

Surface adsorption and collapse transition of linear polymer chains

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Abstract. The critical behaviour of surface adsorption and collapse transition of a flexible self-attracting self-avoiding polymer chain is examined. Depending upon the underlying lattice and space dimensionality, phase diagrams that exhibit many different universality domains of critical behavior are found. We discuss these phase diagrams and the values of the critical exponents found from different theoretical methods.

Keywords. Surface adsorption; polymers chains; fractal lattice; Euclidean lattice.

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1. Introduction

Long neutral flexible polymers in solutions often exhibit remarkably universal properties essentially independent of the chemical nature of the polymer and of the solvent. The universality has found its full recognition and usefulness when polymers have been shown to behave, in the asymptotic limit of infinite molecular weight, as scale invariant critical objects and when the renormalization group ideas have been introduced to polymer theory. The criticality of chain conformation implies not only the existence of critical indices but also of scaling laws for thermodynamic quantities characterizing polymer solution, such as for instance, the osmotic pressure. Since the introduction of an analogy between the polymer theory and a Lagrange field theory of Ginzburg–Landau–Wilson type in the limit where the number of components of the field n goes to zero, many renormalization procedures have been proposed [1].

The physical properties observable on a polymer chain are calculated as statistical averages over all possible configurations of the polymer and these configurations are obtained by mapping the polymer chain onto a walk embedded in an appropriate lattice. Depending upon the physical situation, approximate geometrical restrictions are imposed on these walks. For example, a model of self-avoiding walk (SAW) simulates a polymer chain in a good solvent, while the model of a self-attracting self-avoiding walk (SASAW) represents a polymer chain in a poor solvent that can undergo a collapse transition when the chain contracts from an extended state to a globule state when the temperature is lowered. In a good solvent, monomer–monomer interaction is dominated by short range repulsion (excluded volume interaction), while in a poor solvent the short range repulsion and attraction between monomers at relatively large separation compete with each other.

Therefore the transition from an extended state to a compact globule phase in a poor solvent can be viewed as a gas-liquid transition.

Quantities of interest in the case of one-chain problem are the number of distinct walks C_N of N steps starting at the same origin, the number of closed loops P_N of N steps and the mean radius of gyration $(R^2)^{1/2}$. In the asymptotic limit of infinite molecular weight $C_N = q_{\text{eff}}^N N^{\gamma-1}$, $P_N = q_{\text{eff}}^N N^{-(2-\alpha)}$ and $R \propto N^\nu$ where q_{eff} is system dependent microscopic variable and γ , α and ν are critical indices. All these configurational properties of a polymer on a lattice are deduced from the generating function $G(x, T) = \sum_{N, N_u} \Omega(N, N_u) x^N u^{N_u}$ where $\Omega(N, N_u)$ are the number of different configurations per site of a polymer chain having N monomers, N_u the number of nearest neighbors, x is the fugacity associated with each step of the walk, and the interaction strength u is related to the temperature by $u = \exp(\epsilon_u/k_\beta T)$. Here $\epsilon_u (> 0)$ and k_β denote the attractive energy associated with a pair of nearest neighbor bonds and the Boltzmann constant, respectively.

In critical-phenomena parlance, the infinite random walk (RW) is equivalent to a Gaussian system at its critical point with $\nu = 1/2$ independent of space dimension d (of Euclidean lattice). The SAW is a critical $O(n)$ model with $n \rightarrow 0$ component. The SASAW changes the behavior of the phase transition of the SAW from second order to first order into a collapsed phase at low temperatures [2]. At the intermediate temperature (θ -point) its behavior is described by a tricritical point of $O(n)$; $n \rightarrow 0$ spin system. In this regime the upper critical dimension changes from four to three with the consequence that for $d = 3$, ν is equal to $1/2$ 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 [3-6].

When a polymer chain is in the vicinity of an attractive surface its configurational properties may get strongly modified relative to its 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 and experimental studies [7] 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 as shown in figure 1. The thickness of the adsorbed layer ξ diverges as T_a is approached from below;

$$\left. \begin{aligned} \xi &\propto \left(1 - \frac{T}{T_a}\right)^{-x} & T < T_a \\ \frac{M}{N} &\propto \left(1 - \frac{T}{T_a}\right)^y & T < T_a \end{aligned} \right\} \quad (1)$$

where M is the number of monomers on the surface. M/N goes to zero as T_a is approached. 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 the surface is shown to behave as

$$M \sim \begin{cases} (T_a - T)^{(1/\phi)-1} & T < T_a \\ N^\phi & T = T_a \\ (T - T_a)^{-1} & T > T_a. \end{cases} \quad (2)$$

Linear polymer chains

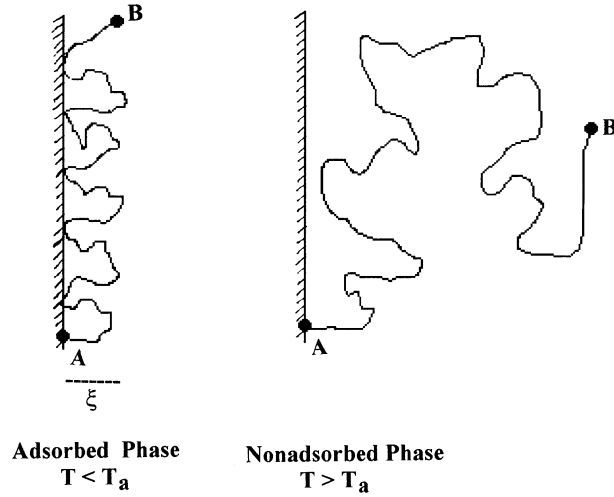


Figure 1. Adsorbed and nonadsorbed phases of a polymer in a good solvent.

Here ϕ is the crossover exponent. Comparing with eq. (1) one gets

$$\left. \begin{aligned} y &= \frac{1}{\phi} - 1 \\ x &= \frac{z}{\phi} \end{aligned} \right\}. \quad (3)$$

The surface also introduces anisotropy in the distribution of monomers. For instance, the radius of gyration parallel and perpendicular to the plane are now different. For the adsorbed layer $R_{\parallel} \propto N^{\nu_{d-1}}$ whereas R_{\perp} is independent of N . Here R_{\parallel} and R_{\perp} represent, respectively, the radius of gyration of a surface adsorbed polymer chain along and perpendicular to the surface. For the distinct walks now we have

$$\left. \begin{aligned} C_N^{\perp} &= q_{\text{eff}}^N N^{\gamma_{\perp}-1} \\ \text{and} \\ C_N^{\parallel} &= q_{\text{eff}}^N N^{\gamma_{\parallel}-1} \end{aligned} \right\}, \quad (4)$$

where C_N^{\perp} and C_N^{\parallel} represent the number of distinct walks when one and both ends are fixed on the surface respectively.

When the polymer chain is in a poor solvent, it exhibits phase diagrams characterized by many different universality domains of critical behavior. This is due to a competition between solvent induced monomer–monomer attraction and the surface–monomer interaction. The two tricritical lines, one corresponding to θ -point and another to the adsorption point, may interact with each other and lead to the existence of higher order critical points. Understanding of these higher order multicritical points and the nature of phase diagrams is one of the challenging problems of this field.

Theoretical methods which have been used to study polymer adsorption include renormalization group [8], transfer matrix [9], Monte Carlo [10, 11], exact enumeration [12, 13], and series expansion techniques [14]. In case of two dimensions many exact results have been found through conformal field theory [15–17] and using conformal invariance prediction in conjunction with the Bethe ansatz solution of associated lattice

models [18]. Many exact results have also been found for the case of fractal lattices using real space renormalization group (RSRG) method [19, 20].

2. Surface interacting polymer chain on a fractal lattice

We first consider a polymer chain immersed in a fractal container represented by a truncated n -simplex lattice. The truncated n -simplex lattice is defined recursively [21]. The graph of the zeroth-order truncated n -simplex lattice is a complete graph on $(n + 1)$ points. The graph of $(r + 1)$ th order lattice is obtained by replacing each of the vertices by the r th order graph by a complete graph on n points. Each of the new 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

$$d_F^{(b)} = \frac{\ln n}{\ln 2}, \quad \tilde{d}^{(b)} = \frac{2 \ln n}{\ln(n + 2)}. \quad (5)$$

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

- 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. (5) where n is replaced by $(n - 1)$.
- The odd simplex lattices do not appear to have collapse transition for a SASAW model [22]. 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.

To perform a RSRG calculation on a polymer chain interacting with a surface, we study how the characteristic quantities describing a walk 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 of a chain in a good solvent are usually calculated using only one parameter, which represents fugacity per monomer of the polymer chain [23]. When the polymer chain is in a poor solvent one needs an additional parameter describing the strength of the nearest neighbor monomer interaction. For surface interacting polymer chain it is convenient to introduce two more parameters describing the strength of the interaction of a monomer in the surface layer and in the adjacent one [19]. Thus for a surface interacting SASAW one needs four parameters.

Let us consider a long flexible neutral polymer chain situated on the truncated n -simplex lattice and make one surface of it attractive. This surface henceforth will be referred to as a (impenetrable) wall. To each N -step walk having N_s steps along the wall, N_t steps lying in the surface layer adjacent to the wall and with N_u number of nearest neighbors we assign the weight $x^N \omega^{N_s} t^{N_t} u^{N_u}$. Here $\omega = \exp(-\epsilon_s/k_\beta T)$ and $t = \exp(-\epsilon_t/k_\beta T)$ are the Boltzmann factors corresponding to surface energy ϵ_s denoting the interaction of a monomer with the wall and ϵ_t the interaction energy of a monomer with the adjacent layer. The other two variables x and u have already been defined. We restrict the attractive interaction to bonds within a first order unit of the fractal lattice. The global generating function for

Linear polymer chains

the problem we want to study can be written as

$$\begin{aligned} G(x, u, \omega, t) &= \sum_{\text{all walks}} x^N \omega^{N_s} t^{N_t} u^{N_u} \\ &= \sum_{N, N_s, N_t, N_u} C(N, N_s, N_t, N_u) x^N \omega^{N_s} t^{N_t} u^{N_u} \end{aligned} \quad (6)$$

where $C(N, N_s, N_t, N_u)$ represents the total number of configurations of all walks.

For fractal lattices it is possible to write the generating function in terms of 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 r th 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 systems depending on the initial conditions, we can find the eigenvalues of the transformation matrix which gives the characteristic exponent of the system.

Here we discuss the results found on truncated 4- and 5-simplex lattices. These two lattices exhibit contrasting behavior and therefore represent two different scenarios which may arise in real systems. The collapsed globule phase transition is found to take place on 4-simplex lattice while the 5-simplex lattice does not show this transition. This is because the geometrical nature (as shown below) of the 5-simplex lattice is such that at least one vertex of each first order unit of the lattice remains unoccupied [22]. Since the surface of the 5-simplex lattice is a truncated 4-simplex lattice, the collapse transition will take place in the adsorbed phase. 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. We therefore have a situation where the container acts as a poor solvent while the surface is a good solvent and in other case the bulk is a good solvent while the surface acts as a poor solvent. Such situations are experimentally realizable.

2.1 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 figure 2. The shaded regions represent the surface. 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. The bulk critical behavior including the θ -point for the SASAW model has been studied by Dhar and Vannimenus [24] and surface adsorption and collapse transition by Kumar and Singh [19]. The results given here are those of Kumar and Singh [19].

For the truncated 4-simplex lattice the generating function can be written in terms of a finite number of restricted partitions shown in figure 3. 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 r th generation one. The variables in

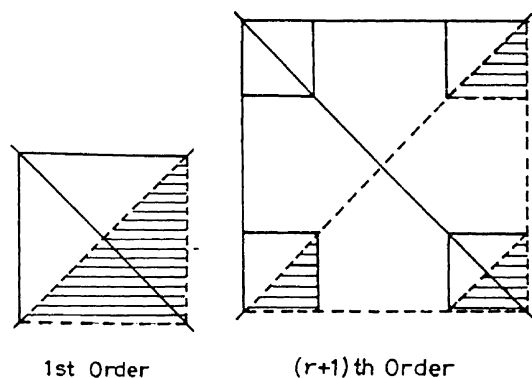


Figure 2. Graphical representation of a truncated 4-simplex lattice of first and $(r + 1)$ th order. The shaded regions represent the adsorbing surface. The nearest neighbor bonds on the surface are shown by dashed lines and those of the bulk by full lines.

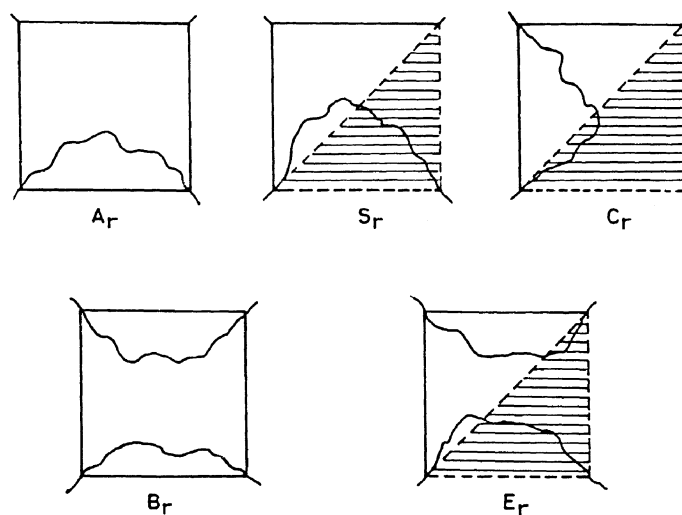


Figure 3. Diagrammatic representation of the restricted partition functions for the r th order tetrahedron. The internal structure of the tetrahedron is not shown. Only the corner vertices and the end points of the walks are shown. Out of five diagrams, two (A_r and B_r) represent the bulk generating functions for the polymer chain and the remaining three (S_r , C_r and E_r) represent the surface functions.

these expressions are just the partial generating functions corresponding to different polymer configurations for a given size of the fractal lattice. Linearizing the recursions near the non-trivial fixed points, the ones reached by the systems depending on the initial conditions, we can find the eigenvalues of the transformation matrix which give the characteristic exponents of the system.

The phase diagrams calculated using RSRG are shown in figure 4 for two different values of t . As has already been mentioned the adsorbed phase in this case is always in a

Linear polymer chains

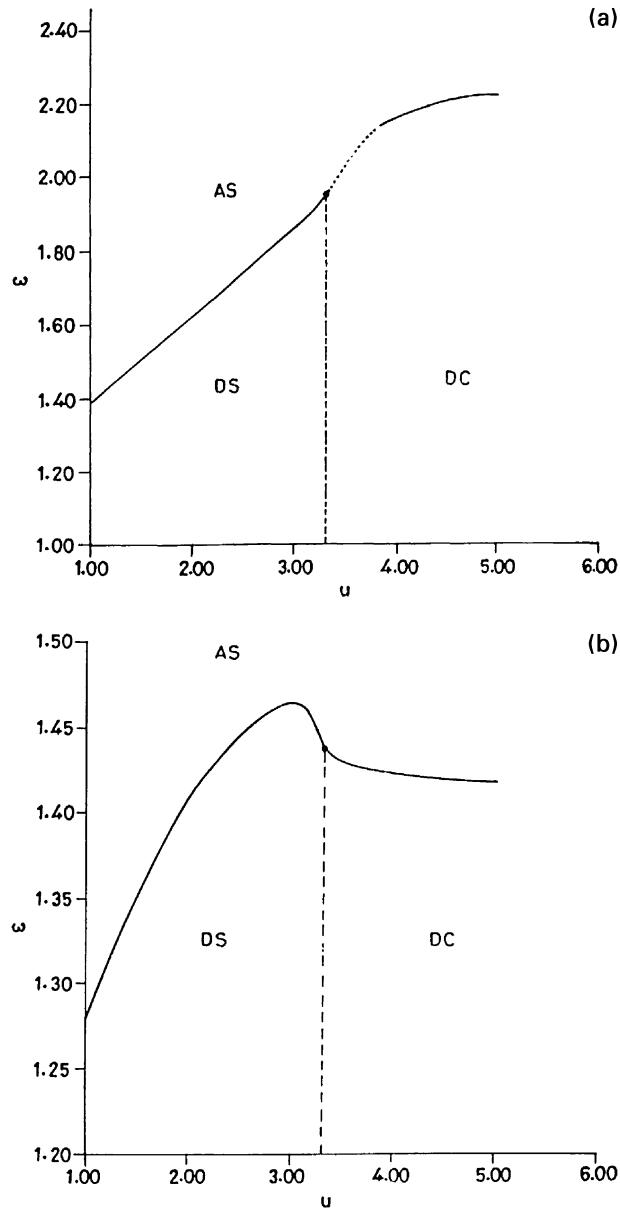


Figure 4. (a) The $\omega - u$ phase diagram at $t = 0.2$ for the truncated 4-simplex lattice. Regions marked by AS, DS and DC represent, respectively, the adsorbed polymer in swollen state, desorbed polymer in swollen and collapsed (globular) state. The dashed line which separates the bulk swollen and collapsed states 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 coexistence of adsorbed SAW and the (bulk) globule phases; (b) The $\omega - u$ phase diagram at $t = 0.5$ for the truncated 4-simplex lattice. Other notations have their meanings as in figure 4a.

swollen state with a radius of gyration exponent equal to that of truncated 3-simplex lattice (i.e. $\nu = 0.7986$). 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 ω -axis, i.e. remains unaffected due to the surface interaction. The point where it meets the adsorption line $\omega = \omega^*(t, u)$ is a multicritical point. This multicritical point is characterized by three different fixed points depending on the value of t which measures the repulsive strength of the adjacent layer to the wall. The nature of the $\omega = \omega^*(t, u)$ line near this multicritical point also depends on the value of t .

When $t < t^* = 0.34115$, the partition of line $\omega = \omega^*(u, t)$ 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 the figure by a dotted line. For $u > u_c(t)$ the line $\omega = \omega^*(u, t)$ 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 $\omega = \omega^*(u, t)$ has a different shape than for $t < t^*$. The line appears to have a maximum at $u \leq u_\theta$. It drops rather sharply (see figure 4b for $t = 0.5$) in contrast to the case of $t < t^*$ at the multicritical point. The tetracritical point is described by a different fixed point. Further, in contrast to the case of $t < t^*$, the line $\omega = \omega^*(u, t)$ for $u > u_\theta$ separating the bulk collapsed and adsorbed phases shows a decreasing tendency as u is increased. The two tetracritical lines on the $\omega - t$ plane meet at 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 $\omega = \omega^*(u, t)$ described above can be understood from contributions of different coexisting polymer configurations to the bulk and surface free energies. When both the adsorbed and desorbed phases are in swollen state, the adsorption line has the same nature in the $\omega - u$ plane for all values t , although the slope of the line decreases as t is increased. At $t = 1$, the adsorption takes place at $\omega = 1$ and the adsorption line in the $\omega - u$ plane has a zero slope. This is due to the fact that at $t = 1$ and $\omega = 1$ the surface is just a part of the bulk lattice. As t is increased, ω has to be increased to have adsorption, and since u in such a situation favors the bulk phase we have to increase the surface attraction 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 figure 3. 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 values of t and u .

When $t < t^*$, the surface layer is strongly repulsive and prohibits the occurrence of the E configurations 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, ω has to be increased. However, at $t > t^*$ the surface is only moderately

Linear polymer chains

repulsive and therefore at a certain value of ω the polymer configuration given by E is formed. Thus a lower value of ω 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 pentacritical effect.

A casual look at figure 4b may give the impression of the existence of a re-entrant adsorbed phase as u is increased. One should, however, realize that these figures are merely a projection on the $\omega - u$ plane of three dimensional figures in which the third dimension is given by x . The value of crossover exponent ϕ for the 4-simplex lattice is 0.7481.

2.2 Truncated 5-simplex lattice

The basic geometrical unit of the construction of a truncated 5-simplex lattice is the hyper tetrahedron of five corner vertices and bonds between every pair of vertices termed as nearest neighbor [23]. The hyper tetrahedron of the first and $(r + 1)$ th order are shown in figure 5. The shaded region represents 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 4D Sierpinski gasket whose surface is a 3D Sierpinski gasket. The restricted partition functions relevant to write the required generating function are shown in figure 6.

The phase diagram as found by Kumar and Singh [19] and reproduced in figure 7 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 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.

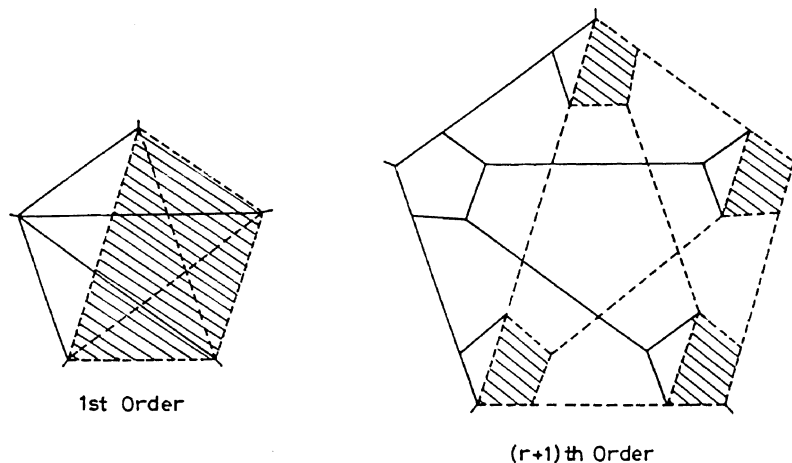


Figure 5. Graphical representation of a truncated 5-simplex lattice of first and $(r + 1)$ th order. The shaded regions represent the adsorbing surface. The nearest neighbor bonds on the surface are shown by dashed lines and those of the bulk by full lines.

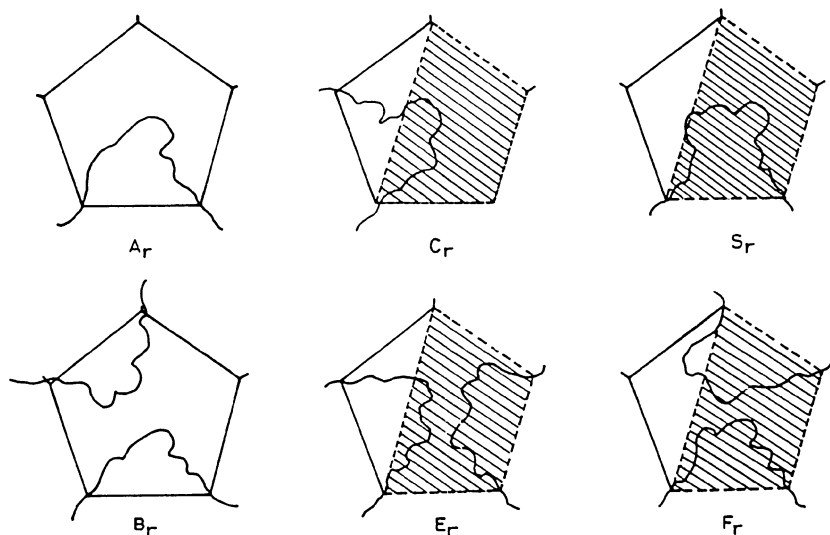


Figure 6. Diagrammatic representation of the restricted partition functions for the r th order hypertetrahedron. Out of six diagrams, two (A_r and B_r) represent the bulk generating functions for the polymer chain and the others (S_r , C_r , E_r and F_r) represent the surface functions.

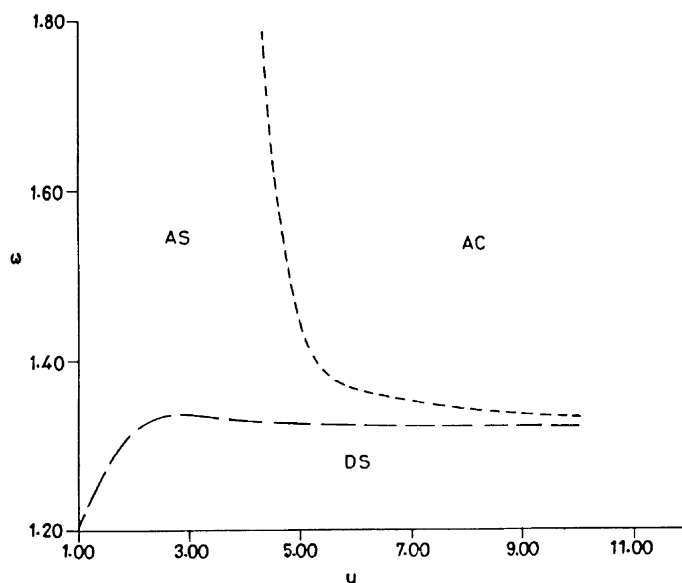


Figure 7. The $\omega - u$ phase diagram at $t = 0.5$ for the truncated 5-simplex lattice. The two tricritical lines are indicated by long dashes (adsorption line) and short dashes (θ -line). These two lines do not appear to meet at any finite value of u .

3. Surface interacting polymer chain on Euclidean lattices

In most calculations of critical behavior of surface interacting polymers on Euclidean lattices the model of SAW interacting with penetrable as well as impenetrable surfaces has been considered. The impenetrable surface corresponds to the adsorption of polymers at a solid–liquid interface, while the penetrable surface may correspond to the problem of polymer adsorption at a liquid–liquid interface. The crossover exponent ϕ , defined near the critical point in each model to describe the behavior of the phase transition, is believed to take different values for the two cases. For impenetrable surfaces, series analysis [13], the result of transfer matrix approach [24], and the conformal invariance theory [25] are consistent with a value for ϕ of 0.5 for $D = 2$; for $D = 3$, series analysis and Monte Carlo estimates [12, 26] give $\phi = 0.59$. For penetrable surface the scaling prediction $\phi = 1 - \nu$ gives $\phi = 0.25$ for $D = 2$ and $\phi = 0.41$ for $D = 3$.

The suitability of a cell RSRG to study the scaling behavior of surface interacting polymer chain described by a lattice SAW has recently been examined by Kumar and Singh [8]. They found that the method based on the central rule in which the starting point of the SAW is taken to be in the middle of one cell edge and which is also taken to be the surface (see figure 8), provides a suitable framework to account for the difference in the nature of the penetrating and impenetrating surfaces. On the other hand the method based on corner rule (see figure 9) which has been used by several workers [27] is not able to account for the change in distribution of monomers in the vicinity of an impenetrable surface. It is easy to realize that once a monomer lies on the surface, due to the surface being impenetrable the following segment has a restricted choice of orientation. This causes an entropy loss per monomer on the surface. The penetrable in which a walk spanning through the surface is allowed and there is no loss of entropy per monomer to take into account can therefore also be described by the corner rule.

The RSRG method is expected to give good results when the rescaling parameter (or the edge of a cell) $b \rightarrow \infty$. The value of ϕ found by Kumar and Singh [8] using the central rule and cell to cell transformation is close to 0.5 in agreement with an exact result. For the penetrable surface the value of ϕ has been found to decrease as b is increased. However, the value reported by Kumar and Singh [8] is still large compared to

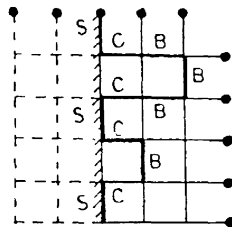


Figure 8. Schematic representation of a polymer configuration on a square lattice (central rule) in the presence of hard wall. The dashed part of the lattice is not present and therefore one half of the lattice is not accessible to the chain. The steps lying on the wall are denoted by S , and those on the layer adjacent to the wall, denoted by C . The steps in bulk are represented by B .

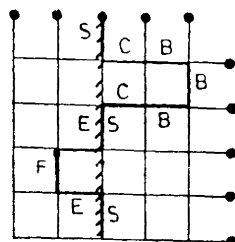


Figure 9. Schematic representation of a polymer configuration on a square lattice (central rule) in case of a penetrable surface where both sides across the surface are accessible to the chain. The steps lying on the wall are denoted by S . B and F represent the bulk partition functions while C and E represent the partition functions corresponding to walks on adjacent layers to the either side of the surface.

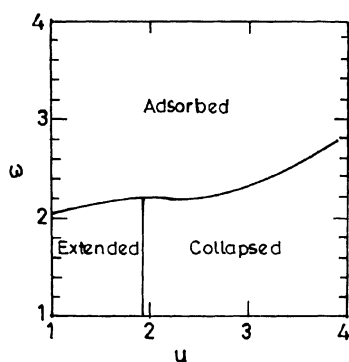


Figure 10. The phase diagram of a surface interacting linear polymer in 2-D space. ω and u axes represent, respectively the Boltzmann factors of surface interaction and monomer-monomer attraction.

the scaling law $\phi = 1 - \nu$. One therefore needs to extend this calculation to still larger values of b and test whether the method of RSRG is good for both penetrable and impenetrable surfaces.

The SASAW model on a square lattice has been considered by Foster *et al* [13]. Since the surface of this lattice is one dimensional, the collapse transition can occur only in the bulk and not on the surface. The phase diagram found by these authors is given in figure 10. One may note that the θ -line does not get affected due to the presence of the surface adsorption line. This result is in agreement with the one found in the case of 4-simplex lattice discussed above.

The phase diagram found for a 3-D cubic lattice using an exact enumeration method [28] is given in figure 11. An interesting feature of this phase diagram is a bend in the θ -line separating the adsorbed swollen and collapsed phases. At very large values of ω , the value of u locating the θ -point is equal to that of 2-D value. The bend in the θ -line on the surface is due to a competition between entropic fluctuations and the monomer-monomer attraction as explained elsewhere [28].

Linear polymer chains

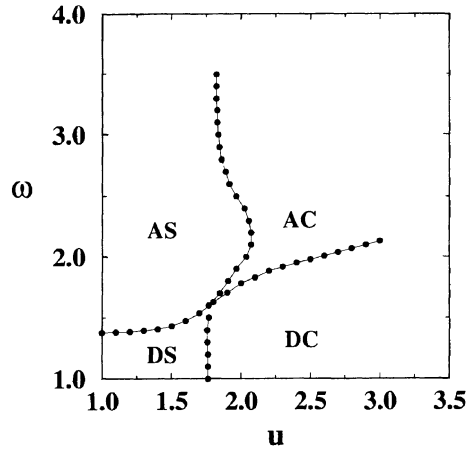


Figure 11. The phase diagram of a surface interacting linear polymer in 3-D space. The surface is 2-D and exhibits collapse transition. Notations are the same as those of figure 10. Regions marked by AS, AC, DS and DC represent, respectively, the adsorbed polymer in swollen state and collapsed (globular) state, desorbed polymer in swollen state and collapsed state.

4. The problem of dirty surface

A surface may become dirty due to the presence of defects. There are two different kinds of defects which may be present on a surface. One is due to defects in geometrical packing, formation of cracks or voids, bumps or steps etc. on the surface. The other kind of defect which a surface may have is substitutional disorder in which some lattice points at random are occupied by impurities.

We consider a fractal space mapped by a truncated 4-simplex lattice (see section 2.1). The surface of this space is a truncated 3-simplex lattice. The fractal nature of the surface may be considered to represent in some approximate sense the self-similar positional disorder of the surface. To represent the substitutional disorder we consider impurity sites distributed on the lattice in such a way that they form a configuration represented by that of an adsorbed polymer chain in a swollen state. This model may be considered to represent approximately the problem of adsorption of a large flexible polymer chain onto a (cell) membrane along which proteins stick out in a spatially uncorrelated manner.

The impurity configuration can be found by the statistics of a single polymer chain on the 3-simplex lattice. For convenience, we represent this configuration (of adsorbed polymer chain) by P_2 . The polymer chain whose adsorption we want to study is represented by P_1 . Therefore the problem of a polymer chain interacting with a dirty surface is projected onto a model of two interacting crossed walks in which one walk is confined to the surface.

The method of RSRG is used to obtain exact results. For this we assign a weight $x_1(x_2)$ to each step of the walk in the bulk (on the surface) and the weight $\sqrt{x_1 x_2} \omega$ to each step taken on the impurity sites on the surface. In other words, when a monomer of chain P_1 visits a site on surface occupied by chain P_2 a weight $\sqrt{x_1 x_2} \omega$ is assigned. If a monomer visits a site on surface not occupied by the monomers of P_2 (i.e. a pure site) the weight

assigned to it is x_2 . The monomers of chain P_1 may attract each other. As above, u represents the Boltzmann factor of this attraction. In order to promote competition between the adsorbed and desorbed phase of chain P_1 , it is desirable to introduce a parameter $t = \exp(-E_t/kT)$ in such a way that $\sqrt{x_1 x_2} t$ is the weight of these steps that are preferred on the lattice points which are nearest neighbors but on an adjacent layer (i.e. in the bulk) to the impurity sites. Hence E_t is the interaction energy between monomer of chain P_1 and an impurity site on the surface.

The global generating function of this model is written in the form

$$\begin{aligned} \Omega(x_1, x_2, \omega, u, t) &= \sum_{\text{all walks}} x_1^{N_1} x_2^{N_2} \omega^{N_s} t^{N_c} u^{N_m} \\ &= \sum_{N_1, N_2, N_s, N_c, N_m} C(N_1, N_2, N_s, N_c, N_m) x_1^{N_1} x_2^{N_2} \omega^{N_s} t^{N_c} u^{N_m}, \end{aligned} \quad (7)$$

where $C(N_1, N_2, N_s, N_c, N_m)$ represents the total number of configurations of all walks. Here N_1 is the total number of monomers in chain P_1 . N_2 represents the total number of impurity sites (i.e. the number of steps of walk P_2). N_s denotes the number of monomers of polymer chain P_1 lying on the adsorbed layer of polymer P_2 . N_c and N_m are the number of steps lying adjacent to the adsorbing layer and number of nearest neighbors respectively.

From the results found by solving this model [29] the following conclusions can be drawn.

The adsorbed polymer chain always remains in swollen state with radius of gyration exponent equal to that of the truncated 3-simplex lattice. The bulk desorbed phase has two regions. The region of swollen state is separated from the collapsed globule state (by tricritical θ -line). The θ -line is at $u_c = 3.316074$ and runs parallel to the ω -axis i.e. remains unaltered due to the surface interaction. The point where it meets the line $\omega^*(t, u)$ is a multicritical point. These multicritical points are characterized by three different fixed points depending on the value of t . When $t = 1$, the value of ω is found to be 1. The ω line runs parallel to the u -axis and meets at the θ -point. The point has five eigenvalues greater than one and corresponds to the ‘‘hexa critical point’’.

When $t = 0$ the value of surface interaction increases with u and meets at θ -line. In this case the polymer chain P_1 forms a layer of monomers over the surface. This may be viewed as a lamellar phase.

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Linear polymer chains

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