Critical behaviour of two interacting linear polymer chains: exact results for a state of interpenetration of chains on a fractal lattice

LETTER TO THE EDITOR

Critical behaviour of two interacting linear polymer chains: exact results for a state of interpenetration of chains on a fractal lattice

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Abstract. A model of two interacting (chemically different) linear polymer chains on a fractal lattice is proposed, to study segregation and interpenetration of chains. Using the real space renormalization group transformation, the value of the contact exponent at the point of the interpenetration transition is calculated exactly for the 2D Sierpinski gasket.

The physical properties observable on a polymer chain length are calculated as statistical averages over all possible configurations of the polymer, and these configurations are obtained by considering the chain as a walk embedded in an appropriate lattice. Several lattice models such as random walk (RW), self-avoiding walk (SAW), true self avoiding walk (TSAW) [1–3], self-attracting self-avoiding walk (SASAW) [4], trails and their silhouettes [5] etc have been proposed to represent a polymer chain in different regimes. All configurational properties of the polymer on a lattice are deduced from the generating function

$$G(x, T) = \sum_{N,P} \Omega(N, R) x^N u^R$$

where $\Omega(N, R)$ is the number of different configurations per site of a polymer having N monomers and R nearest neighbours. Here x is the fugacity associated with each step of the walk and the interaction strength u is related to temperature T by $u = \exp(E/k_\beta T)$, $E > 0$ being the attractive energy associated with a pair of nearest neighbour bonds.

The analogy with critical phenomena [2] allows us to study the issue of universality in polymer statistics in a renormalization group framework. Moreover, if we restrict ourselves to the case of fractal hierarchical lattices, exact solutions of the renormalization group may be worked out and the singular behaviour of the generating functions may be analysed in detail [4–8]. These lattices, like the Sierpinski gasket [8] or truncated n-simplex lattices [6], are defined recursively, and, by splitting the generating functions in a finite subset of partial contributions, it is possible to write a closed set of recursion equations in terms of a finite number of coupling constants. The variables in this set of equations are just the partial generating functions corresponding to different polymer configurations for a given size of the fractal lattice. Linearizing the recursion equations near the non-trivial fixed points one can find the eigenvalues of the transformation matrix which give the characteristic exponents of the system.

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In this letter we study the critical behaviour of a system consisting of two chemically different polymer chains denoted as P_1 and P_2. This system has received considerable experimental and theoretical attention in recent years [9–14]. The problem with which we are basically concerned here is to predict the effect of interactions between the monomers of P_1 and P_2 on their configurations leading to interpenetration or zipping of the chains. It is generally thought that under certain conditions, polymer chains may form a self-similar interpenetrated configuration. With rise in temperature the polymer system may transform to a state where the two chains are segregated from each other. We refer to this transformation as an unbinding transition (in analogy with the surface unbinding transition [15]). The temperature at which the unbinding transition takes place, corresponds to a tri-critical point and in its proximity a crossover regime may be observed. The mean number of monomers M of one polymer in contact with the other polymer at the tri-critical point is assumed to behave as

$$M \propto N^y$$

where N is total number of monomers in the longer chain and y is a contact exponent.

To calculate the exponent y we employ an exact renormalizing-group (RG) calculation for a model on a fractal lattice. For this we consider a Sierpinski gasket in $d=2$ or equivalently a truncated 3-simplex lattice. We want to study the statistics of two interacting walks on this gasket subject to a number of restrictions. Let each walk be a self-avoiding walk (SAW). The different walks are allowed to cross each other at most once at any lattice point. A lattice bond may be occupied either by a step of one or by both walks. With each crossing we may associate contact energy E_c.

The generating function of interest can therefore be written as

$$G(x_1, x_2, \omega, t) = \sum_{\text{all walks}} x_1^{N_1} x_2^{N_2} \omega^{R_1} t^{R_2} \tag{1}$$

where $N_1(N_2)$ is the number of monomers in the polymer $P_1(P_2)$ and $x_1(x_2)$ denotes the fugacity weight factor attached to each step of the polymer $P_1(P_2)$. R_1 is the total number of sites visited by both the walks and R_2 is the number of pairs of sites adjacent to these doubly visited sites. Here $\omega = \exp(E_c/T)$, and $t = \exp(E_t/T)$, where E_c, as mentioned above, is the contact energy and E_t is the energy associated with an unoccupied lattice bond adjacent to the doubly visited site.

The average length of a chain, say P_1, is found from the relation [16]

$$\langle L_1 \rangle = x_1 \frac{\partial \ln G}{\partial x_1}. \tag{2}$$

If we allow the two chains to cross each other on the lattice sites, then the mean number of monomers in direct contact (crossing) with other chain is defined as

$$\langle M \rangle = \omega \frac{\partial \ln G}{\partial \omega} \tag{3}$$

where $\langle M \rangle$ is the number of monomers of one chain in contact with the other.

To calculate G we require a closed set of recursion relations involving four restricted partition functions shown in figure 1. For this case the recursion relations are simple and can be written as

$$A_{r+1} = A^2 + A^3 \tag{4}$$

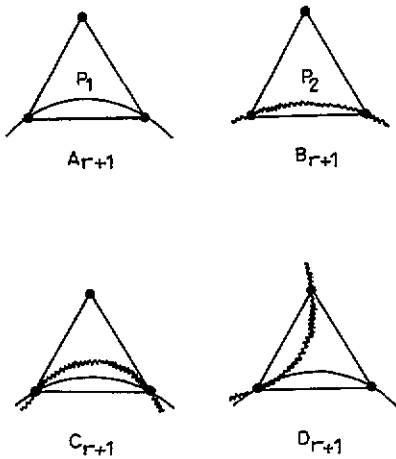$$B_{r+1} = B^2 + B^3 \tag{5}$$

$$C_{r+1} = C^2 + C^3 + D^2(A+B) \tag{6}$$

Figure 1. Diagrams representing the four restricted generating functions for two chains (indicated by smooth (P_1) and wiggle (P_2) lines) on a 2D Sierpinski gasket.

and

$$D_{r+1} = D(A \cdot B + A \cdot C + B \cdot C) + D^3. \tag{7}$$

The suffix r in the RHS of the above equations is dropped for notational simplification. It should be noted that recursion relation for $A(B)$ is independent of $B(A)$, C and D. This is because we ignored, for simplification, the effect of one SAW on the self-avoidance of the other SAW. In a dilute solution, the size of a chain is, however, not expected to change due to interactions between monomers of different chains [12]. The effects of interaction between two chains are taken through C and D. The critical exponents of the individual chains remain as in the dilute case [6]. The starting weight for these walks are

$$A_0 = x_1 \tag{8a}$$

$$B_0 = x_2 \tag{8b}$$

$$C_0 = x_1 x_2 \omega^2 \tag{8c}$$

and

$$D_0 = x_1 x_2 t \omega. \tag{8d}$$

In the asymptotic limit both N_1 and N_2 tend to infinity, and therefore, in that situation $x_1 = x_2$. Thus, $A_{r+1} = B_{r+1}$. For this case we find three non-trivial fixed points whose features are discussed below.

(i) The fixed point $(A^* = B^*, C^*, D^*) = (0.61803, 0, 0)$ corresponds to the bulk segregated state. Linearization around this fixed point gives one eigenvalue greater than one, $\lambda_1 = 2.3819$ which gives the radius of gyration exponent $\nu = 0.7986$ as obtained by Dhar [6]. For $x = x_c(\omega) = 0.61803$ this fixed point is reached for all values of $\omega < \omega_c(t)$.

(ii) The fixed point $(A^* = B^*, C^*, D^*) = (0, 0.61803, 0)$ is reached for all $\omega > \omega_c(t)$ and $x < x_c(\omega)$. This represents interpenetration of chains which may be thought in some appropriate sense to be similar to the formation of the 'double helix' kind of structure of DNA molecules. Linearization around this fixed point yields one eigenvalue greater than one, $\lambda_1 = 2.3819$, with $\nu = 0.7986$. Here it should be noted that in this case the
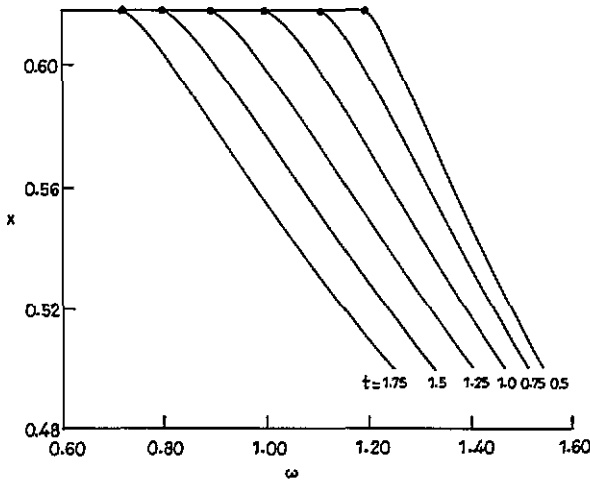
Figure 2. Critical fugacity x as a function of the interaction parameter ω for several values of t for the 2D Sierpenski gasket. The tri-critical points of adsorption are shown by solid circles.

monomers of two different chains are zipped together to form a single composite chain.

(iii) At $\omega = \omega_c(t)$, $x_c(\omega)$ is still equal to its bulk value. We find the fixed point $(A^* = B^* = 0.61803, 0.38196, 0.38196)$. The relation for $A_r(B_r)$ depends only on x, so one has

$$(x_c - x_r) \sim (\lambda_1)^r (x_c - x)$$

while the variation of ω is dominated by the eigenvector associated with the second largest eigenvalue at $(A^* = B^*, C^*, D^*)$:

$$(\omega_r - \omega_c) \sim (\lambda_2)^r (\omega - \omega_c) \qquad \text{with } \lambda_2 = 1.9159.$$

We identify this fixed point as the tri-critical point which gives the contact exponent

$$y = \frac{\ln \lambda_2}{\ln \lambda_1} = 0.7491. \tag{9}$$

In figure 2 we plot the phase diagram in the parameter space of x and ω for a wide range of t. We note that for each value of ω such that $\omega > \omega_c(t)$, an interpenetrated phase is found to occur for $x < x_c$. As t increases $\omega_c(t)$ decreases as shown in figure 3. It thus appears that to have an unbinding transition, one of the interactions should be repulsive.

The existence of chain configurations in a state of interpenetration and the occurrence of an unbinding transition for this simple model of two SAWs on a 3-simplex lattice (or on a 2D-Sierpinski gasket) is a pleasant surprise. We also note that the two fixed points $(A^* = B^*, C^*, D^*) = (0, 0, 1)$ and $(0, 0.61803, 1)$ of equations (4)-(7) cannot be reached starting with the initial condition given by equations (8a)-(8d). The existence of such states, which correspond to a configuration represented by D in figure 1, has not been found experimentally.

It, therefore, seems that the simple model proposed here provides a qualitative description of the phase transition between segregation and interpenetration or zipping of chains of linear polymers. The approach presented here may serve as a starting point
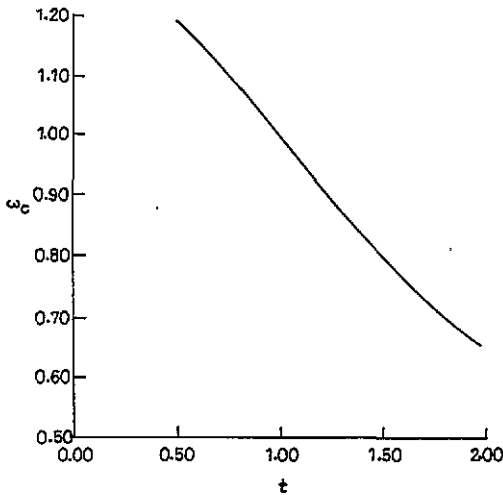
Figure 3. Variation of ω_c as a function of t for 2D Siespinski gasket.

for more thorough investigations of segregation and entanglements in real systems by considering all physically relevant interchain and intrachain interactions.

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