Surface adsorption and the collapse transition of a linear polymer chain: Some exact results on fractal lattices

Sanjay Kumar* and Yashwant Singh

Department of Physics, Banaras Hindu University, Varanasi 221005, India

(Received 5 February 1993)

We study the surface adsorption and collapse transition of a flexible self-attracting self-avoiding polymer chain on truncated 4- and 5-simplex lattices using real-space renormalization-group techniques. We find phase diagrams that exhibit many different universality domains of critical behavior. In the desorbed ordinary bulk regime, the polymer undergoes a collapse transition from a swollen to a compact-globule phase on a 4-simplex lattice, but not on a 5-simplex lattice, where it always remains in the swollen state. In the adsorbed region, on a 4-simplex lattice, the polymer remains in the swollen state with a critical behavior characterized by that of a 3-simplex lattice, whereas, on a 5-simplex lattice, it has both swollen- and compact-globule regions separated by a tricritical (θ) line. The phase diagram of a 4-simplex lattice has a *pentacritical* point which separates a region, where the point at which the adsorbed (swollen) polymer coexists with both the desorbed polymer and desorbed globule is a tetracritical point, from one in which it appears as the intersection of three lines of continuous transition. On a 5-simplex lattice, the adsorbed phase θ line bends in the neighborhood of the special adsorption tricritical line and does not appear to meet it, even for a very large value of the monomer-monomer attraction.

I. INTRODUCTION

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) [1–3], true self-avoiding walk [4], self-attracting self-avoiding walk (SASAW) [5,6], trails and their silhouettes [7], etc., have been proposed to represent a polymer chain in different regimes. For example, the model of a SAW simulates a polymer chain in a good solvent while the model of a SASAW represents a polymer chain in a poor solvent that can undergo a collapse transition, where the chain contracts from an extended state to a globule state when the temperature is lowered.

These lattice models have been the focus of much attention in recent years because from a statistical-mechanics viewpoint they serve as generic examples of analyzing scaling and fractal properties [8–10]. In critical-phenomena parlance, the infinite RW is equivalent to a Gaussian system at its critical point with the radius-of-gyration exponent $\nu = \frac{1}{2}$ independent of space dimension d (of a Euclidean lattice). The SAW is a critical $O(n)$ model with $n \rightarrow 0$ component [2]. The SASAW changes the behavior of the phase transition of the SAW from second order to first order into a collapse phase at low temperature [2]. At the intermediate temperature (θ point) its behavior is described by a tricritical point of $O(n)$, $n \rightarrow 0$, spin system [2]. In this regime the upper critical dimension changes from four to three with the consequence that for $d = 3$, ν is equal to $\frac{1}{2}$ plus a logarithmic correction. The phase diagram for a SASAW

model has been studied on both regular and fractal lattices using a variety of methods [2,5–8].

Configurational properties of polymer chains interacting with a surface may get strongly modified relative to their bulk properties owing to a subtle competition between the gain of internal energy and the corresponding loss of configurational entropy at the surface. The general picture that has emerged from the theoretical [11,12] and experimental [13,14] studies of the surface-interacting polymer chains reveals that under certain conditions, a polymer chain can form a self-similar adsorbed layer near the wall with a decreasing density profile at the critical temperature T_a. The polymer system undergoes a transition from a desorbed state to an adsorbed state as the temperature is lowered. Using the analogy between an adsorbed polymer chain and the magnetic $n \rightarrow 0$ vector model with a free surface it has been shown that the adsorption point T_a corresponds to a tricritical point and in its proximity a crossover regime is observed. In particular the mean number of M monomers at surface is shown to behave as

$$M \sim \begin{cases} (T_a - T)^{1/\phi - 1}, & T < T_a \\ N^\phi, & T = T_a \\ (T - T_a)^{-1}, & T > T_a . \end{cases} \tag{1.1}$$

Here ϕ is the crossover exponent. The value of the exponent ϕ can be found exactly in two dimensions using conformal invariance theory [15] and on fractal lattices using real-space renormalization-group (RSRG) methods [16,17].

A surface-interacting polymer chain in a poor solvent is expected to exhibit a phase diagram characterized by

many different universality domains of critical behavior. The competition between solvent-induced monomer-monomer attraction and the surface-monomer interaction may lead to the possibility of the coexistence of different regimes and multicritical behavior. Attempts have been made to study such phase diagrams on Euclidean lattices using RSRG and phenomenological renormalization methods [18]. However, as a rule these models are not solvable analytically and numerical methods are quite inefficient in the study of multicritical phenomena. Recently, a transfer-matrix method has been used to study the directed and isotropic [19,20] SASAW models of polymer collapse and adsorption. The simultaneous adsorption and collapse transitions which take place at the so-called special (multicritical) θ point have been observed in both models in $d = 2$. In the first case the applicability of the model is, however, physically limited while in the latter, size effects are seriously hindering the possibility of locating and describing precisely the multicritical points.

Fractals which may be considered intermediate between regular and disorder lattice offer a class of system where many nontrivial physical models can be treated exactly. Aside from being interesting in their own right, these results are often in qualitative (and some times even quantitative) agreement with their counterparts for standard Euclidean lattices. The problem of simultaneous adsorption and collapse of a linear polymer chain has recently been studied on a three-dimensional (3D) Sierpinski gasket by Bouchaud and Vannimenus (herein after referred to as BV) [16] and Orlandini et al. [20] using RSRG method.

BV [16] considered a surface-interacting SASAW model and found a phase diagram which qualitatively agreed with the one obtained by Veal, Yeomans, and Jug [19] and the existence of multicritical special θ point is confirmed. Orlandini et al. [20], on the other hand, modeled the polymer chain by a SASAW in the bulk and by a trail silhouette on the surface. In their model, the polymer in the bulk experiences self-attraction due to nearest-neighbor interactions, while on the surface twice visited sites are favored by a suitable fugacity. In their phase diagram the desorbed phase has regions of swollen and collapsed phases separated by a tricritical line and the adsorbed region has the phases of swollen linear chain, branched polymerlike phase and collapsed phase separated by tricritical lines. Thus in the adsorbed region two transitions are found to take place: the first one from linear to branched polymer behavior is followed by a collapse into compact-globule phase.

In this article we consider the problem of simultaneous adsorption and the collapse of a linear polymer chain on truncated n-simplex lattices, which provide a family of fractals in which the fractal dimension can be varied to a wide range while the spectral dimension is held almost fixed. In previous papers [21] we have calculated, using the exact renormalization-group transformation, the bulk critical exponents ν, α, γ and the nature of tricritical point (θ point) corresponding to the transition of collapsed globule phase. In Sec. II we first outline the main features relevant to our present study of these fractal lattices and also the outline of the general formulation of the problem of a surface-interacting polymer chain. The details of calculation of phase diagrams using a RSRG transformation of the chain on truncated 4- and 5-simplex lattices are given in Secs. III and IV, respectively. The paper ends with a brief discussion given in Sec. V.

II. SURFACE INTERACTING POLYMER CHAIN ON A TRUNCATED n-SIMPLEX LATTICE

The truncated n-simplex lattice is defined recursively [22]. The graph of the zeroth-order truncated n-simplex lattice is a complete graph on $(n + 1)$ points. The graph of the $(r + 1)$th-order lattice is obtained by replacing each of the vertices by the rth-order graph by a complete graph on n points. Each of the new n points is connected to one of the lines leading to the original vertex. The fractal and spectral dimensions of this lattice are respectively given as

$$d_F^{(b)} = \frac{\ln n}{\ln 2}, \quad \tilde{d}^{(b)} = \frac{2 \ln n}{\ln(n+2)} . \tag{2.1}$$

The superscripts (b) and (s) (see below) stand for the bulk and surface, respectively. The following features of this family of lattices are of particular interest to us.

(i) The surface of a truncated n-simplex lattice is a truncated $(n-1)$-simplex lattice with fractal $d_F^{(s)}$ and spectral $\tilde{d}^{(s)}$ dimensions given by Eq. (2.1) where n is replaced by $(n-1)$.

(ii) The odd simplex lattices (to be more precise, the lattices with $n = 3$ and 5 [21]) do not appear to have collapse transition for a SASAW model. The polymer chain remains in a swollen state for all values of monomer-monomer attraction on these lattices. Thus for any value of n the collapse transition can take place either in the bulk or in the surface, but not in both.

These features of the truncated n-simplex lattices make it an interesting system for the study of adsorption and collapse transition of a linear polymer chain.

To perform a RSRG calculation on a polymer chain interacting with a surface, we study how the characteristic quantities describing a SASAW change upon repeated length rescaling of the lattice. When these quantities remain invariant, the chain is "self-similar" on all length scales and this is a "fixed point" of the rescaling transformation. The chain and its behavior under rescaling is described with the help of certain parameters. The bulk critical exponents are usually calculated using only one parameter, which represents fugacity per monomer of the polymer chain [3,21]. Here we introduce three more parameters describing the strengths of the nearest-neighbor monomer interaction, the interaction of a monomer in the surface layer and in the adjoint one [16,17].

We consider a polymer chain situated on the truncated n-simplex lattice and make one surface of it attractive. We call this surface a (impenetrable) wall. To each N-step walk having N_s steps along the wall, N_c steps lying in the surface layer adjacent to the wall, and with N_m number of nearest neighbors, we assign the weight $x^N, w^{N_s} t^{N_c} u^{N_m}$. Here x is fugacity associated with each step of the walk and $w = \exp(-E_s / K_B T)$ and

$t = \exp(-E_c/K_B T)$ are Boltzmann factors corresponding to surface energy E_s denoting the interaction of a monomer with the wall and E_c the interaction energy of a monomer with the adjacent layer. u represents monomer-monomer (attractive) interaction strength and is related to the temperature by $u = \exp(+E_m/K_B T)$, $E_m > 0$ being the attractive energy associated with a pair of nearest-neighbor bonds. We restrict the attractive interaction to bonds within a first-order unit of the fractal lattice [6]. The global generating function for the problem we want to study can be written as

$$G(x,u,w,t) = \sum_{\text{all walks}} x^N w^{N_s} t^{N_c} u^{N_m}$$
$$= \sum_{N,N_s,N_c,N_m} C(N,N_s,N_c,N_m) x^N w^{N_s} t^{N_c} u^{N_m}$$

$$(2.2)$$

where $C(n,N_s,N_c,N_m)$ represents the total number of configurations of all walks.

For finitely ramified fractals it has been shown [21] that the relevant generating functions can be expressed in terms of a finite number of restricted partition functions. These partition functions are defined recursively as a weighted sum over all configurations for a given stage of the iterative construction of the fractal lattice. The recursions express the restricted functions for the $(r+1)$th-order lattice in terms of those of the rth-generation one. The variables in these equations are just the partial generating functions corresponding to different polymer configurations for a given size of the fractal lattice. Linearizing the recursions near the nontrivial fixed points, the ones reached by the system depending on the initial conditions, we can find the eigenvalues of the transformation matrix which give the characteristic exponents of the system.

III. THE TRUNCATED 4-SIMPLEX LATTICE

The basic geometrical unit of construction of a truncated 4-simplex lattice is a tetrahedron with 4-corner vertices and bonds between every pair of vertices. Each vertex connected through a direct bond is termed a nearest neighbor. The tetrahedron of first and $(r+1)$th order are shown in Fig. 1. The shaded regions represent the sur-

face. The nearest-neighbor bonds on the surface are shown by dashed lines while those of the bulk are shown by full lines. The surface of the 4-simplex lattice is a truncated 3-simplex lattice. Note that the truncated 4-simplex lattice belongs to the same universality class as the 3D Sierpinski gasket studied by BV [16]. The bulk critical behavior including the θ point for the SASAW model has been studied by Dhar and Vannimenus [6].

The restricted partition functions of our interest are shown in Fig. 2 and corresponding recursion relations are [6,16]

$$A_{r+1} = A^2 + 2A^3 + 2A^4 + 4A^3 B + 6A^2 B^2 , \qquad (3.1)$$

$$B_{r+1} = A^4 + 4A^3 B + 22B^4 , \qquad (3.2)$$

$$S_{r+1} = S^2 + S^3 + A(C^2 + 2C^2 S + 4CSE + 6SE^2) , \qquad (3.3)$$

$$C_{r+1} = AC(1 + 2S + 2S^2) + 2AS^2 E + C^2(2C + 6E)B , \qquad (3.4)$$

and

$$E_{r+1} = AS^2(C + 3E) + (C^3 + 22E^3)B . \qquad (3.5)$$

The subscript r has been dropped out from the right-hand side of above equations. Note that the Eqs. (3.1) and (3.2) correspond to the polymer chain in bulk and have been studied by Dhar [3] and Dhar and Vannimenus [6] in detail. They are decoupled from the surface and remain so under iteration. The initial weight of these functions are

$$A_1 = x^2 + 2x^3 u + 2x^4 u^3 , \qquad (3.6a)$$

$$B_1 = x^4 u^4 , \qquad (3.6b)$$

$$S_1 = x^2 w^2 + x^3 w^3 u + x^3 t^2 u + 2x^4 wt^2 u^3 , \qquad (3.6c)$$

$$C_1 = x^2 t + 2x^3 wtu + 2x^4 w^2 tu^3 , \qquad (3.6d)$$

$$E_1 = x^4 w^2 tu^4 . \qquad (3.6e)$$
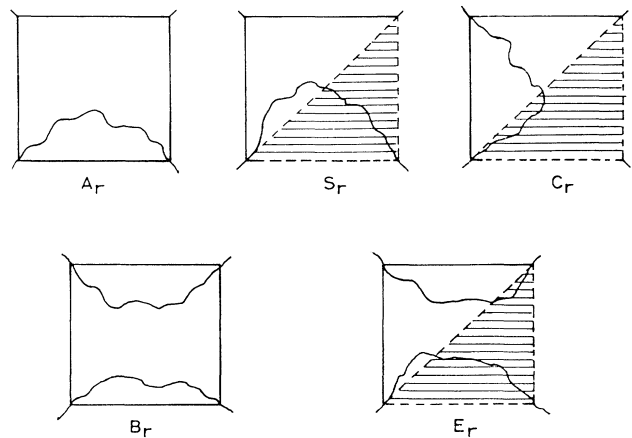
FIG. 2. Diagrammatic representation of the restricted partition functions for the rth-order tetrahedron. The internal structure of the tetrahedron is not shown. Only the corner vertices and the end points of the walks are shown. Out of five diagrams, two (A and B) represent the bulk generating functions for the polymer chain and the remaining three (S, C, and E) represent the surface functions.
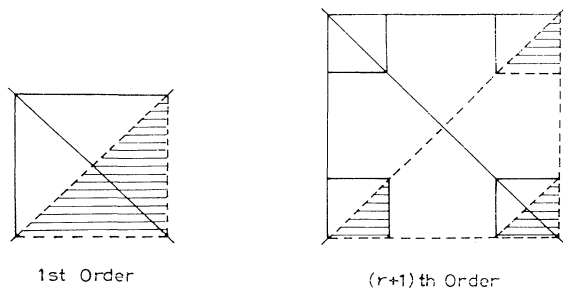

1st Order　　　　　　　(r+1)th Order

FIG. 1. Graphical representation of a truncated 4-simplex lattice of first and $(r+1)$th order. The shaded regions represent the adsorbing surface. The nearest-neighbor bonds on the surface are shown by dashed lines while those of the bulk are shown by full lines.

In writing Eqs. (3.6a)–(3.6e) we associated weights x, xw, and xt, respectively, to each step in the bulk, wall, and the surface adjacent to the wall, and u to each pair of nearest neighbors. More general or complicated initial conditions could be considered by allowing all or some of the interactions to have a different form, but they would not change the qualitative nature of the phase diagram. We, however, note that the initial weight taken by BV for S differs from the one given above by Eq. (3.6c). As a result, the phase diagram found by us has certain additional features not reported by BV [16].

Here our main emphasis is to explore the behavior of the transitions around special line, i.e., $w = w^*(t,u)$ for different values of t. We show that the parameter t plays a crucial role in determining the multicritical behavior of the polymer chain. To make the analysis more simple, we divide the parameter space into three regions depending on the values of surface attraction parameter w.

A. Desorbed phase

For all values of $w < w^*(t,u)$ the polymer chain lies in the bulk. The following features which characterize a bulk phase are found.

(1) For weak monomer-monomer interaction, i.e., $u < u_\theta$ ($= 3.316074$) the fixed point is found to be $(A^*,B^*,S^*,C^*,E^*) = (0.4294,0.0499,0,0,0)$. The linearization of the relevant equations given only one eigenvalue $\lambda_b = 2.7965$ greater than one. The radius of gyration exponent found with this eigenvector is equal to 0.6740, a value already known for the 4-simplex lattice.

(2) At $u = u_\theta = 3.316074$ we have θ-chain behavior for the polymer in the bulk. The fixed point which represents this behavior is $(A^*,B^*,S^*,C^*,E^*) = (\frac{1}{3},\frac{1}{3},0,0,0)$. The linearized equations around this fixed point give two eigenvalues greater than one; $\lambda_{b1} = 3.7037$ and $\lambda_{b2} = 2.2222$. With these eigenvalues we find the critical exponents $\nu_\theta = 0.5293$, $\phi_c = 0.6098$, and $\alpha = 0.3602$. These values characterize the tricritical nature of the θ point.

(3) If we further increase the strength of the monomer interaction, i.e., $u > u_\theta$, the polymer is found in a collapsed (compact globular) phase in which the monomer density per site is finite. This phase is represented by a fixed point $(A^*,B^*,S^*,C^*,E^*) = (0,0.3568,0,0,0)$. Linearization around this fixed point gives only one eigenvalue greater than one. This eigenvalue which is equal to 4.0 leads to $\nu_c = \frac{1}{2}$, corresponding to collapsed phase.

In the phase diagram plotted in Fig. 3 in which we plot w as a function of u, the θ line is found at $u = u_\theta(= 3.316074)$ is shown by dashed line. This line separates the bulk swollen and collapsed phases and terminates at the surface adsorption line $w = w^*(t,u)$. As discussed below, the line $w = w^*(u,t)$ separates the bulk from the absorbed phase. Note that below this line the desorbed phase is not affected by the presence of the surface attraction, except for the θ point turning into a θ line and the critical lines corresponding to swollen and collapsed phases into respective regions.

B. Adsorbed phase

When $w > w^*(u,t)$ the polymer is found in adsorbed phase. The fixed point which represents this state is $(A^*,B^*,S^*,C^*,E^*) = (0,0,0.61803,0,0)$. The linearized equations about this fixed point lead to eigenvalue $\lambda_s = 2.3819$, which gives $\nu_s = 0.7986$, a value equal to the
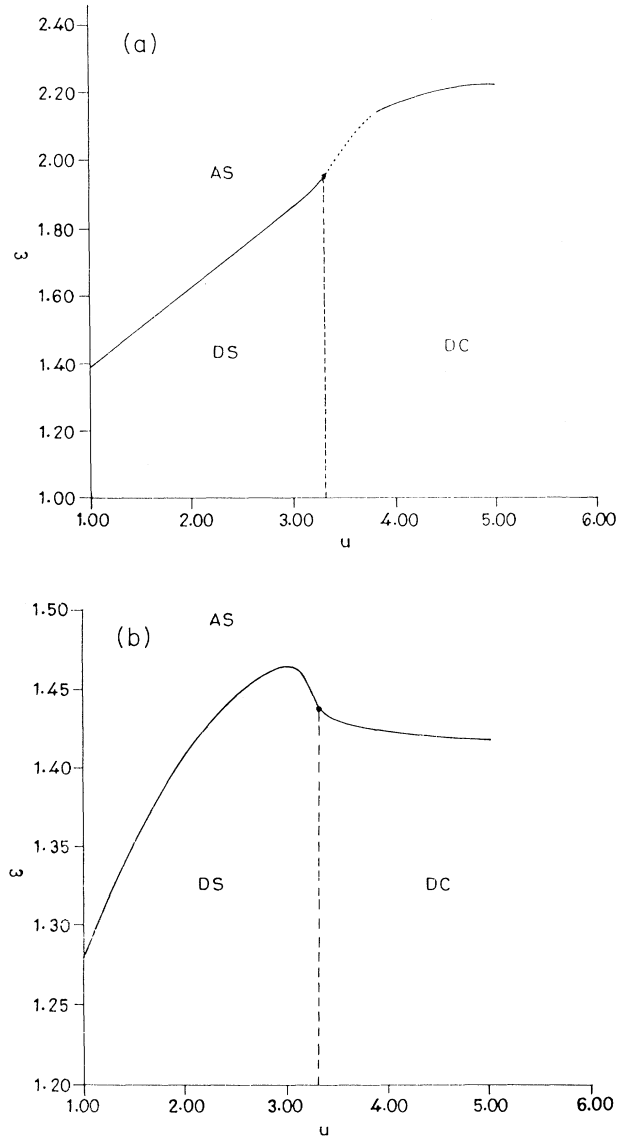

FIG. 3. (a) The w-u phase diagram at $t = 0.2$ for the truncated 4-simplex lattice. Regions marked by AS, DS, and DC represent, respectively, the adsorbed polymer in swollen state, desorbed polymer in swollen, and collapsed (globular) state. The dashed line which separates the bulk swollen and collapsed state of the polymer is the θ line. The special adsorption line is indicated by full line and part of it by dotted line. The point where θ line meets with the adsorption line is a multicritical point. The dotted part of the adsorption line indicates the region of the coexistence of adsorbed SAW and the (bulk) globule phase. (b) The w-u phase diagram at $t = 0.5$ for the truncated 4-simplex lattice. Other notations have the same meanings as in (a).

radius of gyration exponent for a SAW on a 3-simplex lattice.

C. Special adsorption line

When $w = w^*(u,t)$ the polymer is on an adsorption special line. Our aim here is to study the different regions of this line which characterize different multicritical behaviors as a function of u and t. Note that the parameters u and t measure, respectively, the strengths of nearest-neighbor monomer interaction and the repulsive strength of the adjacent layer to the wall.

(4) For weak monomer interaction $u < u_\theta$, the $w = w^*(u,t)$ line corresponds to a fixed point $(A^*, B^*, S^*, C^*, E^*) = (0.4294,\ 0.049\,98, 0.4294, 0.4294,\ 0.049\,98)$ for all values of t lying between 0 and 1. The linearization of the equations about this fixed point gives two eigenvalues, $\lambda_b = 2.7965$ (corresponding to swollen bulk state) and $\lambda_\phi = 2.1583$. Thus the point is the expected symmetrical special point which describes the polymer at the unbinding transition with $\nu = \nu_b$ and the crossover exponent $\phi_s = 0.7481$ and $\alpha = 0.6653$. In the $w - u$ plane, the phase diagram shown in Figs. 3 and 4, the line $w = w^*(u,t)$ corresponding to this point is shown by a full line.

(5) As noted above, the collapse transition in the bulk solution occurs when the initial conditions are such that $A^* = B^* = \frac{1}{3}$. Solving Eqs. (3.1), (3.2), (3.6a), and (3.6b) we find that these values are found for $x_\theta = 0.229\,157\ldots$ and $u_\theta = 3.316\,074.\ldots$ Using these values of $x = x_\theta$ and $u = u_\theta$ in the recursion relations of Eqs. (3.1)–(3.5) we located the other fixed points which lie on the line $w = w^*(u,t)$ and are multicritical.
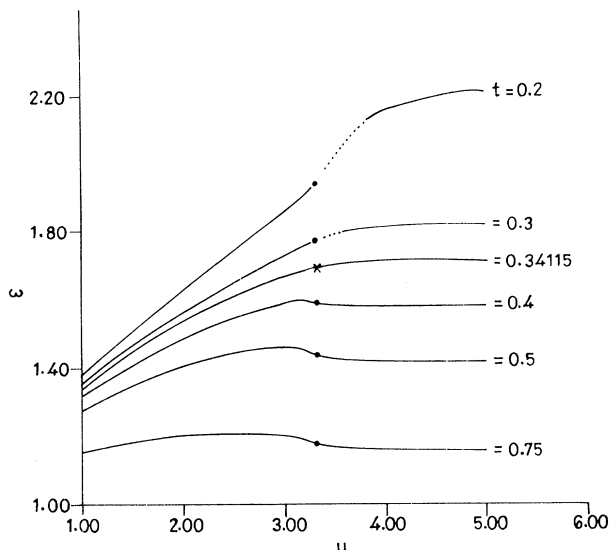
(i) When $w = w^*(u = u_\theta, t)$ and $t < t^*$ (=0.341 15. ...) the iterations of the equations lead to a fixed point $(\frac{1}{3}, \frac{1}{3}, 0.4477, 0.4528, 0.0815)$. The linearized equations have three repulsive directions with eigenvalues

$$\lambda_{SM} = 2.2715, \quad \lambda_{b1} = 3.7037, \quad \lambda_{b2} = 2.2222\ .$$

Note that the last two values are the same as those found for the bulk θ point [see (2) above].

(ii) For $w = w^*(u_\theta, t)$ where $t > t^*$, the fixed point $(\frac{1}{3}, \frac{1}{3}, 0, 0, 0.3693)$ is found. Again we find three eigenvalues greater than one, where $\lambda_{SM} = 3$ and the other two λ_{b1} and λ_{b2} are the same as those given above.

(iii) For $w = w^*(u_\theta, t^*)$ we find the symmetric "desorbed and collapsed" fixed point, i.e., $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. This point has been found to have four eigenvalues greater than one. These values are

$$\lambda_{SM1} = 2.7628, \quad \lambda_{SM2} = 1.4964\ ,$$

and the other two are λ_{b1} and λ_{b2} given above.

All these points are multicritical special θ points and are found at different values of t. In Fig. 5 we plot $w^*(u_\theta, t)$ as a function of t. The line is a multicritical line having a higher-order multicritical point at $t = 0.341\,15$.

(6) For $u > u_\theta$ we have the following situations.

(i) If $t < t^* = 0.341\,15.\ldots$ and $u_\theta < u(t)$ we find the unbinding transition takes place between an adsorbed phase of a SAW and the free collapsed globule phase at $w = w^*(u,t)$. The fixed point that corresponds to this transition is $(0, 0.3568, 0.618\,03, 0, 0)$. BV [16] have reported this feature and have attributed it to the coexistence between the adsorbed SAW and the globule phase.

(ii) For $t < t^*$ and $u > u_c(t)$ the transition at $w = w^*(u,t)$ is governed by the fixed point $(0, 0.3568, 0, 0, 0.3568)$. There are two relevant eigenvalues associated with this point. They are $\lambda_1 = 4.0$ and $\lambda_2 = 3.0$. Note that λ_1 corresponds to the bulk collapse phase and $\lambda_2 = \lambda_{SM}$ found in (5 ii) above.

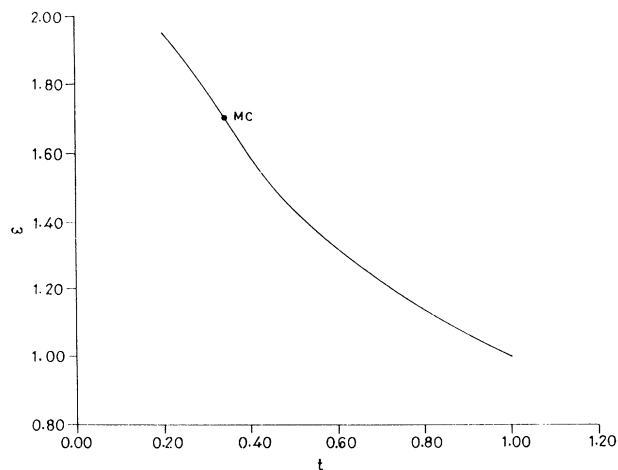(iii) For $t > t^*$ we do not find the behavior given in (i).

FIG. 4. Special adsorption lines are shown in w-u plane for several values of t. The multicritical (tetracritical) point is shown by a full circle. The region (indicated by dotted line) of coexistence of the adsorbed SAW and the (bulk) globule phase is shown to exist for $t < t^* = 0.341\,15.\ldots$ At $t = t^*$ the multicritical point shown by the cross represents a special symmetric desorbed and collapsed fixed point and is of higher order (pentacritical) than at other values of t.

FIG. 5. Critical values of w as a function of t corresponding to the multicritical points. The point MC, which is a pentacritical point, separates the two tetracritical lines.

Instead, for the whole range of $u > u_\theta$ we find the behavior given in (ii).

IV. THE TRUNCATED 5-SIMPLEX LATTICE

The basic geometrical unit of the construction of a truncated 5-simplex lattice is hypertetrahedron of five corner vertices and bonds between every pair of vertices, termed as nearest neighbor [21]. The hypertetrahedron

of first and $(r+1)$th order are shown in Fig. 6. The shaded regions represent the surface and nearest-neighbor bonds on the surface are shown by dashed lines while those of the bulk are shown by full lines. It is equivalent to a 4D Sierpinski gasket whose surface is a 3D Sierpinski gasket. The restricted partition functions relevant to our present study are shown in Fig. 7 and their corresponding recursion relations are given below:

$$A_{r+1}= A^2+3A^3+6A^4+6A^5+18A^2B^2+96A^2B^3+12A^3B+78A^3B^2+30A^4B+132AB^4+132B^5 , \tag{4.1}$$

$$B_{r+1}= A^4+2A^5+13A^4B+4A^3B+32A^3B^2+88A^2B^3+22B^4+220AB^4+186B^5 , \tag{4.2}$$

$$S_{r+1}=132E^4B+44AE^2F^2+88CE^3B+32C^2E^2B+C^2A+12C^3EB+2C^4B+12SAE^2+64SAE^2F+8SCAE$$
$$+24SCAEF+4SC^2A+4SC^2AF+S^2+6S^2F^2+42S^2AE^2+24S^2CAE+6S^2C^2A+2S^3+4S^3F+2S^4 , \tag{4.3}$$

$$C_{r+1}=132E^3FB+CA+18C^2EB+6C^3B+6C^3FB+132SE^3B+96SCE^2B+3SCA+54SC^2EB+12SC^3B$$
$$+6S^2AE+18S^2AEF+6S^2CA+6S^2CAF+12S^3AE+6S^3CA , \tag{4.4}$$

$$E_{r+1}=22E^3B+186E^3FB+22AEF^3+66CE^2FB+C^3B+132SE^3B+22SAEF^2+66SCE^2B+16SC^2EB$$
$$+3SC^3B+3S^2AE+16S^2AEF+S^2CA+3S^2CAF+7S^3AE+2S^3CA , \tag{4.5}$$

$$F_{r+1}=22F^4+186E^4B+132AE^2F^2+88CE^3B+C^4B+88SAE^2F+32S^2AE^2+12S^2CAE+2S^2C^2A+4S^3F+S^4 . \tag{4.6}$$

We have dropped the subscript r from the right-hand side of the equations.

Equations (4.1) and (4.2) correspond to the polymer chain in the bulk and have already been studied by us [21] in detail. They are decoupled from the surface and remain so under iteration. The starting weights of these equations are

$$A_1=x^2+3x^3u+6x^4u^3+6x^5u^6 , \tag{4.7a}$$

$$B_1=x^4u^4+2x^5u^7 , \tag{4.7b}$$

$$S_1=x^2w^2+2x^3w^3u+x^3t^2u+4x^4wt^2u^3$$
$$+2x^4w^4u^3+6x^5w^2t^2u^6 , \tag{4.7c}$$

$$C_1=x^2t+3x^3wtu+6x^4wtu^3+6x^5w^3tu^6 \tag{4.7d}$$

$$E_1=x^4w^2tu^4+2x^5w^3tu^7 , \tag{4.7e}$$

$$F_1=x^4w^4u^4+2x^5w^2t^2u^7 . \tag{4.7f}$$

In contrast to the case of 4-simplex lattice, the phase diagram for 5-simplex lattice remains qualitatively unaltered due to variation in the value of t. All the results reported here are, therefore, for only one value of t, i.e., $t=0.5$. Once again our main motivation is to explore the multicritical behavior of the polymer chain around the special (adsorption) line $w=w^*(u,t)$. For simplicity, we divide the parameter space into three regions depending on the value of surface attraction parameter.

A. Desorbed phase

When $w<w^*(u,t)$, the polymer remains in desorbed phase. The fixed point $(A^*,B^*,S^*,C^*,E^*,F^*)$ $=(0.3265,0.0279,0,0,0,0)$ corresponds to bulk state with

$\nu=0.6049$ and $\alpha=0.5934$ as reported earlier [21]. This fixed point is reached when $w<w^*(u,t)$ at $x=x_c(u)$. In Fig. 8 we plot x_c as a function of u and note that the polymer chain is in swollen state for all values of u [21].

B. Special adsorption line

At $w=w^*(u,t)$ and $x=x_c(u)$ the fixed point $(0.3265,0.0279,0.3265,0.3265,0.0279,0.0279)$ is reached. The linearization of equations about this fixed point gives two eigenvalues greater than one. The point is identified as the tricritical point of adsorption transition. The two eigenvalues are

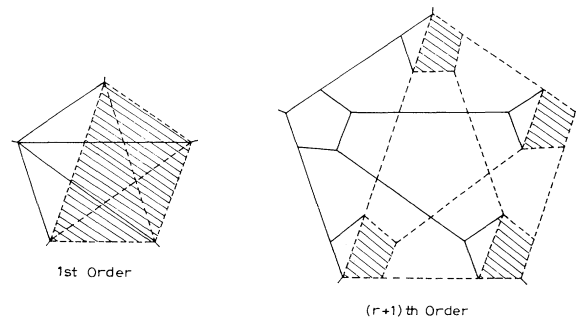$$\lambda_b=3.1319, \quad \lambda_{ST}=2.5858 .$$

1st Order

(r+1)th Order

FIG. 6. Graphical representation of a truncated 5-simplex lattice of first and $(r+1)$th order. The shaded regions represent the adsorbing surface. The nearest-neighbor bonds on the surface are shown by dashed lines while those of the bulk are shown by full lines.
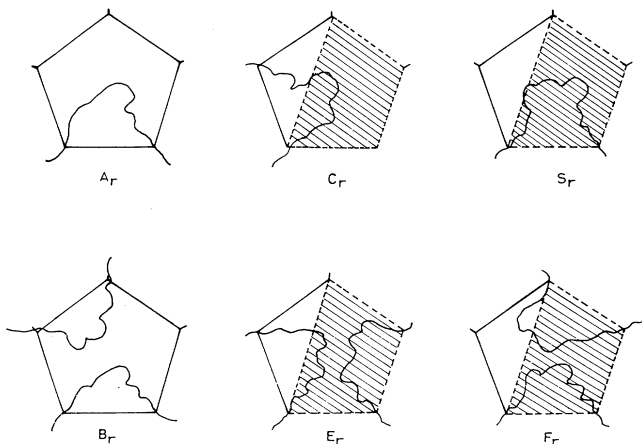
FIG. 7. Diagrammatic representation of the restricted partition functions for the rth-order hypertetrahedron. Out of six diagrams, two (A and B) represent the bulk generating functions for the polymer chain and the others (C, S, E, and F) represent the surface functions.

The crossover exponent

$$\phi = \frac{\ln\lambda_{ST}}{\ln\lambda_b} = 0.8321 \ .$$

In Fig. 9, in which we have plotted x_c as a function of w for different u, the tricritical point forms a line shown by the dashed line. We note that for each u we have a value of $w = w^*(u,t)$ such that for $w > w^*(u,t)$ the adsorbed phase (discussed below) is found to exist for $x < x_c(u)$. For a given $u,w < w^*(u)$, and $x = x_c$, part of the curve represents the desorbed phase and the point $w = w^*(u,t)$ and $x = x_c(u)$ is a tricritical point. We also note the existence of another curve indicated by the dotted line in Fig. 9. This is a tricritical line of surface collapse transition.
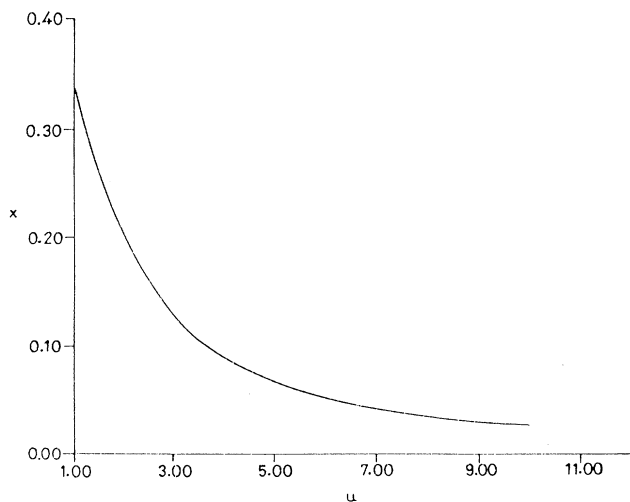

FIG. 8. Critical fugacity x for a linear polymer chain on the truncated 5-simplex lattice as a function of the monomer-monomer attraction parameter u.

C. Adsorbed phase

When $w > w^*(u,t)$ the polymer chain is in adsorbed phase. As shown in Fig. 9, the adsorbed region of the phase diagram on x-w plane has the swollen and collapsed globule phases separated by the θ line. For $w \gg w^*(u,t)$ the θ line is found at $u = u_\theta = 3.316\,074$. The adsorbed phase for $u < u_\theta$ is in a swollen state and for $u > u_\theta$ it is in the collapsed globule phase. These results are in agreement with the bulk region of the phase diagram of the 4-simplex lattice. However, in contrast to the bulk 4-simplex lattice result, the θ line of the adsorbed phase does not meet the special adsorption line at $u = u_\theta$. Our calculation indicates that as $w \geq w^*(u,t)$, the θ line bends and approaches very slowly the line $w = w^*(u,t)$ as the value of u is increased. Even for $u \geq 200$ we find that the two lines have not merged. However, the separation between the two at such a large value of u is very small and may not be detectable by any experiment. This feature of the phase diagram is also clear in Fig. 10 in which we plot the two tricritical lines on u-w plane. The region of coexistence of three phases
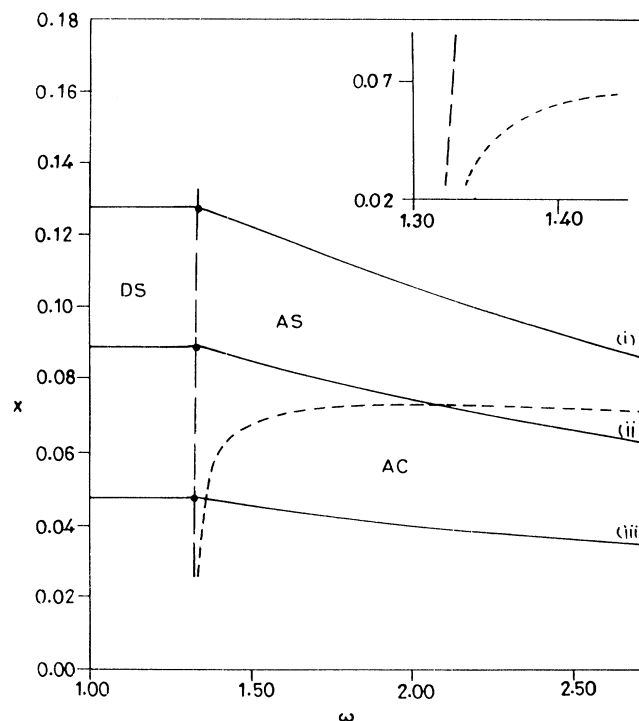

FIG. 9. The x-w phase diagram at $t = 0.5$ for the truncated 5-simplex lattice. The special adsorption line is indicated by the long-dashed line and the θ line which separate the adsorbed polymer chain in swollen (AS) and collapsed (AC) (globular) phases are indicated by the short-dashed line. Full lines marked (i), (ii), and (iii) represent the critical value of the fugacity for the polymer chain for different values of $u = 3.0$, 4.0, and 6.3885, respectively. Note that the value of x remains constant in the desorbed region and decreases as w is increased in the adsorbed region for each u. The tricritical point of adsorption is indicated by full circle. The insertion on the top right-hand side of the figure gives on a magnified scale the position of the two tricritical lines.
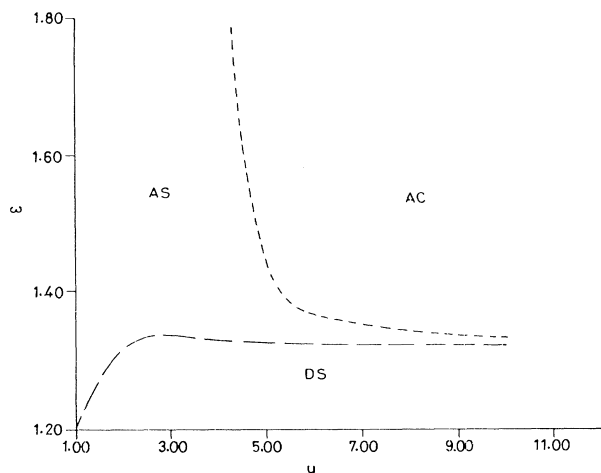
FIG. 10. The w-u phase diagram at $t = 0.5$ for the truncated 5-simplex lattice. The two tricritical lines are indicated by long-dashed (adsorption line) and short-dashed (θ line) lines. These two lines do not appear to meet at any finite value of u.

of the polymer chain, viz. the bulk swollen, the adsorbed swollen, and the collapsed globule phases are separated by these lines. We find that the line $w = w^*(u,t)$ at small u rises and attains a maxima at around $u = 2.3$ for $t = 0.5$. For $u > u_\theta$ the line $w = w^*(u,t)$ becomes almost independent of u.

V. DISCUSSIONS

The truncated 4- and 5-simplex lattices considered here exhibit contrasting behaviors. The collapsed globule phase transition is found to take place on a 4-simplex lattice while the 5-simplex lattice does not show this transition. This is because the geometrical nature of the 5-simplex lattice is such that at least one vertex of each first-order unit of the lattice remains unoccupied. Since the surface of the 5-simplex lattice is a truncated 4-simplex lattice, the collapse transition will take place in adsorbed phase of this lattice. On the other hand, the surface of the 4-simplex lattice is a truncated 3-simplex lattice; this transition cannot take place in the adsorbed phase. These features of the two lattices are obvious in the phase diagrams plotted above.

In the w-u phase diagram of a surface interacting SASAW models on 4-simplex lattice plotted in Figs. 3 and 4, the adsorbed phase is always in a swollen state with a radius of gyration exponent equal to that of a truncated 3-simplex lattice. The bulk phase has two regions; the region of swollen state separated from the collapsed globule state [by a tricritical line (θ line)]. The θ line is at $u = u_\theta = 3.316074$ and runs parallel to the w axis, i.e., remains unaffected due to the surface interaction. The point where it meets the adsorption line $w = w^*(t,u)$ is a multicritical point. This multicritical point is characterized by three different fixed points depending on the values of t which measures the repulsive strength of the adjacent layer to the wall. The nature of the $w = w^*(u,t)$ line near this multicritical point also depends on the value of t.

When $t < t^* = 0.34115$, the portion of line $w = w^*(u,t)$ which separates bulk swollen from the adsorbed phase is almost linear with positive slope. At the multicritical (tetracritical) point the line rises rather sharply. In a region specified by $u_\theta < u < u_c$, where the value of u_c depends on t, we have the coexistence between the adsorbed SAW and the collapsed globule phase. This region is shown in Figs. 3 and 4 by a dotted line. For $u > u_c(t)$ the line $w = w^*(u,t)$ becomes almost flat. The value of $u_c(t)$ decreases as t is increased and becomes equal to that of u_θ at $t = t^* = 0.34115$. At $t = t^*$ the multicritical point becomes a symmetric "desorbed and collapsed" pentacritical point having four eigenvalues greater than one.

For $t > t^*$ the line $w = w^*(u,t)$ has a different shape than for $t < t^*$. The line appears to have a maximum at $u \lesssim u_\theta$. It drops rather sharply [see Fig. 3(b) for $t = 0.5$] in contrast to the case of $t < t^*$ at the multicritical point. The multicritical (tetracritical) point in this region is described by a different fixed point. Further, in contrast to the case of $t < t^*$, the line $w = w^*(u,t)$ for $u > u_\theta$ separating the bulk collapsed and adsorbed phases shows the decreasing tendency as u is increased. In Fig. 5 we display on the w-t plane the two tetracritical lines separated by a *pentacritical* point. This pentacritical point separates a region where the point in which the adsorbed (swollen) polymer coexists with both the desorbed polymer and the desorbed globule is a tetracritical point from one in which it appears as the intersection of three lines of a continuous transition.

The behavior of special adsorption line described above can be understood from contributions of different coexisting polymer configurations (see Fig. 2) to the bulk and surface free energies. When both the adsorbed and desorbed phases are in swollen state, the adsorption line has same nature in the w-u plane for all values of t, although the slope of the line decreases as t is increased. At $t = 1$ the adsorption takes place at $w = 1$ and the adsorption line in the w-u plane has a zero slope. This is due to the fact that at $t = 1$ and $w = 1$ the surface is just a part of the bulk lattice. As t is increased, w has to be increased to have adsorption, and since u in such a situation favors the bulk phase [owing to presence of some B configuration (Fig. 2)] we have to increase the surface interaction to counteract this tendency. In the other extreme, i.e., when $u \gg u_\theta$, the adsorption line has a zero slope. Here the coexisting polymer configurations are those given by B and E in Fig. 2. The free energies due to these two configurations balance each other at all u values and therefore the line remains insensitive to the value of u. It is only in the neighborhood of the special θ point that the line becomes sensitive to the value of t and u.

When $t < t^*$, the surface layer is strongly repulsive and prohibits the occurrence of the E configuration in the neighborhood of the θ point. The adsorbed state is still given by the configuration S, although the bulk is in the globular compact phase. Thus to balance the free energy w has to be increased. However, at $t > t^*$ the surface is only moderately repulsive and therefore at certain value of w the polymer configuration given by E is formed. This lower value of w is needed to balance the bulk free

energy at the special θ point. The formation of B and E configurations near the θ point gives rise to pretransitional effects [shown in Figs. 3(b) and 4] for $t > t^*$.

A casual look at Fig. 3(b) and 4 may give the impression of the existence of a reentrant adsorbed phase as u is increased. One should, however, realize that these figures are merely a projection on the w-u plane of three-dimensional figures in which the third dimension is given by x. BV [16] have reported the phase diagram given in Fig. 3(a). Because of the initial weights given to different chain configurations, they did not find the other features of the phase diagram.

The phase diagram on the 5-simplex lattice given by Fig. 10 has features which differ from those of the 4-simplex lattice. As already pointed out, the whole bulk region of the phase diagram is in a swollen state. The adsorbed region has swollen and collapsed globule phases separated by a θ line shown by a dashed curve. This line does not meet the adsorption tricritical line even for a very large value of u. Since the special adsorption line is described by only one fixed point, the parameter t has no qualitative effect on the phase diagram.

However, if we assume that a polymer chain is at criticality for a given x_a and u in bulk and we put $A^* = 0.3265. . .$ and $B^* = 0.0279. . .$ in other recursions and then iterate the system, the situation and corresponding phase diagram change drastically. Here we will concentrate ourselves once again on the adsorption special line and its neighborhood. Our findings are as follows.

(i) At $w = w^*(t,u)$, $x = x_c(u)$, and $u < u_c = 6.3885$, the fixed point (given in Sec. IV B) is found and the characteristic exponents remain the same.

(ii) A fixed point $(A^*, B^*, S^*, C^*, E^*, F^*)$ $= (0.3265, 0.0279, 0, 0, 0, 0.3568)$ is reached at $w = w^*(t,u)$, $x = x_c(u)$, and $u > u_c = 6.3885$. This implies the coexistence with the bulk swollen and the surface collapsed. Linearization around the fixed point yields two eigenvalues greater than one, i.e., $\lambda_1 = 3.1319$ and $\lambda_{SM} = 4$, which gives the crossover exponent $\phi = 0.8235$.

(iii) When $w = w^* = 1.4929. . .$, $x = x_c(u) = 0.4744. . .$, and $u = u_c = 6.3885. . .$ the fixed point $(A^*, B^*, S^*, C^*, E^*, F^*) = (0.3265, 0.0279, 0.2823, 0.1686, 0.0521, 0.3327)$ is achieved. Linearization around the fixed point gives three eigenvalues greater than one. We identify it as the multicritical point where three phases become identical. The eigenvalues are

$$\lambda_1 = 3.1319, \quad \lambda_{SM1} = 3.7370, \quad \lambda_{SM2} = 2.2308 .$$

It should be noted that the last two eigenvalues are very close to the eigenvalues discussed in the 4-simplex lattice at the θ point. This indicates that the adsorbed phase tricritical line (corresponding to collapse transition) seems to meet at this point. However, as discussed in Sec. IV, the fluctuations may not allow this to happen.

ACKNOWLEDGMENTS

*Present address: Department of Physics, Tripura University, Agartala 799 004, India.

[1] The Wonderful World of Stochastics (Studies in Statistical Mechanics 12), edited by M. F. Shiesinger and G. H. Weiss (North-Holland, Amsterdam, 1988).

[2] P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, 1979); J. Phys. (Paris) 36, 155 (1975).

[3] D. Dhar, J. Math. Phys. 19, 5 (1978).

[4] D. Amit, G. Parisi, and L. Peliti, Phys. Rev. B 27, 1635 (1983).

[5] D. J. Klein and W. A. Seitz, J. Phys. (Paris) Lett. 45, L241 (1984).

[6] D. Dhar and J. Vannimenus, J. Phys. A 20, 199 (1987).

[7] I. S. Chang and Y. Shapir, J. Phys. A 21, L903 (1988).

[8] Ferenc Iglói, Phys. Rev. A 43, 3194 (1991).

[9] Scaling Phenomena in Disordered System, Vol. 133 of NATO Advanced Study Institute, Series B: Physics, edited by R. Pymn and A. Skjeltorp (Plenum, New York, 1986).

[10] Fractals in Physics, edited by L. Pietronero and E. Tosatti (North-Holland, Amsterdam, 1986).

[11] P. G. de Gennes, Adv. Colloid Interface Sci. 27, 189 (1987).

[12] E. Bouchaud, A. Aurvray, J. P. Cotten, M. Daoud, B. Far-

noux, and G. Jannink, Prog. Surf. Sci. 27, 5 (1988).

[13] D. Napper, Polymeric Stabilization of Collidal Dispersions (Academic, New York, 1983).

[14] M. D. Housley and K. K. Statruly, Dynamics of Biological Membranes (Wiley, New York, 1982).

[15] J. L. Cardy, Nucl. Phys. B 240, 514 (1984); T. W. Burkhardt and E. Eisenriegler, ibid. 316, 559 (1989).

[16] E. Bouchaud and J. Vannimenus, J. Phys. (Paris) 50, 2931 (1989).

[17] S. Kumar, Y. Singh, and D. Dhar, J. Phys. A (to be published).

[18] S. Cattarinussi and G. Jug, J. Phys. A 23, 2701 (1990).

[19] A. R. Veal, J. M. Yeomans, and G. Jug, J. Phys. A 23, L109 (1990); Oxford University Report, 1991 (unpublished).

[20] E. Orlandini, F. Seno, A. L. Stella, and M. C. Tesi (unpublished); D. P. Foster, E. Orlandini, and M. C. Tesi, J. Phys. A 25, L1211 (1992).

[21] S. Kumar, Y. Singh, and Y. P. Joshi, J. Phys. A 23, 2987 (1990); S. Kumar and Y. Singh, ibid. 23, 5118 (1990); Phys. Rev. A 42, 7151 (1990).

[22] D. Dhar, J. Math. Phys. 18, 577 (1977); D. R. Nelson and M. E. Fisher, Ann. Phys. (N.Y.) 91, 226 (1975).