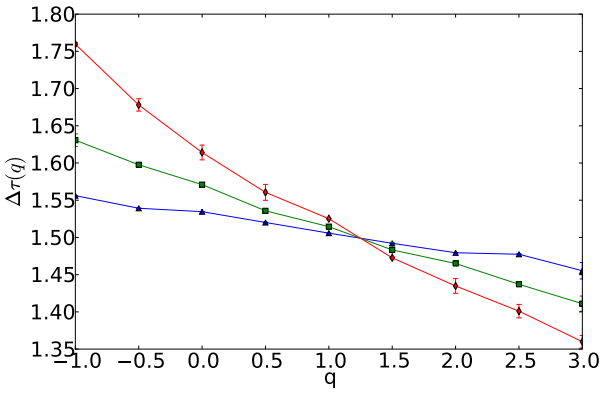


FIG. 5. (Color Online) The results of simulations to determine the multifractal dimensions for for different obstacle densities $n_0 = 0.1$ (triangles), 0.2 (squares), and 0.3 (diamonds) in three dimensions.

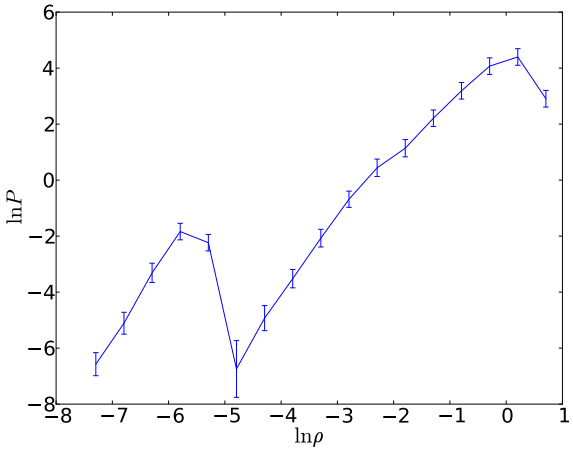


FIG. 6. (Color Online) The distribution of the TAMD natural logarithm of ρ for 40 chains, an obstacle density of $n_0 = 0.2$ in three dimensions with $N = 128$, $L = 32$. The vertical axis the natural logarithm of the probability distribution.

Therefore is appears that in three dimensions, our simulations and analysis also support the idea that the TAMD is multifractal for obstacle densities away from the percolation.

V. MANY CHAINS

The internal statistics of a self avoiding walk (SAW) in a much larger lattice of quenched random obstacles was shown to be equivalent to that of an annealed average and hence that of a SAW without disorder [1]. For the case of a many chain solution, extending this result is not completely straightforward. The difficulty in this case is that the polymer solution extends throughout the entire lattice.

We could considered the problem of an infinite lattice with a set of chains that were mobile but were required to always be close to each other. In other words, one can add the constraint that all chains are within a finite size box whose center of mass is arbitrary. In this case the argument of Cates and Ball [1] could be extended to this many-chain case. Therefore with an infinite size lattice and with this many chain problem, the annealed and quenched averages should be equivalent. Unfortunately this does not give any indication of the size of the lattice where these two types of averages become equivalent.

However, this problem is easily amenable to numerical simulation. Various equilibrium internal averages for chains were calculated and found to be almost entirely unaffected by the disorder. As an example, we considered $m = 40$ chains each of length $N = 128$ with an obstacle density of $n_0 = 0.2$ in a box of size $L = 32$. Excluding obstacles, this corresponds to a chain filling fraction of 20%. $R_g^2 = 49.190 \pm 0.013$ in this case. In comparison $R_g^2 = 48.785 \pm 0.006$ when run with no obstacles. The difference between these two cases is less than 1%. As the obstacle density approaches the percolation point, one would expect the difference between these two cases to increase due to the increasing likelihood of islands that are inaccessible, similar to the single chain case [4, 8].

In contrast to internal chain statistics, such as the average radius of gyration, we expect that the TAMD for the many chain case to be greatly affected by the presence of disorder, as it was for the single chain case.

For a system of chains at finite density in three dimensions, the fluctuations in chain density will be quite different than for a single chain. Above the correlation length, correlations in density will decrease rapidly. Therefore the distribution of the TAMD is no longer expected to be multifractal over these scales. This problem was simulated using the same approach as above.

The distribution of the TAMD was averaged over lattice sites and different realizations of the obstacle density in three dimensions. This is displayed in Fig. 6 for the same system as discussed above: $m = 40$ chains each of length $N = 128$ with an obstacle density of $n_0 = 0.2$ in a box of size $L = 32$. The distribution is plotted with logarithmic axes (base e). The results were averaged over 155 different realizations of the random obstacles, and each simulation was run for a total of 8×10^9 steps. The TAMD ρ was normalized so that $\langle\rho\rangle = 1$.

The results show that the distribution $P(\log\rho)$ has two peaks. One peak is close to $\rho = 1$ and most values of the density are clustered around that value. However, there is another peak for very small values of the obstacle density $\rho = 0.003$. The second peak is unexpected because it implies that there are intermediate values of the density that are much less probable.

The same feature persists when the obstacle density n_0 is reduced to 0.1 and in both cases it is clear that this

second peak is not due to random statistical fluctuations. This is likely due to the presence of some particular local configurations of obstacles, for example a cul-de-sac. In this case there will be entropic exclusion of chain for such a region leading to a lower monomer density.

The distribution in Fig. 6 is is not compatible with the prediction of multifractal statistics (Eq. 1) as the distribution must be convex. In addition, the coarse graining analysis of the last two sections does not yield a spectrum of exponents. $\Delta\tau(q)$ over the same range as Fig. 5 varies by less than 0.05. The lack of large fluctuations is to be expected due to the presence of a screening length. Although it is likely that the TAMD is multifractal below this scale, it is not possible to investigate this numerically because the accessible sizes only cover a small range in scales.

VI. DISCUSSION

This work has studied the problem of polymer chains in a disorder medium using a lattice model for self avoiding walks with some sites excluded. Many of the statistics for the polymer are exactly the same as if there were no disorder, for a single chain in the limit of an infinite lattice. For a finite sized lattice quantities such as average radius of gyration appear to be almost unaffected by the presence of disorder. In contrast, the time average monomer density (TAMD) in both two and three dimensions becomes very heterogeneous. For a single polymer chain, our results provide evidence that this density obeys multifractal statistics for length scales smaller than the radius of gyration of the chain. This appears to be true for disorder far away from the percolation transition.

The fact that the statistics of the average density are multifractal suggests that the dynamics are even more complex. And because a spectrum of exponents govern the density correlation functions, the extensions to dynamical properties must take this into account. Certain properties such as the diffusion coefficient of a self avoiding chain in a disordered environment have been previously investigated [18, 19] indicating that the diffusion coefficient and hence the relaxation time, have a power law scaling.

In the case of many chains, it is known that the effects of screening lead to a slowing down in the dynamics of chains and that for long enough chains, the relaxation time is proportional to $\exp(const \times N^p)$ [20, 21], where p is believed to be $2/3$. The effects of the random environment are screened out for distances longer than the correlation length, therefore such long relaxation times are also expected in the many chain case studied here.

The fact that even a low amount of disorder causes the TAMD to become highly fluctuating should be taken into account when considering other processes that often occur in polymeric systems. For example, if a low concentration of polymeric solution has not phase separated, considering a similar situation but in a disordered medium such as a gel, could had significant consequences. As the above results imply, the polymers will all be attracted to the same regions of the gel. This will mean the effective concentration in those regions will be considerably higher. This could then enhance the degree of phase separation.

A disordered medium should have an interesting effect on a polymer moving in an applied field, for example as is seen during electrophoresis [22]. If we consider the field to be very weak, the chain will tend to spend most of its time in a small subset of the volume available to it, even for low disorder, as a consequence of the large fluctuations in density found here. It would be interesting to explore how the mobility varies as a function of the applied field in this case. Even very weak applied fields are capable of stretching long chains [23, 24]. This should dramatically change the TAMD in this situation.

Another potential application of this work concerns the positions of macromolecules inside a living cell. We have seen that a self avoiding walk will be much more likely to be found in some disordered regions rather than in others despite the fact that the chain is capable of sampling almost all regions. This is despite a lack of complex chemical interactions and is entirely due to excluded volume effects. There are situations where molecules such as DNA plasmids move in a heterogeneous environment that has much in common with our much simpler problem. For example, DNA plasmids in prokaryotic cells nucleoids move in what is effectively a highly disordered network-like environments [25]. It appears that the diffusion of these plasmids is restricted to certain regions in the bacteria nucleoid [26] suggesting that there are regions not readily accessible to chains. It would be interesting to investigate further to what extent phenomena such as these are a result of the mechanism studied here.

VII. ACKNOWLEDGMENTS

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