Adsorption and collapse transitions of a linear polymer chain interacting with a surface adsorbed polymer chain

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Abstract

We study the problem of adsorption and collapse transition of a linear polymer chain situated in a fractal container represented by a 4-simplex lattice and interacting with a surface adsorbed linear polymer chain. The adsorbed chain monomers act as pinning sites for the polymer chain. This problem has been solved exactly using real space renormalization group transformation. The resulting phase diagram and critical exponents are given.

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1 Introduction

The problem of surface effects on conformation statistics of long flexible polymer chains has been widely studied both because of its merit as an interesting problem in statistical mechanics and because of its important role in many physical processes like colloidal stabilization, adhesion, or lubrication, etc [1, 2]. The statistical mechanics approach to this problem has successfully been applied, particularly in case of good solvent that contains only one linear polymer chain interacting with an impenetrable wall [3-7]. The essential physics is derived from a model of self-avoiding walk (SAW) on a semi-infinite lattice, with an energy contribution $\epsilon_a$ for each step of the walk along the lattice boundary. This leads to an increased probability characterized by the Boltzmann factor $\omega = \exp(-\epsilon_a/k_B T)$ of making a step along the attractive wall, since $\epsilon_a < 0$, $\omega > 1$ for any finite temperature $T$. At low temperatures due to the attraction between the polymer chain and the surface, the chain gets adsorbed on the surface while at high temperatures all polymer configurations have almost same weight and a non-adsorbed behaviour prevails. The transition between these two regions is marked by a critical adsorption temperature $T_a$, with a desorbed phase for $T > T_a$ and an adsorbed phase for $T < T_a$. The asymptotic behaviour of the average number $M$ of steps of the walk along the boundary can be summarized in the following way [7]

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

(1.1)

where $N$ denotes the average number of monomers and $\phi$ is the crossover exponent.

When the polymer chain is in a poor solvent, it exhibits a phase diagram characterized by many different universality domains of critical behaviour. This is due to the competition between solvent-induced monomer-monomer attraction and the surface-monomer interaction. In this case the essential physics is derived using a model of self-attracting self-avoiding walk (SASAW) on a semi-infinite lattice [8, 9].

Theoretical methods which have been used to study polymer adsorption include renormalization group [10, 11], transfer matrix [12], Monte Carlo [13, 14], exact enumeration [15] and series expansion techniques [16]. In case of two dimensions many exact results have been found through conformal field theory [17-20] and using conformal invariance prediction in conjunction with the Bethe ansatz solution of associated...
Many exact results have also been found for the case of fractal lattices using real space renormalization group (RSRG) \cite{8, 23-25}. In this article, we consider the adsorption and collapsed transition of a long flexible polymer chain interacting with another long flexible polymer chain adsorbed on a surface. The monomers of the adsorbed chain act as pinning (or interaction) sites for the chain of our interest. The situation is shown in Figure 1. A polymer chain shown by zigzag line lies on the surface. Its monomers shown by black circles act as a pinning sites for the other polymer chain which is shown by wiggle line. The monomers of this floating chain shown by open circles get attracted to the surface because of the pinning sites. When a monomer of the floating chain gets adsorbed on the pinning sites (shown by shade circle) there is a gain of energy $\epsilon_a$. The model which we describe below also has two other interactions; (i) attraction between nearest neighbours formed by monomers of floating chain which are separated by relatively large distance along the chain and (ii) the interaction between nearest neighbours formed by a pinning site and a monomer of the floating chain occupying the neighbouring sites. These interactions are shown by $\epsilon_u$ and $\epsilon_t$, respectively, in the Figure 1. This situation is similar to the problem of adsorption of a long flexible polymer chain onto a (cell) membrane along which protein stick out in a spatially uncorrelated manner.

The paper is organized as follows. In section 2, we describe a model of two interacting chains in which one is adsorbed on a surface of a fractal container. The motivation of choosing a fractal space is that the model can be solved exactly apart from having its own practical applications. The results found by solving the model exactly are given in section 3. The paper ends with conclusions listed in section 4.

## 2 Model and its solution

We consider a fractal space mapped by truncated 4-simplex lattice. The basic geometrical unit of construction of this lattice is a tetrahedron with 4-corner vertices and bonds between every pair of vertices. Each vertex connected through a direct bond is termed as nearest neighbour. The fractal and spectral dimensions of the 4-simplex lattice are 2 and 1.5474, respectively. The tetrahedron of first and $(r + 1)$th order are shown in Figure 2. The shaded region represents the surface. The surface is a truncated 3-simplex lattice with fractal and spectral dimensions, 1.5849 and 1.3652 respectively. The bulk critical behaviour including $\theta$-point and the phase diagram of
surface interacting polymer chain using SASAW model has been studied recently [8].

In the model proposed here we represent the pinning sites by the monomers of an adsorbed polymer chain on a 3-simplex lattice. The configuration of the pinning sites can, therefore, be found by the statistics of single polymer chain on the 3-simplex lattice. For convenience we represent this configuration (of adsorbed polymer chain) by $P_2$. The floating polymer chain in a fractal container whose adsorption we want to study is represented by $P_1$. Therefore the problem is projected on to a model of two interacting crossed walks [26-28] in which one walk is confined to the surface and act as pinning sites for the other chain.

We assign the weight $x_1(x_2)$ to each step of the walk in the bulk (on the surface) and the weight $\sqrt{x_1x_2\omega}$ to each step taken on the pinning sites on the surface. In other words, when a monomer of chain $P_1$ visits a site on the surface occupied by chain $P_2$ a weight $\sqrt{x_1x_2\omega}$ is assigned. If a monomer visits a site on the surface not occupied by the chain $P_2$ (i.e. a pure site) the weight assigned to it is $x_1$. The monomers of chain $P_1$ may attract each other. We denote the Boltzmann factor associated with this interaction by $u$, where $u = \exp(-\epsilon_u/k_BT)$ ($\epsilon_u < 0$ being the attractive energy associated with a pair of near-neighbour bonds on the lattice). In order to promote competition between the adsorbed and desorbed phases of chain $P_1$ it is desirable to introduce a parameter $t = \exp(-\epsilon_t/k_BT)$ in such a way that $\sqrt{x_1x_2t}$ is the weight of those steps that are performed on the lattice points which are the nearest neighbour but in a adjacent sites to the pinning sites. Here $\epsilon_t$ is the interaction energy between a pair formed by a monomer of chain $P_1$ in the adjacent site and a pinning site on the surface.

The global generating function of this model can be written in the form

$$\Omega(x_1, x_2, \omega, u, t) = \sum_{all\, walks} x_1^{N_1} x_2^{N_2} \omega^{N_s} t^{N_c} u^{N_m}$$

$$= \sum_{N_1 N_2 N_s N_c N_m} C(N_1, N_2, N_s, N_c, N_m) x_1^{N_1} x_2^{N_2} \omega^{N_s} t^{N_c} u^{N_m}$$

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 monomers in adsorbed polymer chain ($P_2$), $N_s$ denotes the number of monomers of polymer chain $P_1$ adsorbed on the pinning sites. $N_c$ and $N_m$ are number of monomers lying adjacent to the surface and forming the nearest neighbour with the pinning sites, and number of nearest neighbours in chain $P_1$, respectively.

The generating function for the 4-simplex lattice can be expressed in terms of finite
number of restricted partition functions [29]. We show in Figure 3 all the possible restricted partition functions which appear in this problem. This can be seen from Figure 4 in which we draw one of the possible configurations of walks on the \( r \)-th order of the lattice. The surface adsorbed chain \( P_2 \) is shown by zigzag line while the chain \( P_1 \) by wiggle line. These partition functions are defined recursively as weighted sum over all possible configurations for a given stage of the iterative construction of the 4-simplex lattice. The variables in these equations are just the partial generating functions corresponding to different polymer configurations for a given size of the fractal. Linearizing the recursion equations near the fixed points, the one 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.

The recursion relations for the restricted partition functions can be written as (see Figure 5)

\[
A_{r+1} = A^2 + 2A^3 + 2A^4 + 4A^2B + 6A^2B^2 \quad (2.3)
\]

\[
B_{r+1} = A^4 + 4A^3B + 22B^4 \quad (2.4)
\]

\[
H_{r+1} = H^2 + H^3 \quad (2.5)
\]

\[
C_{r+1} = C^2 + C^3 + AD^2(H + 2C + 2F + 2G + 2 + 2A) + 4A^2G(C + F) + 2AG^2(A + C) + 4ACFG + HD^2 \quad (2.6)
\]

\[
D_{r+1} = ABD(4G + 2F + 2E) + A^2D(G + F + E + C + H) + AD(C + H + C^2 + H^2) + BDE(2F + 4G) + ACD(F + G + H) + AHDE + D^3(2B + A) \quad (2.7)
\]

\[
E_{r+1} = AD^2(4B + 2G + 2E + 2H + 2A) + BD^2(2F + 4G) + AH^2(A + E) + 6B^2E^2 + 2BE^3 + 2A^2HE \quad (2.8)
\]

\[
F_{r+1} = AD^2(2B + E + 2G) + B^2(8G^2 + 6F^2 + B(8G^3 + 2F^3) + 8BFG(B + G) + ACF(2A + C) + BED^2 + 4BGF^2 + A^2C^2 \quad (2.9)
\]

\[
G_{r+1} = AD^2(2B + A + G + F + C) + AG(2AC + C^2) + 12B^2FG + 6BGF^2 + 10BFG^2 + 10B^2G^2 + 6BG^3 + BD^2E \quad (2.10)
\]

A notational simplification in which the index \( r \) is dropped from the right hand side of the recursion relations is adopted here. It may be emphasized here that the
recursion relations written above are exact for the model defined above.

Eq.(2.5) which represents the recursion relation for the adsorbed chain $P_2$ is independent of configuration of chain $P_1$. The effect of $P_2$ on chain $P_1$ is taken through $C$, $D$, $E$, $F$ and $G$. Since all interactions involved in the problem are restricted to bonds within a first order unit of the fractal lattice, $\omega$, $t$, and $u$ do not appear explicitly in the recursion relations. They appear only in initial values given below.

\[
A_1 = x_1^2 + 2x_1^3u + 2x_1^4u^3 \quad (2.11)
\]
\[
B_1 = x_1^4u^4 \quad (2.12)
\]
\[
C_1 = x_1^2x_2^3\omega^2t^2 + x_1^3x_2^3(\omega^6u + t^2\omega^2u) + 2x_1^4x_2^3\omega^4t^2u^3 + x_1^2x_2^3\omega^4 + 2x_1^3x_2^3t^2\omega^2u + 2x_1^4x_2^3t^2\omega^2u^3 \quad (2.13)
\]
\[
D_1 = x_1^2x_2^3\omega + x_1^3x_2^3(t\omega u + t^3u) + x_1^4x_2^3(u^3\omega^3 t^3 + u^3\omega^5 t) + x_1^2x_2^3\omega^3t^2u^3 + x_1^3x_2^3\omega^3tu^3 + x_1^3x_2^3\omega^3tu^3 \quad (2.14)
\]
\[
E_1 = x_1^2x_2^3 + 2x_1^3x_2^3\omega^2t^2u + 2x_1^4x_2^3\omega^2u^3 + x_1^2x_2^3 + 2x_1^3x_2^3u + 2x_1^4x_2^3u^3t^2 \quad (2.15)
\]
\[
F_1 = x_1^4x_2^3\omega^4u^4 + x_1^4x_2^3\omega^4t^2u^4 \quad (2.16)
\]
\[
G_1 = x_1^4x_2^3\omega^2t^2\omega^2u^4 + x_1^4x_2^3\omega^2t^2\omega^2u^4 \quad (2.17)
\]

Here index 1 and 2 on the right hand side of Eq.(2.11)-(2.17) correspond to chain $P_1$ and pinning sites (chain $P_2$) respectively. The fixed points corresponding to different configurations of polymers in the asymptotic limit are found by solving Eq.(2.3) and (2.4) for polymer chain $P_1$ and Eq.(2.5) for chain $P_2$ respectively. A complete phase diagram obtained from Eqs.(2.3) - (2.4) and from Eq.(2.5) are given elsewhere \[3\].

The state of polymer chain $P_1$ depends on the quality of the solvent and on the temperature and can therefore be in any of three states; swollen, compact globule and at $\theta$-point described in the asymptotic limit by the fixed points $(A^*, B^*) = (0.4294, 0.0498), (0.0, 22^{-1/3})$ and $(1/3, 1/3)$ respectively. The fixed point corresponding to the swollen state is reached for all values of $u < u_\theta$ at $x_1 > x_\theta$. The end to end distance for a chain of $N_1$ monomers of $P_1$ in this state varies as $N_1^{\nu_1}$ with $\nu_1 = 0.7294$ \[8, 29\] and connectivity constant $\mu = 1/x$ is found to be 1.5474. The fixed point corresponding to the compact globule state is reached for all values of $u > u_\theta$ at $x_1(u) < x_\theta$. At $u_\theta = 3.31607..$ and $x_\theta = 0.22913..$ the system is found to be at its tricritical point or $\theta$-point. The fixed point $H^* = 0.61803..$ is found by solving Eq.(2.5). It corresponds
to a pattern with fractal dimension equal to 1.266.

In a system of polymer chain interacting with a surface adsorbed chain, we have three different combinations of the individual state. Using the fixed points of \((A^*, B^*)\) corresponding to three different states of polymer chain \(P_1\) and \(H^* = 0.61803\) (for surface adsorbed chain \(P_2\)), we solve the coupled non-linear equations [Eqs. (2.6) - (2.10)].

3 Results

For all values of \(\omega < \omega_c(u, t)\), the polymer chain \(P_1\) lies in the bulk. The critical behaviour of polymer chain \(P_1\) does not get affected by the presence of the surface or pinning sites. In the phase diagram shown in Figure 6, \(\omega\) is plotted as a function of \(u\) for three values of \(t = 0, 0.5\) and \(1.0\). The \(\theta\)-line which separates the bulk swollen and collapsed phases and terminates at the surface adsorption line \(\omega = \omega_c(u, t)\) is found at \(u = u_c = 3.316074\). The \(\theta\)-line in Figure 6 is shown by dashed line. \(\omega = \omega_c(u, t)\) separates the bulk from the adsorbed phase. Below this line the desorbed phase does not get affected by the presence of the surface attraction, except for the \(\theta\)-point turning into a \(\theta\)-line and the critical lines corresponding to swollen and collapsed phases into respective regions.

When \(\omega > \omega_c(u, t)\) the polymer gets adsorbed. Depending on the value of \(t\) the chain may lie on the pinning sites or avoids them. For \(t \sim 1\) the polymer chain may get adsorbed on the pinning sites acquiring the configuration as that of the pinning sites.

When \(\omega = \omega_c(u, t)\) the chain \(P_1\) is on the adsorption special line. The different regions of this line characterize different multicritical behavior as a function of \(u\) and \(t\). Note that the parameter \(u\) and \(t\) measure, respectively, the strengths of nearest neighbour interaction and the repulsive strength of a monomer on the adjacent layer and forming a nearest neighbour with a pinning site on the surface.

(I) The fixed point \(A^*, B^*, C^*, D^*, E^*, F^*, G^*\) = (0.4294, 0.04998, 0.2654, 0.2654, 0.2654, 0.0391, 0.0391) is reached for all values of \(u < u_c\) and \(\omega = \omega_c\) at \(t > 0\). Linearization around this fixed point gives one eigenvalue (other than \(\lambda_b = 2.7965\)) \(\lambda_\theta = 1.7914\) greater than one. From the eigenvalues \(\lambda_b\) and \(\lambda_\theta\) one gets the crossover exponent

\[
\phi = \frac{\ln \lambda_\theta}{\ln \lambda_b} = 0.5669 \sim 0.57
\]
This fixed point corresponds to special line $\omega = \omega_c(u, t)$ for $u < u_c$ and $t > 0$. The polymer chain at the adsorption line (tricritical line) fluctuates among configurations corresponding to $A$ (bulk), $C$, $D$, $E$ (surface) [see Figure 3].

For $t = 0$ the fixed point $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (0.4294, 0.04998, 0.0, 0.0, 0.1164, 0.0, 0.0)$ is reached for all values of $u < u_c$. Linearization about this fixed point does not yield any eigenvalue (except $\lambda_b$) greater than one. Therefore there is no crossover from bulk to surface.

(II) When $u > u_\theta (= 3.316074)$ and $x < x_\theta (= 0.229157...)$ the polymer chain is in the collapsed state in the bulk. At $t = 0$, we choose $u = 3.3333..$ and $x = 0.2282..$ and solve Eqs.(2.3) - (2.9). This leads to a fixed point $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (0.0, 0.3568, 0.0, 0.0, 0.7652, 0.0, 0.0)$ at $\omega = \omega_c = 1.5751...$. This corresponds to configuration in which compact globule formed in the bulk container gets stuck to the surface in such a way that monomers avoid touching the sites of the surface occupied by the chain $P_2$. Linearization around this fixed point gives in addition to $\lambda_b$ an eigenvalue greater than one i.e $\lambda_\phi = 2.4233$. With this eigenvalue the crossover exponent is found to be

$$\phi = \frac{\ln \lambda_\phi}{\ln \lambda_b} \simeq 0.64.$$ 

(III) When $t > 0$ and $\omega = \omega_c$ (for $u > u_\theta$ and $x < x_\theta$), we get a fixed point $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (0.0, 0.3568, 0.0, 0.0, 0.0, 0.0, 0.2206,0.2206)$. Linearization around this fixed point gives $\lambda_\phi = 2.3073$. The crossover exponent in this case is $\phi \simeq 0.60$. In this case the surface configurations attained by the polymer chain are those which correspond to the configurations $F$ and $G$ shown in Figure 3. It means that the globule gets attached to the site occupied by the chain $P_2$ on the surface.

(IV) When $u = u_\theta = 3.316074.....$ and $x = x_\theta = 0.229137...$ the polymer chain (in bulk) is at $\theta$-point. For this we have three distinct fixed points depending on the values of $t$. We now discuss these three fixed points.

(A) For $t = 0$ and $\omega = \omega_c = 1.5772$ the fixed point achieved by the system is $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (1/3, 1/3, 0.0, 0.0, 0.0, 0.613, 0.8228.., 0.0)$. Linearized equations around this fixed point give three eigenvalues greater than one. These values are

$$\lambda_1 = 2.4511,$$

and

$$\lambda_{b1} = 3.7037, \quad \lambda_{b2} = 2.2222$$
Note that the last two eigenvalues are the same as those found for the bulk $\theta$-point. 

The crossover exponent is

$$\phi = \frac{\ln \lambda_1}{\ln \lambda_{b1}} \sim 0.65.$$ 

This is a tetracritical point. The adsorbed phase corresponding to configurations which forms a layer on the surface occupied by the pinning sites.

(B) For $0 < t < 1$ we have fixed point $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (1/3, 1/3, 0.0510.., 0.0, 0.613, 0.2364.., 0.2364)$. This point has been found to have three eigenvalues greater than one. These values are

$$\lambda_1 = 2.3311,$$

and the other two are $\lambda_{b1}$ and $\lambda_{b2}$ given above. The crossover exponent, $\phi$ found in this case is equal to 0.61. This tetracritical point differs from the previous one in the sense that the adsorbed phase has configuration which is combination of both $F$ and $G$ as shown in Figure 3 whereas at $t = 0$ the adsorbed phase has the configuration corresponding to $E$.

(C) At $t = 1$ and $\omega = 1$ we find the symmetrical fixed point $(A^*, B^*, C^*, D^*, E^*, F^*, G^*) = (1/3, 1/3, 0.2061, 0.2061, 0.2061, 0.2061, 0.2061)$. This point has four eigenvalues greater than one. Apart from the two known eigenvalues $(\lambda_{b1}, \lambda_{b2})$ the two additional eigenvalues are

$$\lambda_1 = 2.1269 \text{ and } \lambda_2 = 1.1947$$

This is a pentacritical point. Note that for $t > 1$, corresponds to $\omega < 1$. Therefore the tetracritical line as a function of $t$ is symmetrical about the point $t = 1$.

## 4 Conclusions

In this paper we studied the critical behaviour of polymer chain interacting with a surface adsorbed chain. It is shown that this model differs from the usual polymer adsorption and also from the problem of two interacting chains studied in past [15,23-28]. We find a very rich $\omega - u$ phase diagram plotted in Figure 6. The adsorbed polymer chain representing the pinning sites always remain in swollen state with radius of gyration exponent equal to that of truncated 3-simplex lattice. We therefore have pinning sites forming pattern with fractal dimension 1.266. The bulk desorbed phase has two regions: the region of swollen state separated from the collapsed globule...
state (by a tricritical $\theta$-line). The $\theta$-line is at $u = u_\theta = 3.316074..$ and runs parallel to the $\omega$ 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 multi-critical points are characterized by three different fixed points depending on the value of $t$. When the value of $t = 1$ the value of $\omega$ is found to be 1. The $\omega$ line runs parallel to the $u$-axis and meets at the $\theta$-point. This point has four eigenvalues greater than one and corresponds to the pentacritical point. This is a point at which two tetracritical lines corresponding to $0 < t \leq 1$ and $t > 1$ meet. When $t > 1$, $\omega$ has to be less than 1.

When $t = 0$, the value of surface interaction increases with $u$ and meet at $\theta$-line. The Figure 6 gives the impression of the existence of reentrant adsorbed phase as $u$ is increased. One should, however, remember that these figures are merely a projection on the $\omega - u$ plane of three dimensional figures in which the third dimension is given by $x$.

When the value of $t$ lies in between 0 and 1 the slope increases, but we do not find any “frustrated phase” as observed in usual situation of surface adsorption. The behaviour of special adsorption line described above can be understood from contributions of different coexisting polymer configurations (see Figure 3) to the bulk and surface free energies. When both adsorbed phase (as by definition) and bulk phase are in swollen state, the adsorption line has same nature in $\omega - u$ plane for all values of $t$, although the slope of line decreases as $t$ increases and at $t = 1$ the slope becomes zero and line runs parallel to $u$ axis. This is due to the very fact that at $t = 1$ and $\omega = 1$ the surface behaves as a part of bulk and distribution of monomers are isotropic.

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**FIGURE CAPTION**

**Figure 1** Schematic representation of all possible interactions appearing in Generating Function defined by Equation 2.2.

**Figure 2** Graphical representation of a truncated 4-simplex lattice of first order and $(r + 1)$th order. The shaded regions represent the surface.

**Figure 3** Diagrammatic representation of all the restricted partition functions which appear in the generating function defined by Eq.(2.2). Polymer chain $P_1$ in the bulk is represented by wiggle line while adsorbed polymer chain $P_2$ is shown by zigzag line.

**Figure 4** Diagrammatic representation of one of possible configurations of a polymer interacting with surface confined polymer chain on third order of 4-simplex lattice. All the possible partition functions contributing to the generating function are shown.

**Figure 5** Diagrams representing the recursion relation for the restricted partition functions given by Eqs. 2.3-2.9. Some of the possible configurations contributing to the recursion relations are shown.

**Figure 6** Special adsorption lines are shown in $\omega$ - $u$ plane for $t = 0$, 1 and 0.5.
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Figure 2:
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