Density Fluctuations of Self-Avoiding Walks in Random Systems

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We analyze density fluctuations of a self-avoiding chain in a random environment by a computer simulation. The density at a site is obtained by computing the number of times a monomer visits a particular site on a finite lattice. Although the chain obeys self-avoiding-walk statistics, the density measure appears to be multifractal. We compute $\tau(q)$ and $f(\alpha)$.

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The properties of polymers in disordered media have recently received much attention.[1-5] There are a variety of physical situations in which a polymer is placed in a highly disordered medium. For example, in a porous medium, such as a gel, this situation arises as a first step in a separation process, such as gel electrophoresis.[6] Biological systems also often involve long macromolecules in a highly inhomogeneous environment.

To understand this problem theoretically, an appropriate model must be introduced. The chemical conditions are often such that the polymer is self-avoiding, and therefore the polymer can be represented over a wide range in length scale as a self-avoiding walk (SAW). The interaction between the polymer and the disordered medium is most simply represented by a random potential, with short-range correlations. In analytical work, Gaussian statistics for the potential are most frequently assumed;[2] in numerical work, hard-core repulsion between the chain and the medium is most often employed.[3] Physical differences between these two choices may arise, coming from the fact that there is a lower bound to the value that the potential can assume, when these hard-core statistics are taken.[2]

Statistical properties of this model can be understood by taking appropriate ensemble averages. There are two kinds of averages that can be done: an average over different chain conformations and an average over different random media. The average over different random media has been frequently performed first, to reveal how the statistics of the SAW are modified by the random potential. Annealed and quenched averages have both been considered. In the case of a random potential with a lower bound, general arguments of Cates and Ball[2] show that the annealed and quenched averages are equivalent.[7]

Their argument can be summarized as follows. In a large enough system, a single polymer chain in a fixed (quenched) environment will explore many different environments. Averaging the statistics of the polymer in these different locations is equivalent to averaging the chain over different realizations of the same random potential. Since these realizations in different locations will be uncorrelated, this is equivalent to taking an annealed average.

The annealed statistics of a chain in a short-range random potential can be easily computed. For the case of soft local intrachain interactions, the random potential introduces an attractive two-body term, leading to a tricritical point as the local repulsive term is decreased.[3] For the case of a complete self-avoidance, the disorder can be integrated out giving no effect on the statistics of the chain. In summary, we know the following: The quenched statistics of an SAW in a short-range random potential whose probability distribution has a lower bound has the same statistics as an SAW without any random potential. These results have been confirmed by computer simulation.[4] Here we are not considering hard-core disorder close to the percolation transition which introduces complications. Aside from this case, averaging over the random potential does not lead to any new physical effects in the systems described above.

There are, however, important properties that are left out by averaging out over disorder first, and one might expect that some properties of the system are very sensitive to the presence of a random potential. For example, one might be interested in the frequency at which an arbitrary site on the lattice is visited. Physically, one could measure this by averaging the density in some region over time, say by the use of fluorescence, and from this compile a map of frequency as a function of position. This quantity, the time-averaged monomer density (TAMD), should be greatly affected by the presence of a random potential, since in the absence of a potential the averaged density is constant.

A Gaussian chain in the presence of a random potential will essentially collapse to fit into regions of low potential energy. Its density outside these regions will be exponentially suppressed. When one includes strong enough excluded volume interactions the chain is no longer collapsed but is now extended with the fractal dimension of the usual SAW. However, it will still avoid regions of high potential, and so it is expected that the

time-averaged monomer density will still show large fluctuations. Because the chain is self-similar over distances much greater than the correlation length of the random potential and the persistence length, and distances much smaller than the radius of gyration of the polymer, we expect the TAMD to be self-similar over the same range. Because we expect the TAMD of a long chain to be self-similar and to show large fluctuations, it is an obvious candidate for a "multifractal measure."[8-10]

In fact, one can speculate via a simple heuristic argument that the behavior of the TAMD is multifractal. Consider a long chain that can take on all conformation with the restriction that its center of mass is a constant value. We expect that if we were to cut the chain into smaller chains that have a radius of gyration R_g equal to D, then the TAMD for these smaller chains should be very closely related to the TAMD of the chain we started with. In fact, if we were to pin the center of mass of a cut chain to some location, the TAMD in that region, of size D, should be almost the same as the TAMD of the entire uncut chain, up to a multiplicative constant. To determine this constant, coarse grain the TAMD of the uncut chain into regions of size D. This coarsed-grained TAMD in the region of the pinned smaller chain gives the desired multiplicative constant. This is precisely the structure one finds in multifractal measures. The measure can be constructed by subdividing the support into successively finer scales, with the measure on a smaller scale determined by the physics that occurs locally, times a multiplicative constant that is determined from behavior on the next larger scale.

In what follows we present numerical evidence that the TAMD is multifractal and numerically determine $\tau(q)$. As mentioned above, a real system where these results can be applied is a dilute solution of polymers inside a gel. If we observe the TAMD then it should look multifractal up to a length scale of the radius of gyration R_g. The density when coarsed grained on length scales much larger than R_g should become smooth, and fluctuations in density should cease to obey multifractal scaling.

While many previous studies have concentrated on the critical behavior at the percolation threshold,[4,5] this work shows that even at dilute concentrations far below the percolation threshold the TAMD is drastically different than when no impurities are present.

The simulations were carried out in two dimensions because of the large amount of computer time involved. All computations were carried out on a Cray X-MP. The system chosen was a polymer chain on a square lattice with hard-core on-site repulsion. The environment was represented by obstacles also with hard-core on-site interactions. These were randomly positioned and 20% of the sites were filled. This value is far enough away from the percolation threshold as to make the probability of starting the chain on a finite cluster rather small. If this happened, the run was aborted and new initial conditions were chosen. This eliminated the possibility of the chain being trapped and spending all its time in a small region of the system rather than sampling all the available realizations.

The chain was grown on a lattice using a "slithering snake" algorithm as developed by Wall and Mandell.[11] The algorithm consists of removing a chain end at random and reattaching it to the other end. If the excluded volume criterion is met and if there is no impurity at the new position of the end then the move is accepted, otherwise the chain end is put back in its original position. Periodic boundary conditions were used in the simulation. The simulation was run for 10^4 Monte Carlo steps, where each step involved N^2 attempted movements of the chain, N being the length of the chain used. All the chains were grown from a point source and were given five N^2 movements to equilibrate. At the end of each subsequent Monte Carlo step, properties of the chain such as the radius of gyration, the distribution of the radius of gyration, and the monomer density distribution were calculated. The simulation was first run for a lattice of size 512×512 to check whether we recovered SAW statistics in the presence of disorder. We found that the exponent ν was not affected in agreement with previous simulations,[4] with $\nu=0.722\pm0.027$. In order to estimate the fluctuations in the chain's radius of gyration, we computed the distribution of the radius of gyration. We found very little effect of disorder on the distribution,[12] at least for the concentration of impurities studied in this simulation. We also looked at the monomer-monomer correlation to see if there was any effect of disorder but could not find any noticeable difference.

Next we obtained the TAMD by considering a finite-size lattice and counting the number of times a site on the lattice was visited by the polymer. In order to make sure that the statistics of the chains were not affected by the use of this smaller lattice we again computed the scaling exponent ν and found it unchanged. The lengths of the chains that were used in these calculations were such that chain overlap due to periodic boundary conditions was unlikely, but the end-to-end distance of the chain almost spanned the lattice. A typical conformation of the TAMD is shown in Fig. 1. This is for a lattice of size 32×32. As can be seen there are huge fluctuations from site to site on the lattice. The range of density is almost 4 orders of magnitude for this particular plot.

We used a variety of different lattice sizes in our simulations, 24×24, 32×32, 40×40, 44×44, and 64×64 and the corresponding chain sizes were 45, 60, 80, 100, and 120. The concentration of impurities was kept at 0.2 for all system sizes. The results were then averaged over ten realizations of disorder. Our results are most accurate at the largest lattice size 64×64, as finite-size effects are least important here. Results for smaller lattices are quite similar.

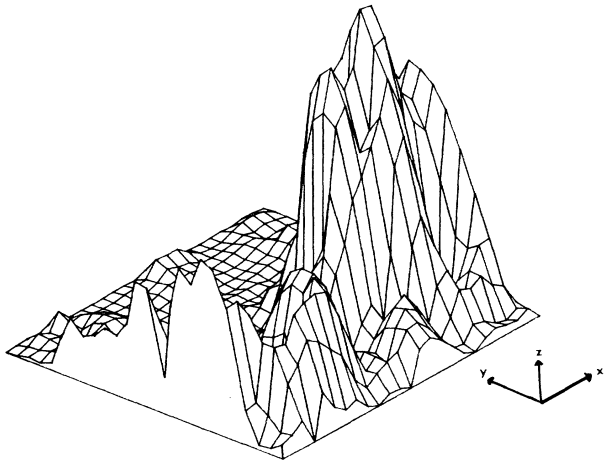

FIG. 1. A density surface obtained from the Monte Carlo simulation. Density is on the z axis. The points of maximum density correspond to "holes" in the cage. This contour was obtained for a chain of 60 links in a 32×32 cage with a density of impurities of $p=0.2$.

We denote the TAMD at site i by ϕ_i, which has been normalized so that $\sum_i \phi_i = 1$. Multifractal behavior in a system of size $L\times L$ can be characterized by the sequence of mass exponents $\tau(q)$ defined as

$$\sum_{i=1}^{L^2} \phi_i^q \sim L^{-\tau(q)}. \tag{1}$$

We calculated $\tau(q)$ two ways and obtained similar results. The first was by averaging the density ϕ_i over regions of size $L \leq R_g$ for lattices and chain lengths of different sizes. Our most accurate determination of $\tau(q)$ was obtained by considering the lattice of size 64×64, and coarse graining ϕ_i over intermediate length scales l, defining $\tilde{\phi}_i$ to be the density ϕ_i coarse grained over a box of size $l\times l$. It is easily shown that $\sum \tilde{\phi}_i^q \sim l^{\tau(q)} l^{-dq}$, where d is the spatial dimension. The scaling behavior of the TAMD as a function of l is shown in Fig. 2 for $q=+2$ and $q=-2$, where q is the order of the moment. These curves are well described by power laws for coarse-graining scales l except for when $l \gg R_g$ and l is equal to the lattice spacing, where in both cases one expects deviations from power-law behavior. These plots are therefore strong evidence for self-similarity in the TAMD.

From the power-law dependence on l, the value of $\tau(q)$ can be extracted from the above plots at different values of q. In order to satisfy multifractal scaling the $\tau(q)$ curve should be a nonlinear function of q. This can be easily seen in Fig. 3. The point $\tau(q=0)$ corresponds to the negative of the fractal dimension of the system.

Another quantity that is used to characterize multifractal behavior is the singularity spectrum $f(\alpha)$. $f(\alpha)$ can be interpreted as the negative of the Legendre trans-

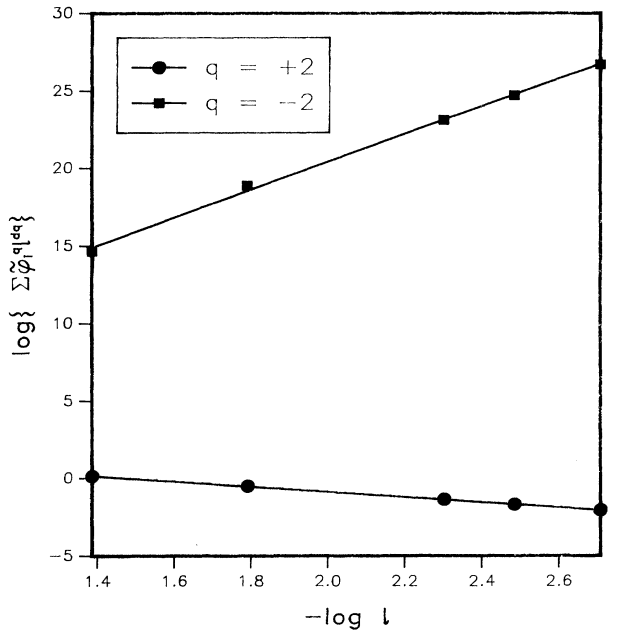

FIG. 2. The scaling behavior of the TAMD for $q=+2$ and $q=-2$. The scaling behavior was computed from the data for a chain of length 120 in a lattice of size 64×64 averaged over ten realizations of disorder. $\tilde{\phi}_i$ is the density coarse grained over various length scales l from $l=4$ to $l=R_g$. q is the order of the moment, while d is the spatial dimension.

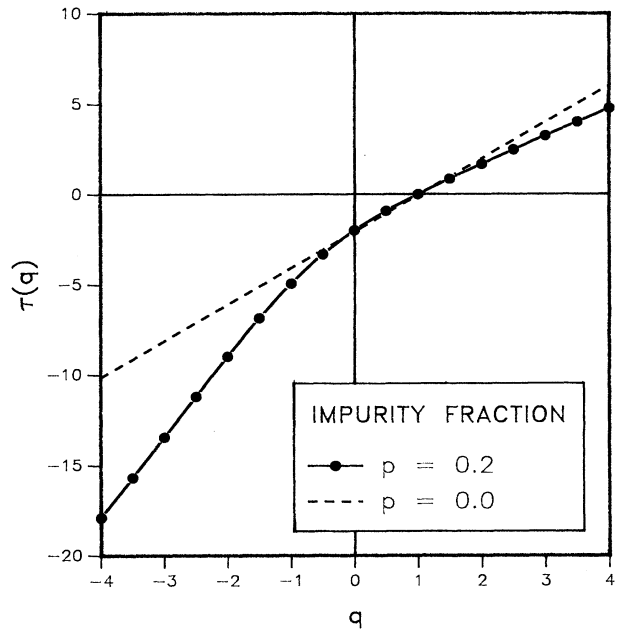

FIG. 3. The scaling of the moments $\tau(q)$ with the order of the moment q. As can be seen the solid line is a continuous curve indicating an infinite hierarchy of exponents. The concentration of impurities is 0.2. The dashed line is the curve obtained when there is no disorder present. The point $\tau(q=0)$ corresponds to -2.

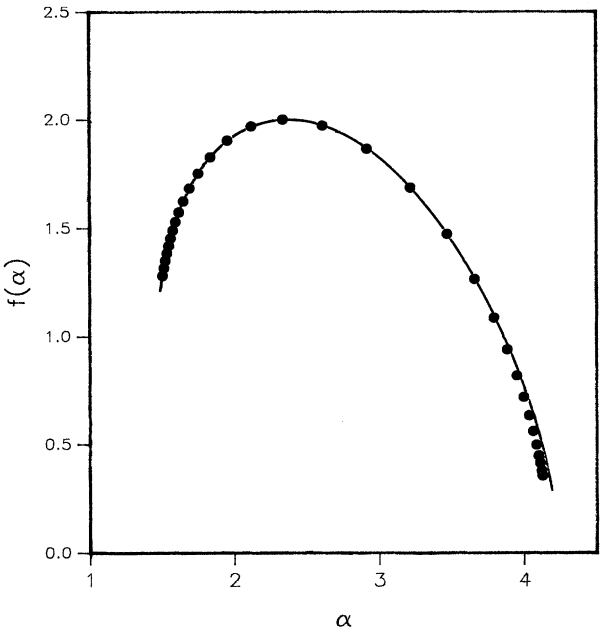

FIG. 4. The $f(\alpha)$ curve from the simulations calculated by two methods. The solid circles represent the $f(\alpha)$ curve calculated by first smoothing the $\tau(q)$ curve and then taking its Legendre transform. The solid line represents the $f(\alpha)$ curve calculated by the method of Chhabra and Jensen (Ref. 13). The point $f(\alpha)_{\max}$ is at $+2$.

form of $\tau(q)$:

$$f(\alpha(q)) = -[\tau(q) - q\alpha(q)], \tag{2}$$

where

$$\alpha(q) = \frac{d\tau(q)}{dq}. \tag{3}$$

From Eqs. (2) and (3) we calculated $f(\alpha)$ and the curve is shown in Fig. 4. Because we were able to work with a reasonably large system size, this method gives almost identical results to the method of Chhabra and Jensen.[13]

It is important to note that, if when one averages the density in regions of size $L \gg R_g$, the nonlinearity of $\tau(q)$, as seen in Fig. 3, disappears and the TAMD can now be characterized by simple fractal behavior. To show the effect of the random potential on the TAMD, we have also calculated $\tau(q)$ for the case of zero disorder. In the absence of a random potential every site on the lattice has the same probability of visitation and so the $\tau(q)$ curve now becomes a linear function of q. This is shown in Fig. 3 where the dashed curve represents the $\tau(q)$ curve for the case of no disorder. If one were to study the polymer in a system of periodic obstacles, the TAMD would be the same as the case of no disorder.

In conclusion, we have shown that the statistics of self-avoiding walks in random environments show unusual properties that are lost when the regular kind of averaging over disorder is performed. The amount of time a monomer spends in a particular location has large fluctuations that satisfy multifractal scaling. This should have applications to a variety of different physical situations, and should be observable experimentally by fluorescence techniques or by measuring reaction rates of macromolecules in gels.

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[1]G. F. Al-Noaimi, G. C. Martinez-Mekler, and R. M. Velasco, J. Chem. Phys. **78**, 3316 (1983); B. Derrida, Phys. Rep. **103**, 29 (1984); S. F. Edwards and M. Muthukumar, J. Chem. Phys. **89**, 2435 (1988); J. D. Honeycutt and D. Thirumalai, J. Chem. Phys. **90**, 4542 (1989); J. Machta and R. A. Guyer, J. Phys. A **22**, 2539 (1989).

[2]M. E. Cates and R. C. Ball, J. Phys. (Paris) **49**, 2009 (1988).

[3]B. Duplantier, Phys. Rev. A **38**, 3647 (1988).

[4]S. B. Lee and H. Nakanishi, Phys. Rev. Lett. **61**, 2022 (1988), and references therein.

[5]Y. Meir and A. B. Harris, Phys. Rev. Lett. **63**, 2819 (1989).

[6]J. Tinoco, K. Sauer, and J. C. Wang, *Physical Chemistry, Principles and Applications in Biological Systems* (Prentice-Hall, Englewood Cliffs, NJ, 1985), pp. 252–261.

[7]Although this paper (Ref. 2) does not discuss self-avoidance explicitly, their arguments carry through in this case also.

[8]T. C. Halsey, M. H. Jensen, L. P. Kadanoff, I. Procaccia, and B. I. Shraiman, Phys. Rev. A **33**, 1141 (1986); R. Benzi, G. Paladin, G. Parisi, and A. Vulpiani, J. Phys. A **18**, 3521 (1984).

[9]M. E. Cates and J. M. Deutsch, Phys. Rev. A **35**, 4907 (1987).

[10]A. W. W. Ludwig, Nucl. Phys. **B285**, 97 (1987).

[11]F. T. Wall and F. Mandell, J. Chem. Phys. **63**, 4592 (1975).

[12]D. Gersappe (unpublished).

[13]A. Chhabra and R. V. Jensen, Phys. Rev. Lett. **62**, 1327 (1989).