Structural crossover of polymers in disordered media

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We present a unified scaling theory for the structural behavior of polymers embedded in a disordered energy substrate. An optimal polymer configuration is defined as the polymer configuration that minimizes the sum of interacting energies between the monomers and the substrate. The fractal dimension of the optimal polymer in the limit of strong disorder (SD) was found earlier to be larger than the fractal dimension in weak disorder (WD). We introduce a scaling theory for the crossover between the WD and SD limits. For polymers of various sizes in the same disordered substrate we show that polymers with a small number of monomers $N \ll N^*$ will behave as in SD, while large polymers with length $N \gg N^*$ will behave as in WD. This implies that small polymers will be relatively more compact compared to large polymers even in the same substrate. The crossover length N^* is a function of ν and a, where ν is the percolation correlation length exponent and a is the parameter which controls the broadness of the disorder. Furthermore, our results show that the crossover between the strong and weak disorder limits can be seen even within the same polymer configuration. If one focuses on a segment of size $n \ll N^*$ within a long polymer ($N \gg N^*$) that segment will have a higher fractal dimension compared to a segment of size $n \gg N^*$.

The study of polymers [1–8] in the presence of disordered media is of broad scientific interest and is relevant to many fields such as protein folding [1], polymers in porous media [2], and spin glasses [3]. It also has many important applications such as in enhanced oil recovery, drug delivery, and DNA sorting [6]. A polymer embedded in a disordered energy substrate, at low temperatures, will settle down in the optimal configuration, i.e., the configuration with the minimum energy.

In this Rapid Communication we study the scaling of the structural properties of such an optimal configuration. A linear polymer of N monomers, under disorder, can be modeled by an N step self-avoiding walk (SAW) on a lattice where each site (or bond) in the lattice is assigned an energy ϵ taken from a given distribution. The optimal configuration in such a model is the SAW of length N for which the sum of the energies along its path is minimal. For generating a broad disorder, it is common to use the distribution $P(\epsilon)=1/(a\epsilon)$ ($\epsilon < e^a$) where the parameter a controls the broadness of the disorder [9–12]. Such a distribution generates an exponential disorder where the energy value of each site i on the lattice is given by $\epsilon_i = \exp(ar_i)$ where r_i is a random number taken from a uniform distribution between [0, 1]. For $a \to \infty$, we obtain the strong disorder (SD) limit and for small values of a the weak disorder (WD) limit. In the WD limit, essentially all sites contribute to the total sum of ϵ_i, while in the SD limit the total sum is dominated by a single site with the maximum energy [9,13].

Smailer *et al.* [8] studied the properties of a linear polymer in the WD limit using both a uniform and a Gaussian energy distribution. They found that for two-dimensional (2D) the end-to-end distance of the polymer R scales with N as $N \sim R^{d'_\text{opt}}$, where the fractal dimension is $d'_\text{opt} \cong 1.25$. This result is different from that found by Braunstein *et al.* [11] for the SD limit. Braunstein *et al.* used the exponential dis-

order $\epsilon_i = \exp(ar_i)$ and obtained $N \sim R^{d_\text{opt}}$ with $d_\text{opt} \cong 1.5$. Thus, the polymer is more compact in the presence of strong disorder compared to weak disorder.

In this Rapid Communication we present a unified scaling theory for the crossover between WD and SD limits. We claim that the crossover between strong and weak disorders for the optimal polymer problem depends on the characteristic size a^ν, where ν is the correlation length exponent from percolation theory [14–16].

This claim can be explained as follows. Consider an infinite lattice where each site i has a value p_i where $p_i \in [0, 1]$. In a percolation process, an increasing fraction p of the sites with the lowest values is occupied (the others are removed) until the point $p = p_c$ is reached where the lattice undergoes a phase transition. For $p > p_c$, an infinite number of the lattice sites are connected, while for $p < p_c$ the lattice is separated into small finite clusters.

Now assume each site is associated with an energy $\epsilon_i = \exp(ap_i)$ and an infinite polymer is observed on the lattice. In SD the highest energy ϵ_max along a polymer configuration dominates the total energy. The energy $\widetilde{\epsilon}_\text{max}$, which is the highest energy along the *optimal* polymer configuration, cannot be smaller than $\exp(ap_c)$ and cannot be larger than $\exp(ap_c)$ and therefore must be equal to $\exp(ap_c)$. If $\widetilde{\epsilon}_\text{max} < \exp(ap_c)$ then according to the percolation theory, only a cluster with a finite number of sites exists and an infinite polymer cannot be embedded inside this cluster. If $\widetilde{\epsilon}_\text{max} > \exp(ap_c)$ then according to percolation theory the polymer is not optimal since there exists a polymer with a lower-energy configuration for which $\widetilde{\epsilon}_\text{max} \equiv \exp(ap_c)$. Thus, the optimal configuration is achieved for $\widetilde{\epsilon}_\text{max} \equiv \exp(ap_c)$ since p_c is the lowest value for which an infinite cluster that all its sites have energies lower than $\widetilde{\epsilon}_\text{max}$ exists.

For a finite lattice of size R, the value p_c for which the percolation transition occurs is distributed as a narrow distri-
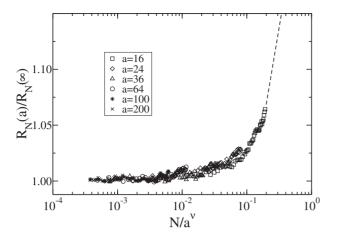
FIG. 1. Simulation results for the scaling of $R_N(a)/R_N(\infty)$ as function of $N/a^{\nu'}$ for different values of a. The dashed lines represent the asymptotic expected value of the slope $x^{1/d'_{opt}-1/d_{opt}}$ [Eq. (1)].

bution with a mean p_c and a standard deviation of $\sigma = R^{-1/\nu}$ [17]. Let $\epsilon_1 = \exp(ap_1)$ be the largest energy and $\epsilon_2 = \exp(ap_2)$ the second largest energy on the lattice. Since $\log(\frac{\epsilon_1}{\epsilon_2}) \sim a(p_1 - p_2)$ and p_1 and p_2 are both from the same narrow distribution, it follows that $\log(\frac{\epsilon_1}{\epsilon_2}) \sim a(p_1 - p_2) \sim a\sigma \sim aR^{-1/\nu}$. Therefore, the SD limit ($\epsilon_1/\epsilon_2 \gg 1$) is obtained for $R \ll a^\nu$ while the WD limit is obtained for $R \gg a^\nu$.

Similar considerations were presented by Buldyrev *et al.* [17] for the crossover from SD to WD in the optimal path problem. Yet, the optimal polymer problem is significantly different from the optimal path problem. The optimal path problem explores the optimal path between two fixed points (fixed R) where the path length varies. In the optimal polymer problem, the polymer length is fixed and one tries to minimize the sum of the interaction energies between the monomers and the substrate, while the end-to-end distance varies. While the complexity of the optimal path problem is $O(N^2)$, finding the optimal polymer is a nondeterministic polynomial [(NP) time] problem since nearly all the possible configurations need to be explored in order to find the optimal configuration. To reduce the computational time of our simulations we have used the following optimizations. (a) During the calculation of the optimal polymer of length N, the optimal polymers of length 1 to N are also calculated. (b) A new site in the lattice is explored only if the path until that point does not exceed the optimal total energy of length N obtained until that point. The second optimization is only useful for the SD limit, where one energy dominates the total sum [18]. On the other hand, for the SD limit the accuracy of the floating point (double) variable in conventional computers is limited to $a \sim 36$. We have overcome this limitation by using the external software that enables unlimited floating point accuracy but demands significantly more computational time. These computational problems are the reasons why our simulation results are limited to polymer configurations of length $N = 50$.

Next, we propose a single scaling function for the dependence of $R \equiv R_N(a)$ on N that includes both the SD and WD regions. We expect that the scaling function will depend on
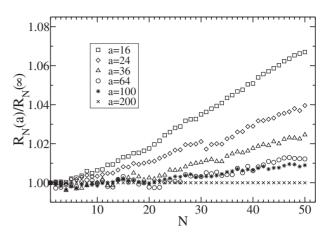

FIG. 2. Simulation results of $R_N(a)/R_N(\infty)$ as function of N for several values of a. For small values of N, all the polymers behave as in the SD limit and independent of the disorder have the same fractal dimension. For larger values of N, $R_N(a)/R_N(\infty)$ increases toward the WD region. The results are limited to $N=50$ because calculating $R(a)$ for large a slows down the calculations significantly.

the ratio R/a^ν which represents the relative strength of the disorder. Since the polymers are of length N, we use instead of R/a^ν the scaling parameter $N/a^{\nu'} \equiv N/a^{\nu d_{opt}}$ which is related to R/a^ν by $\frac{R}{a^\nu} \equiv \frac{N^{1/d_{opt}}}{a^\nu} \equiv (\frac{N}{a^{\nu d_{opt}}})^{1/d_{opt}}$. Thus, we propose that

$$R_N(a) \sim R_N(\infty) f\left(\frac{N}{a^{\nu'}}\right), \tag{1}$$

with $f(x)$ a scaling function given by

$$f(x) = \begin{cases} const, & x \ll 1 \\ x^{1/d'_{opt} - 1/d_{opt}}, & x \gg 1, \end{cases} \tag{2}$$

where $d_{opt} \simeq 1.5$ (SD), $d'_{opt} \simeq 1.25$ (WD), and $R_N(\infty) \sim N^{1/d_{opt}}$.

Indeed from Eqs. (1) and (2) follows that for $N \ll a^{\nu'}$ (SD) $R_N \sim N^{1/d_{opt}}$, while for $N \gg a^{\nu'}$ (WD) limit, we obtain $R_N \sim N^{1/d'_{opt}}$ the known result for the WD limit. Figure 1 presents simulation results supporting the scaling function of Eqs. (1) and (2). The SD region can be seen clearly in the flat area for $N/a^{\nu'} \ll 1$, while the sharp increase in the slope indicates the crossover to WD until the point where the slope fits the asymptotic expected value $1/d'_{opt} - 1/d_{opt}$ (dashed line) [see Eq. (2)].

Until now, we have been relating to SD and WD as if the polymers were in different substrates. But actually the crossover between the SD and WD is present even on the same energy substrate as can be seen from the scaling function of Eqs. (1) and (2). In other words, for a given a, a small enough polymer ($N \ll a^{\nu'}$) will behave as in SD, while a large enough polymer ($N \gg a^{\nu'}$) will behave as in WD. This property is demonstrated in Fig. 2 where we plot the ratio $R_N(a)/R_N(\infty)$ as a function of N for different values of a. For small values of N, the polymers behave as in SD since $R_N(a)/R_N(\infty) \simeq 1$ [recall that $R_N(\infty)$ is the SD limit]. In con-
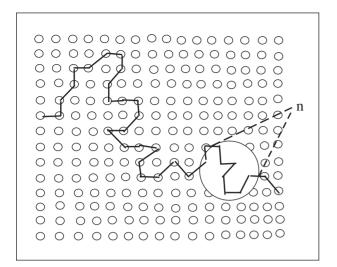
FIG. 3. (a) Illustration for the crossover between WD and SD inside the same polymer. Inside a segment of length $n < a^{\nu'}$, the polymer is more compact (has a higher fractal dimension) compared to a larger segment or the full polymer.

trast, for $N \gg 1$, a crossover towards WD occurs represented by the larger R values. Note that the crossover value $N^*(a)$ increases for larger a.

Next we show that such a crossover also exists within the same polymer configuration. We argue that a segment of monomers of length $n \ll a^{\nu'}$, within a polymer of length $N \gg a^{\nu'}$, will behave as in SD and will be more compact compared to a segment of size $n' \gg a^{\nu'}$ that will behave as in the WD limit. An illustration of this property is shown in Fig. 3. In Fig. 4 we present simulation results showing that the same scaling relations describing the crossover between SD and WD for polymers of different sizes is also correct within the same polymer. Here the simulations were performed for different segments of size n of the same polymer and $R_n(a)$ is the end-to-end distance of these segments.

When studying the probability density function of polymers $\rho \equiv \rho(R,N,a)$, we obtain an interesting result. The width of the distribution does not depend on the crossover
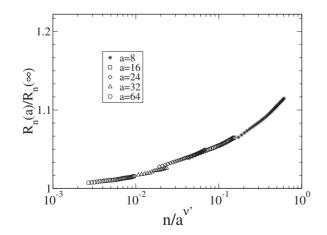

FIG. 4. Simulation results for the scaling of $R_n(a)/R_n(\infty)$ as function of $n/a^{\nu'}$ for different values of a. The different values of n represent different segments within the same polymer.
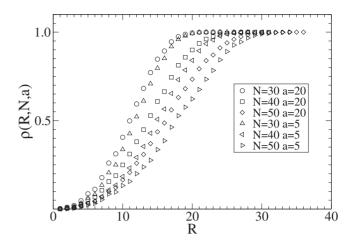

FIG. 5. Simulation results for the cumulative probability density function, $\rho(R,N,a)$ as function of R for different values of N and a in the region $0.075 \leq N/a^{\nu'} \leq 2$.

parameter of the disorder $N/a^{\nu'}$, only on the normalization parameter $R/\langle R \rangle$. This is different from the results obtained in optimal path where the probability density function depends on the disorder crossover parameter [17]. This difference can be understood by the fact that the polymer configuration is of fixed length N. While the length of an optimal path between any two nodes within a distance R may be very long, enabling a broader distribution of the path lengths in SD, the end-to-end distance R in the optimal polymer configuration is limited from above by the fixed length N (in the optimal path, one measures the distribution of the length N, while in polymers we measure the distribution of R). Therefore, the scaling relation for the probability density function of the optimal polymer depends only on the normalization parameter $R/\langle R \rangle$ while the dependence of N and a are determined by $\langle R \rangle$

$$\rho(R,N,a) = f\left(\frac{R}{\langle R \rangle}\right). \tag{3}$$

Indeed, Fig. 5 shows the simulation results for the cumulative distribution of $\rho(R,N,a)$ for different values of R,N,a
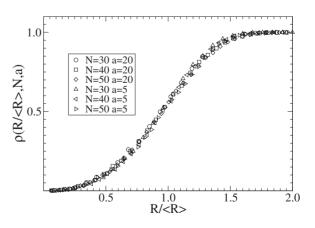

FIG. 6. Simulation results for the cumulative probability density function, $\rho(R/\langle R \rangle,N,a)$ as a function of $R/\langle R \rangle$. When normalizing by $R/\langle R \rangle$, the different curves collapse into a single curve.

that correspond to both the strong and weak disorder regions. In Fig. 6 the scaling of these lines is presented, showing that all the different distributions both for SD and WD collapse into a single curve.

Summarizing, we have presented a unified scaling theory for the optimal polymer configuration embedded in a disordered energy substrate. The structure of the polymer at the minimal energy depends on the strength of the disorder. We find that the crossover between the SD limit and the WD limit occurs at $N^*(a) = N/a^{\nu'}$. For $N/a^{\nu'} \gg 1$ the WD is obtained, while for $N/a^{\nu'} \ll 1$ the SD limit is obtained. We present the simulation results showing that this transition occurs even inside the same polymer. Therefore, a segment of n monomers where $n/a^{\nu'} \ll 1$ (the SD limit region) will be more compact compared to the full polymer where $N/a^{\nu'} \gg 1$ (the WD region).

Our results of the crossover between the SD limit and the WD limit may be observed in neutron-scattering experiments. Since the structure factor decays with a power (equal to the fractal dimension) of the wave vector, we expect to see a crossover in the structure factor at the wavelength for which the transition between the SD and WD occurs. For 3D, the crossover would occur from $d_{\text{opt}} \cong 1.82$ in SD limit [11] to $d'_{\text{opt}} \cong 1.4$ in the WD limit [8]. Recently, experimental studies of the scaling properties of the linear-chain configuration of DNA knots adsorbed onto a mica surface under weak trapping [19] have shown that R scales with N with a fractal dimension of 1.51. This value is significantly different from the classical Flory result $d_f = 4/3$. The fractal dimension $d_f = 1.51$ found in 2D might be explained by Eq. (1) in the limit of strong disorder.

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