

## Static and dynamic properties of polymers in random media

J. Machta

*Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01003*

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The properties of polymers in a disordered environment are studied with emphasis on the effect of trapping due to fluctuations in the porosity of the environment. Results are obtained for  $Z_N$ , the number of self-avoiding walks of length  $N$  starting at the origin, and  $D$ , the diffusion coefficient for the center of mass of the polymer. The two most important new results are that  $\langle \ln Z_N \rangle \approx N - a_1 N^\alpha$ , with  $\alpha = 2 - d\nu$  and  $\nu$  the Flory exponent, and that the leading behavior of the diffusion coefficient is  $D \approx \exp(-a_2 N^\alpha)$ .

In this Rapid Communication, I discuss the static and dynamic properties of a polymer chain in a quenched random environment. The question of whether the presence of disorder qualitatively changes the static properties of polymer chains has been controversial.<sup>1-6</sup> Harris<sup>2</sup> presented a simple argument that the size  $R$  of a self-avoiding walk (SAW) is unmodified by a random environment and this result is supported by recent numerical work.<sup>6</sup> The situation is less clear for the number of SAW's of length  $N$  which start at the origin,  $Z_N$ . In the absence of disorder,  $Z_N \approx \mu^N N^{\gamma-1}$ . Derrida<sup>3</sup> has pointed out that in the presence of a random medium,  $\langle Z_N \rangle$  and  $\langle \ln Z_N \rangle$  may exhibit different critical behavior. While  $\langle Z_N \rangle$  is only trivially changed by disorder, there have been suggestions<sup>4</sup> that  $\langle \ln Z_N \rangle$  displays an essential singularity so that  $\gamma$  fails to exist. In the present work, we show that this is the case and, for the first time, identify the exponent describing the essential singularity with the "specific-heat" exponent,  $\alpha = 2 - d\nu$ .

de Gennes<sup>7,8</sup> has shown that the dynamics of a polymer in a random network is strongly affected by the entanglement of the chain with the network so that the motion of the chain is primarily along its own length with new regions explored only by the ends of the chain. He termed this motion "reptation" and showed that it leads to a diffusion coefficient for the chain which behaves as  $N^{-2}$ . Recent numerical work,<sup>9</sup> however, indicates that the diffusion coefficient for chains in a random environment decreases more rapidly in  $N$  than the reptation prediction. In the present work we study the effect of fluctuations in the environment on the diffusion coefficient. The most important and novel conclusion of this analysis is that the diffusion coefficient diminishes as  $\exp(-N^\alpha)$  for large  $N$ .

Static density fluctuations in the environment lead to wide spatial variations in the local number of conformations available to the chain—regions with unusually small numbers of scatterers support vastly more conformations and behave as "entropic traps." As a consequence of these entropic traps, the equilibrium spatial distribution of the polymer is strongly inhomogeneous and the asymptotic behavior of the typical and average values of  $Z_N$  differ. Because of the long release times from deep entropic traps, the approach to equilibrium is very slow and the diffusion coefficient is exponentially smaller than the reptation prediction. Simple calculations based on the distribution

of entropic traps yield results for the statistics of  $Z_N$  and for both the short- and long-time diffusive motion of the chain. Related notions of entropic trapping have been discussed in Refs. 9-11.

The model studied here is a self-avoiding walk on a site-diluted lattice. The polymer chain is described by a connected sequence  $\phi$  of  $N$  sites such that no site may be visited more than once. Each site in an environment is classified as "allowed" with probability  $p$  or "forbidden" with probability  $1 - p$ . Each configuration of the environment contains  $V$  sites and is described by a set  $c$  of forbidden sites. The sites are uncorrelated and the probability  $P(c)$  of a configuration is given by the binomial distribution. A chain  $\phi$  in configuration  $c$  is allowed if  $\phi$  and  $c$  do not intersect.

As first shown by Harris,<sup>2</sup> the statistics of the size of a SAW is unaffected by site dilution. The argument is very simple and we repeat it here. Consider, for example, the root-mean-squared end-to-end distance  $R_N(c)$  of a chain which is in equilibrium in a given random environment  $c$ ,

$$[R_N(c)]^2 = \frac{\sum_{\phi} r_{\phi}^2 \chi(c, \phi)}{\sum_{\phi} \chi(c, \phi)}. \quad (1)$$

The sum over  $\phi$  is over all SAW's of fixed length  $N$ ;  $r_{\phi}$  is the end-to-end vector of the chain, and  $\chi(c, \phi)$  is an indicator function, which is zero if  $\phi$  and  $c$  intersect and one otherwise. In the limit  $V \rightarrow \infty$  with  $N$  fixed, self-averaging holds for the numerator and denominator on the right-hand side of Eq. (1) so that the size  $R_N$  is independent of  $c$  and given by the ratio of configuration averages,

$$R_N^2 = \frac{\sum_{\phi, c} r_{\phi}^2 P(c) \chi(c, \phi)}{\sum_{\phi, c} P(c) \chi(c, \phi)}. \quad (2)$$

Since each SAW occupies  $N$  sites, the sum over  $c$  is independent of  $\phi$ , and for  $V \rightarrow \infty$  one has

$$\sum_c P(c) \chi(c, \phi) = p^N, \quad (3)$$

which cancels out of the numerator and denominator. Thus, the size of the chain is unaffected by the disorder and  $R_N \approx AN^{\nu}$  with  $A$  independent of  $p$  and  $\nu \cong 3/(d+2)$  the usual Flory exponent.

Though the size of the chain is unaffected by the random environment, the equilibrium spatial distribution of the chain is strongly correlated with the disorder for  $d < 4$ . The chain is effectively trapped in regions where

the density of allowed sites or “local porosity” is significantly above average. To understand this phenomena quantitatively, coarse grain the system into cells of volume  $\Omega = aN^{dv}$  with  $a$  order one so that the chain more or less occupies a single cell at any given time. Divide the set of cells into classes according to the local porosity,  $m = M/\Omega$ , where  $M$  is the number of allowed sites in the cell. Consider each class of cells to be a subsystem and compute the relative number of conformations per cell of the polymer within each class. To do this, choose a single conformation of the polymer and count the number of cells with porosity  $m$  which are compatible with that conformation. This number is independent of the conformation, thus the probability  $\psi(m)$  that a SAW is compatible with a cell of porosity  $m$  is

$$\psi(m) = \begin{cases} \frac{M!(\Omega - N)!}{\Omega!(M - N)!}, & M \geq N, \\ 0, & M < N. \end{cases} \quad (4)$$

In the appropriate limit for a SAW,  $\Omega \approx M \gg N \gg 1$ , this reduces to

$$\ln \psi(m) = N \ln m - \frac{N^2}{2\Omega} \frac{1-m}{m} + \dots \quad (5)$$

In equilibrium the chain spends a time-proportional  $\psi(m)$  per cell in the subsystem with porosity  $m$  and, for large  $N$ , the chain strongly prefers to reside in the cells with larger than average porosity. On the other hand, cells which deviate significantly from the expected porosity  $p$  are extremely rare for large  $\Omega$ . The probability density  $\rho(m)$  for  $m$  is well approximated by the Gaussian,

$$\rho(m) \left[ \frac{\Omega}{2\pi p(1-p)} \right]^{1/2} \exp \left[ -\frac{\Omega(m-p)^2}{2p(1-p)} \right]. \quad (6)$$

The product of  $\rho$  and  $\psi$  is sharply peaked for large  $N$  and the chain spends almost all its time in the class of cells with the porosity  $m_N$ , which maximizes  $\rho(m)\psi(m)$ ,

$$m_N = p + \frac{1-p}{a} N^{1-dv}. \quad (7)$$

The fraction of space in which the chain spends most of the time is given by

$$\rho(m_N) \approx \exp \left[ -\frac{1-p}{2pa} N^\alpha \right], \quad (8)$$

where

$$\alpha = 2 - dv. \quad (9)$$

Using the Flory result for  $v$  we have  $\alpha \cong (4-d)/(d+2)$ . For  $d < 4$ , the chain spends almost all the time in a very small fraction of space. Henceforth, our results will apply to the case  $d < 4$ . It should also be noted that extremely large systems are needed to fully observe this effect. The requirement is that at least one cell of class  $m_N$  is likely to be found in a system of size  $V$  so that  $V\rho(m_N)/\Omega$  must be order one and the minimum size  $V_{\min}$  is

$$\ln V_{\min} \approx \frac{1-p}{2pa} N^\alpha. \quad (10)$$

For smaller systems we expect the chain to be localized in

the cell with the maximum porosity.

Let  $Z_N(c)$  be the number of SAW's of length  $N$  which start at the origin of configuration  $c$  [ $Z_N(c) = 0$  if the origin of  $c$  is forbidden]. In an undiluted system,  $c = \emptyset$ , the two leading terms in an asymptotic expansion of  $\ln Z_N(\emptyset)$  are

$$\ln Z_N(\emptyset) \approx N \ln \mu + (\gamma - 1) \ln N. \quad (11)$$

The exponent  $\gamma$  is universal while the connective constant  $\mu$  is not.

There are two averages to consider, the quenched average,  $\langle \ln Z_N \rangle$ , and the annealed average,  $\ln \langle Z_N \rangle$ . The annealed average is easily evaluated by multiplying Eq. (3) by  $Z_N(\emptyset)$  and taking the logarithm,

$$\begin{aligned} \ln \langle Z_N \rangle &= \ln Z_N(\emptyset) + N \ln p \\ &\approx N \ln p \mu + (\gamma - 1) \ln N + \dots \end{aligned} \quad (12)$$

For the annealed average the only effect of the disorder is to modify the connective constant.<sup>4</sup>

To estimate the quenched average note that chains attached to the origin explore a region of size  $R_N$  around the origin and approximate  $Z_N(c)$  by  $\psi(m_0)Z_N(\emptyset)$  where  $m_0$  is the porosity in the cell containing the origin,

$$\begin{aligned} \langle \ln Z_N \rangle &\cong \ln Z_N(\emptyset) + \int_0^1 dm \rho(m) \ln \psi(m) \\ &\approx N \ln p \mu - \frac{1-p}{2pa} N^\alpha. \end{aligned} \quad (13)$$

The quenched average measures the typical value of  $Z_N$  which is much smaller than the average value because the origin is not typically found in a region of unusually high porosity.

We may endow the chain with dynamics and, above the percolation threshold for the allowed sites, study the macroscopic diffusive motion of the center of mass of the chain. The precise nature of the dynamics is not important, so long as there is a time scale  $\tau$  for the chain to completely change its conformation. The dynamics must be local so that the new conformation is chosen from among those conformations which are within  $R_N$  of the original conformation. Finally, the chain distribution must approach the correct equilibrium distribution, that is, each allowed conformation is visited with equal probability. A physically plausible dynamics which simulates the effect of entanglement present in any real random medium is “reptation dynamics;”<sup>12</sup> here, the chain moves along its own contour and randomly explores new positions at its ends. In this case  $\tau$  is the renewal time for the tube and scales as  $N^3$ .

On large scales, the motion of the center of mass of the polymer is a random walk among the coarse-graining cells described by the master equation,

$$\frac{dc_i(t)}{dt} = \sum_j W_{ij} c_j - W_{ji} c_i, \quad (14)$$

where  $c_i(t)$  is the occupation probability for cell  $i$  at time  $t$ ,  $W_{ij}$  is the transition rate from cell  $j$  to cell  $i$ , and the sum is over the nearest neighbors of site  $i$ . An estimate for the transition rates can be obtained by making the assumption that after time  $\tau$  the chain attempts to enter one of the  $2d$  neighboring cells, and also that the attempt is

successful in proportion to the ratio of the number of conformations available in the two cells,

$$W_{ij} \approx (d\tau)^{-1} \frac{\psi(m_i)}{\psi(m_i) + \psi(m_j)}. \quad (15)$$

Note that this form for the transition rates leads to the correct equilibrium occupation probabilities,

$$c_i(t \rightarrow \infty) = \psi(m_i) / \sum_{j \in V} \psi(m_j). \quad (16)$$

What is the nature of the random walk described by Eqs. (14) and (15)? The variance  $\sigma^2$  of  $m$  scales like  $N^{-d\nu}$ , so the typical cell-to-cell fluctuations in  $\ln\psi$  scale like  $N^{d/2}$ . For  $d < 4$  and large  $N$ , neighboring values of  $\psi$  vary widely and the transition rates can be approximated by

$$d\tau W_{ij} \approx \begin{cases} 1, & m_i > m_j, \\ \psi(m_i)/\psi(m_j), & m_j > m_i. \end{cases} \quad (17)$$

Thus, local maxima of the porosity serve as trapping centers. These traps are separated by a distance of several times  $R_N$  and have waiting times which can be estimated as  $\tau\psi(m_i)/\psi(p)$ , where  $m_i$  is the value of the porosity at the trap. The important disorder in the system is the wide distribution of waiting times in the trap and we ignore other kinds of disorder such as the random positions of the traps, the anisotropy in leaving the traps, and the random heights of the barriers between traps. The result is a random walk in an environment with random traps having a distribution of waiting times. The diffusion coefficient  $D$  for this model is given by the ratio of the square of the distance between traps and the average waiting time  $T$  (Ref. 13),

$$D = bR^2/T, \quad (18)$$

where  $b$  is a constant of order one and

$$T \approx \frac{\tau}{\psi(p)} \int_p^1 dm \rho(m) \psi(m). \quad (19)$$

Using Eqs. (9) and (10) the integral is easily evaluated by steepest descents with the result

$$D \approx \frac{bR^2}{\tau} \exp\left[-\frac{1-p}{2pa} N^\alpha\right]. \quad (20)$$

We see that the diffusion coefficient is exponentially suppressed for  $d < 4$ , due to entropic trapping.

The equilibration time scales as  $\exp(N^\alpha)$  and is astro-

nomical for long chains. It is thus of interest to find the intermediate time behavior of a polymer introduced at random in the medium. Let  $L(t)$  be the size of the region explored by the chain up to time  $t$ . The time scale for escaping this region is set by the deepest trap in the region,

$$t = \tau\psi(m)/\psi(p), \quad (21)$$

where  $m$  is the porosity of the deepest trap. The depth of this trap can be estimated from

$$(L^d/\Omega)\rho(m) \approx 1. \quad (22)$$

Eliminating  $m$  from Eqs. (21) and (22) yields

$$\ln L \approx \frac{ap}{2d(1-p)} N^{-\alpha} \ln^2(t/\tau). \quad (23)$$

This behavior holds over length scales from several times  $R_N$  up to  $V_{\min}^{1/d}$ . The growth law of Eq. (23) mimics anomalous diffusion,  $L \approx t^\delta$ , with  $\delta$  slowly increasing to  $\frac{1}{2}$ .

In summary, we have seen that the most important effect of a random environment on the static and dynamic properties of a polymer chain is to create entropic traps in which the polymer resides in equilibrium. The effects of these traps appears as an essential singularity in the  $N$  dependence of both the typical number of chains starting at the origin and the chain diffusion coefficient. Within the magnetic phase transition language for describing SAW's,<sup>8</sup> the exponent  $\alpha$  is identified via hyperscaling with the specific-heat exponent. It is noteworthy that the Harris criterion holds in the sense that the disorder leads to a relevant essential singularity when  $\alpha > 0$ . The presence of the essential singularity explains the nonexistence of a perturbative fixed point in a field-theoretic formulation of the problem.<sup>14</sup>

Although our results are derived for a simple model of a self-avoiding walk on a lattice, they should remain valid for more general situations where there are short-range correlations in the environment. For example, the environment may consist of a random network. The crucial feature is that porosity fluctuations should be Gaussian on length scales longer than the size of the polymer. Similarly, it is not necessary for the polymer to be strictly self-avoiding as long as the self-repulsion is sufficient to prevent the collapse of the chain in the random environment. The conditions for this are discussed in Refs. 5 and 11.

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<sup>1</sup>K. Kremer, Z. Phys. B **45**, 149 (1981).

<sup>2</sup>A. B. Harris, Z. Phys. B **49**, 347 (1983).

<sup>3</sup>B. Derrida, Phys. Rep. **103**, 29 (1984).

<sup>4</sup>J. P. Nadal and J. Vannimenus, J. Phys. (Paris) **46**, 17 (1985); J. Vannimenus and M. Knezevic, Europhys. Lett. **3**, 21 (1987).

<sup>5</sup>J. Machta and R. A. Guyer, J. Phys. A (to be published).

<sup>6</sup>S. B. Lee and H. Nakanishi, Phys. Rev. Lett. **61**, 2022 (1988), and references therein.

<sup>7</sup>P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971).

<sup>8</sup>P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cor-

nell Univ. Press, Ithaca, 1979).

<sup>9</sup>M. Muthukumar and A. Baumgartner, Macromolecules **22**, 1937 (1989); **22**, 1941 (1989).

<sup>10</sup>M. E. Cates and R. C. Ball, J. Phys. (Paris) **49**, 2009 (1988).

<sup>11</sup>J. D. Honeycutt and D. Thirumalai, J. Chem. Phys. **90**, 4542 (1989).

<sup>12</sup>F. T. Wall and F. Mandel, J. Chem. Phys. **63**, 4592 (1975).

<sup>13</sup>J. W. Haus and K. W. Kehr, Phys. Rep. **150**, 263 (1987).

<sup>14</sup>G. C. Martinez-Mekler and M. A. Moore, J. Phys. (Paris) **42**, L413 (1981).