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LETTER TO THE EDITOR

Polymer chains in porous media

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Abstract. Static and dynamical properties of polymer molecules with and without excluded volume in porous media are investigated by Monte Carlo simulations. The exponents characterising the shape of the polymer approach their asymptotic values extremely slowly. The dynamical information indicates that the chain is trapped in local free-energy minima for random times, t_D, which have a very broad distribution. These properties are compared with those found in regular networks formed by various periodic distributions of obstacles.

It has been suggested that the properties of a polymer molecule trapped in a porous medium are important in many practical situations including filtration, enhanced oil recovery processes, gel permeation chromatography, and transport of solute through membranes [1, 2]. Numerous experiments of partitioning and diffusion of flexible polymer coils in porous glass, in membranes and under a variety of different random physical conditions have been carried out [3–5]. In these situations the polymer molecule is trapped in a random environment created by the distribution of molecules of the medium. The confinement of the polymer chain to a restricted portion of phase space leads to a loss in entropy. The shape of the polymer is determined mainly by the loss in configurational entropy and transport (diffusion) of the chain proceeds by overcoming the entropic bottlenecks generated by the random media.

Several of the experiments have been analysed using the scaling theory which was developed for the case of a polymer molecule confined to pores with regular geometry [6]. However, when randomness becomes relevant it is clear that the pore structure has to be described using a distribution of length scales [7]. In this case, the precise dependence of various quantities such as the mean square end-to-end distance, probability distribution of the end-to-end vector, and relaxation times on the parameters of the system is difficult to obtain analytically.

In this letter, we report the properties of freely jointed chains in random porous media using Monte Carlo simulations. Scaling arguments are used to analyse the results. The porous medium is modelled using the site percolation method. The model we have used is a modification of the one recently introduced by Baumgärtner and Muthukumar (BM) [8]†. Following these authors, we introduce a cubic lattice each of whose sites is occupied by an obstacle with probability p or unoccupied with probability $(1-p)$. A freely jointed chain consisting of N beads (where in our simulations N varies from 5 to 160) is placed in an unoccupied region of the lattice.

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† Note that the P of [8] corresponds to $(1-P)$ in the present letter.

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The chain is free to move in continuous space. The interaction between a bead at r_i and an obstacle at R_j is assumed to be a Gaussian-like potential,

$$\phi(r) \equiv \varepsilon f(r) = \varepsilon\left[1 - 3\left(\frac{r}{r_c}\right)^4 + 2\left(\frac{r}{r_c}\right)^6\right]\exp(-(r/\sigma)^2) \qquad r < r_c \qquad (1)$$

and is zero for $r > r_c$ where $r = |r_i - R_j|$. The factor in square brackets ensures that the potential and its first derivative approach zero continuously as $r \to r_c^-$. The parameters used in the present simulations are $\varepsilon/k_BT = 39.0$, $\sigma = 0.5a$ and $r_c = 0.7a$, where a is the lattice spacing. Neglecting overlap effects, the excluded volume per obstacle for this choice of parameters is $1.053a^3$. For the freely jointed chain with no excluded volume (NEV), the only constraint on the conformations of the chain is that the bond length, l, between successive beads is fixed at a value $l = 0.6a$. We have also studied the effect of excluded volume (EV), and in this case the monomers have an additional pairwise repulsive interaction given by $V(|r_i - r_j| = r) = \varepsilon_{12}(\sigma_{12}/r)^{12}$ with $\varepsilon_{12}/kT = 2.0$ and $\sigma_{12} = 0.3a$. The simulations were performed using both the 'slithering snake' algorithm [9] and the kink-jump technique [10]. The former was used to enhance the efficiency of exploration of configuration space and the latter to obtain dynamical information.

The Hamiltonian for a Gaussian chain in a porous medium can be written as

$$\beta H = \frac{3}{2l}\int_0^L \dot{r}^2(s)\,\mathrm{d}s + \beta\varepsilon\int \mathrm{d}^3r\,\rho(r)\int_0^L \mathrm{d}s\, f[r(s) - r] \qquad (2)$$

where $\rho(r) = \Sigma_{i=1}^{M} s_i\delta(r - R_i)$ with M being the total number of lattice sites and s_i is either 0 or 1. The distribution of the obstacles is taken to be [13]

$$P[\delta\rho(r), s_i] \sim P_0[\delta\rho(r)][(1-p)\delta(s_i) + p\delta(1 - s_i)]$$

where

$$\delta\rho(r) = \rho(r) - \rho_0 \qquad P_0[\delta\rho(r)] \sim \exp\left(-\tfrac{1}{2}\int \delta\rho^2(r)\,\mathrm{d}^3r/\rho_0\right)$$

and

$$\rho_0 = (1/V)\int \rho(r)\,\mathrm{d}^3r$$

is the mean density. The free energy is obtained by averaging the logarithm of the partition function, Z, using the above distribution. This can be done using the replica trick [11] and the result for $[Z^n]_P$ is (neglecting factors that do not survive in the $n \to 0$ limit)

$$[Z^n]_P \sim \int \prod_{\alpha=1}^{n} D[r_\alpha(s)\exp\left(-\frac{3}{2l}\sum_{\alpha=1}^{n}\int_0^L \mathrm{d}s\,\dot{r}_\alpha^2(s) + U_{\mathrm{eff}}\right) \qquad (3a)$$

where α and β label the replicas and

$$U_{\mathrm{eff}} = \ln\left\{1 + p\left[\exp\left(\frac{\rho_0\varepsilon^2\beta^2}{2}\sum_{\alpha,\beta}\int_0^L \mathrm{d}s\int_0^L \mathrm{d}s'\int \mathrm{d}^3r f(r_\alpha(s) - r)f(r_\beta(s') - r)\right) - 1\right]\right\}. \qquad (3b)$$

For the theory given by (3) dimensional analysis suggests that the appropriate coupling constant scales as $p\sqrt{N}$. The same conclusion has been reached by BM using different arguments†. Using this as the scaling variable one can write the mean square end-to-end distance averaged over disorder as

$$[\langle R^2\rangle] \sim \langle R^2\rangle_0 f(p\sqrt{N}) \tag{4}$$

where $\langle R^2\rangle_0 = Nl^2$. By excluding certain regions of configuration space the obstacles induce an effective attractive interaction between the monomers. The chain is expected to shrink in size with respect to $\langle R^2\rangle_0$ and is localised in an optimal pocket. For sufficiently large N we find that $[\langle R^2\rangle]^{1/2} \sim N^{1/5}$. This implies that $f(x) \sim 1/x^{3/2}$. When excluded volume effects are taken into account the situation is more difficult because of the competition between the repulsive energy arising due to self-avoidance and the effective attractive interaction due to the obstacles. In this case the present simulations are consistent with (4) with $\langle R^2\rangle_0 \sim N^{6/5}l^2$. We have not been able to obtain the asymptotic form of the scaling function $f(p\sqrt{N})$ because, as shown below, the approach to the asymptotic behaviour is extremely slow. The physical limit of shrinkage is a compact globule and thus we can conjecture that for the EV case the asymptotic behaviour is given by $[\langle R^2\rangle] \sim N^{2/3}(1/p)^{16/15}$. The scaling of $[\langle R^2\rangle]$ with N (for both the EV and NEV case) can be easily obtained using the standard Flory argument, if the form of the attractive potential, U_{A}, as a function of $[\langle R^2\rangle]$ is known. The calculation of U_{A} does not appear straightforward. An estimate of U_{A} can be obtained from the scattering function and this will be considered elsewhere.

Assuming that scaling holds, the distribution of the end-to-end vector, R, is expected to have the following general functional form [13]:

$$P(x) \sim \exp(-(|x|/\sigma_{\mathrm{eff}})^{\delta}) \tag{5}$$

where x is the cartesian component of R and σ_{eff} is the appropriate scaling length. This form should be valid as long as σ_{eff} is larger than the percolation connectedness length, ξ. In our simulations, values of p are typically well below the site percolation threshold, $p_{\mathrm{c}} = 0.6883$, and so ξ is small and (5) should be valid with $\sigma_{\mathrm{eff}} \sim [\langle R^2\rangle]^{1/2}$. When the functional form given by (5) is correct, $\delta = 1/(1-\nu)$ where ν is the correlation length exponent for $[\langle R^2\rangle]$ [13]. When $p = 0$, $\delta = 2.0$ for the NEV case and $\delta \approx 2.5$ for the EV case. Although (5) is expected to hold only asymptotically it is useful to consider δ as a function of N. We have calculated the scaling length σ_{eff} and the exponent δ as functions of both p and N by obtaining the best fits to the moments (up to the eighth) of the distribution function obtained from the simulations. Figure 1 shows that the functional form given by (5) fits our Monte Carlo distribution functions remarkably well, for N as small as 10 and arbitrary p. Although we have performed simulations of polymers in random media with N as large as 80, we have presented the results $P(x)$ for smaller N values in figure 1 to illustrate that even for these small values the expected scaling behaviour for $P(x)$ is obtained! The approach to the asymptotic value of δ can be inferred by considering the dependence of $\delta_N - \delta_\infty$ on N, where δ_N is the effective exponent for a given N and δ_∞ is the asymptotic ($N \gg 1$) value. The simulations as well as analysis suggest that [14] $\delta_N - \delta_\infty \sim N^{-\alpha(p)}$ where $\alpha(p)$ is an exponent that depends in general on both p and the self-avoidance criterion. The exponent, $\alpha(p)$, is obtained by considering values of N up to 80. First consider

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† A different distribution has been considered in [12].

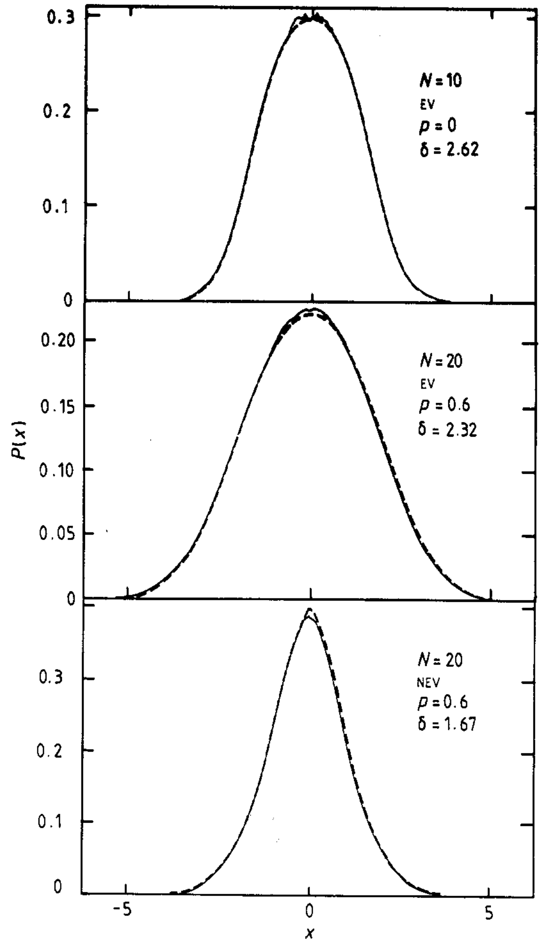

Figure 1. Distribution function of the x component of the end-to-end distance. Results for only small values of N are displayed to show that even for short chains the expected scaling behaviour for $P(x)$ (see equation (5)) is obtained. In each case the full curve denotes Monte Carlo data and the broken curve a best fit to (5).

the case of $p=0$, for which values of δ_∞ and ν are known (almost) exactly. The exponent $\alpha(p=0)$ for the freely jointed chains, computed using the exact distribution function [15] for arbitrary N, is found to be 1.0. For the EV case, $\alpha(p=0)$ is estimated to be at least unity based on the present simulations. We reached a similar conclusion by reanalysing the moments obtained by Wall and Hioe [16] for self-avoiding walks on the diamond lattice.

When p is non-zero the chains, both with and without excluded volume, show a considerably different behaviour. The asymptotic behaviour is expected to be reached only when the length of the polymer is much larger than the characteristic length due to disorder. Therefore, we expect the approach to the asymptotic behaviour to be slower than for the $p=0$ case. Because the polymer prefers to be in a region free of the obstacles, the relevant length scale which has to be exceeded is some characteristic distance between the clusters of obstacles, l_p. It is obvious that l_p monotonically decreases with increasing p. This suggests that the asymptotic value for δ_N should be

reached faster as p increases. For the case of no self-avoidance we find that our results are consistent with the above expectations. Specifically, if $\delta_\infty = 1.25$, the simulations indicate that $\alpha(p = 0.2) \sim 0.3$ and $\alpha(p = 0.6) \sim 0.5$. The competition between the repulsive interaction due to excluded volume and the effective attractive interaction between monomers, which is induced by disorder, forces the approach to the asymptotic value of δ_N to be even slower when self-avoidance is taken into account. The chains will shrink to a compact globule with $[\langle R^2\rangle] \sim N^{2/3}$ only when p is large enough or N becomes very large [14]. Because of the very slow approach to the asymptotic value we have not been able to determine $\alpha(p)$ accurately. We do find that δ_N decreases with increasing p but in all cases studied δ_N is quite far from the expected asymptotic value of 1.5. To probe the onset of the asymptotic behaviour we would have to consider chains of much larger size than we have been able to simulate.

For comparison purposes, we have considered the properties of a polymer chain in various other media where the obstacles are arranged in the following regular configurations. (i) Obstacles of volume a^3 or $8a^3$ form a periodic cubic array with the spacing between the centre of each cube being either $2a$ or $3a$, respectively. (ii) The obstacles form a three-dimensional cubic network. The edge of each cube has length $2a$. The polymer chain is forbidden to cross the edges of the cubes. (iii) The obstacles are arranged so that they form a network of hollow cubes in a cubic array with a hole of length a in each face†. We were motivated to consider this configuration (iii) because the dynamics of a polymer chain in such an environment is controlled by well characterised entropic bottlenecks. In cases (i) and (ii) we find that the freely jointed chain shrinks relative to its free size but the amount of shrinkage is considerably less than found in the random medium. This is expected because optimal configurations that maximise entropy can be readily found. The distribution function, $P(x)$, shows unusual behaviour in these cases. Pronounced peaks exist at distances commensurate with lattice spacing, i.e. at $x = n\bar{l}$ where $\bar{l}$ is the distance between the obstacles and n is an integer. A theoretical analysis will be presented in a future communication [14].

We now discuss the motion of the chains in the porous medium as well as in the network of hollow cubes arranged in a cubic array, focusing on the displacement of the centre of mass, R_{CM}, of the chain. Other aspects of the dynamics will be reported elsewhere [14]. In both our work and that of Baumgärtner and Muthukumar, the quantity $\langle (R_{\mathrm{CM}}(t) - R_{\mathrm{CM}}(0))^2\rangle$, as a function of t exhibits three distinct regimes: (i) initial diffusive behaviour with diffusion coefficient D_0; (ii) subdiffusive behaviour for intermediate times $t_R < t < t_p$ where t_p is a function of p and N; (iii) normal diffusive behaviour for times greater than t_p with diffusion constant D_∞ which is less than D_0. In order to obtain a microscopic picture of the chain dynamics we followed the components of R_{CM} as a function of time for polymer chains in the hollow cubic network and in the porous medium. The time scale t_p is typically about 10^5 and thus we focus on the behaviour of the chain dynamics for times less than t_p to probe the effect of the expected free-energy barriers. The results are displayed in figure 2. There are two key features we have observed. (a) For both cases, R_{CM} undergoes a random motion about a mean position corresponding to a minimum in the free energy. This is followed by sudden excursions to other free-energy minima at random intervals. The jump in both cases occurs over a distance which is an appreciable fraction of the size of the chain. For the random case this yields an approximate distance separating

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† After this work was completed, we received a preprint from BM [17], in which essentially the same model is considered.

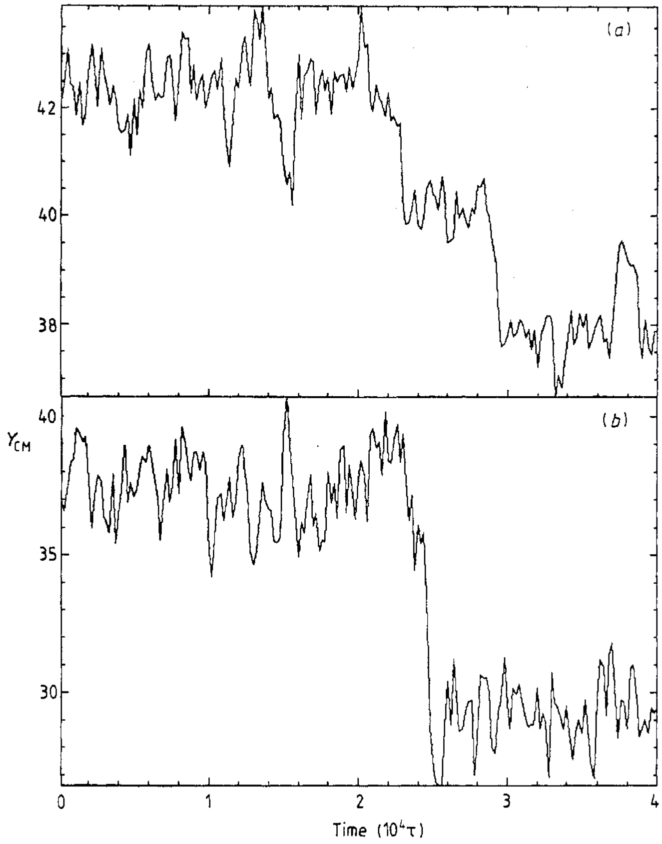

Figure 2. Single component of the centre of mass of a polymer as a function of time for: (*a*) chain with $N = 40$ in a random porous medium; (*b*) chain with $N = 10$ in a lattice of hollow cubes.

the free-energy minima. (b) The residence time (the time the chain spends in the local free-energy minimum in which it is trapped) for the random case shows a broader distribution than for the regular network. As a consequence several dynamic correlations are expected to exhibit non-exponential behaviour [14] for the polymer in a random medium. These observations have been used to construct a phenomenological two-state random-walk model. The calculations based on this model yield results in qualitative agreement with the simulations [14]. The behaviour shown in figure 2 provides further evidence that the hollow cubic network may be a useful caricature of motion seen in the more complex porous medium [14, 17].

The model considered here can be generalised to include more than one polymer molecule in the porous medium. This problem is not only of relevance to experiments but is also useful in characterising entanglement effects in random media. It is interesting to speculate on the effect of quenched randomness on the simplest case of the many-chain problem, namely the polymer melt. Here, in analogy with the corresponding excluded-volume problem, one expects that the effective attractive potential, U_A, will be screened out. Thus, one would conclude that, at least for the polymer melts in porous media, randomness is irrelevant and that molten chains are ideal. Further work is required to clarify this point.

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