Polymer adsorption on curved surface

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Abstract:
Lattice model of directed self avoiding walk is used to investigate adsorption properties of a semiflexible sequential copolymer chain on an impenetrable curved surface on a hexagonal lattice in two dimensions. Walks of the copolymer chains are directed in a direction away from the surface at a suitable value of monomer surface attraction, the copolymer chain gets adsorbed on the surface. To calculate exact value of monomer surface attraction, the directed walk model have been solved analytically using generating function method to discuss results when one type monomer of the copolymer chain has attractive, repulsive or no interaction with the surface. Results obtained show that adsorption transition point is independent of bending energy of the copolymer chain.

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1 Introduction:
The copolymer adsorption is a subject of theoretical and experimental investigations due to its applications in biophysics, biosensors, pattern recognition, adhesion and surface protection. For example, in the case of biophysics, Since protein molecule is made of heterogeneous sequence of hydrophobic and hydrophilic residues, therefore, it can be treated as a random copolymer and its stiffness may be in between flexible and stiff chains. Whence, protein is a semiflexible random copolymer molecule. The conformational properties of such polymer molecules have attracted considerable attention in recent years due to advancement in the experimental methods in which it has become possible to pull and stretch single bio-molecule to measure its elastic properties [1, 2]. These study reveal a wealth of information about the conformational behaviour of biopolymers and therefore of biological importance. In addition to it, study of adsorption of the copolymer chain on a surface is also useful in determining the relation between their compositions with their adsorption
characteristics.

The problem of random copolymer adsorption has been extensively studied using numerical methods, see, [3, 4, 5, 6, 7, 8] and references quoted therein. However, analytical methods for adsorption of copolymer chain with self avoidance effect are limited to directed walk like models. In past few years sequential copolymer adsorption has also received attention [9] due to location of its adsorption transition point and calculation of crossover exponent. Adsorption of the copolymer chain merits somewhat differently from homopolymer chain in a sense that different type of monomers of the copolymer chain need not have attractive interaction with the surface.

Lattice model of self avoiding walks and directed self avoiding walks have been used extensively to derive essential physics associated with the behaviour of a surface interacting polymer chain in a good solvent in two and three dimensions [9, 10, 11, 12]. If surface is attractive, it contributes an energy $\epsilon_s (<0)$ for each step of walk lying on the surface. This leads to an increased probability defined by a Boltzmann weight $\omega = \exp(-\epsilon_s/k_B T)$ of moving a step on the surface ($\epsilon_s < 0$ or $\omega > 1$, $T$ is temperature and $k_B$ is the Boltzmann constant). The polymer chain gets adsorbed on the surface at a suitable value of $\epsilon_s$. The transition between adsorbed and desorbed regimes is marked by a critical value of adsorption energy or $\omega_c$. One may define the crossover exponent $\phi$ at the adsorption transition point as, $N_s \sim N^{\phi}$, where $N$ is the total number of monomers in the polymer chain and $N_s$ the number of monomers adsorbed on the surface.

In this paper, we have extended directed self avoiding walk model, introduced by Privman et al. [12] for homopolymer chain, to study the adsorption desorption phase transition behaviour of the semiflexible sequential copolymer chain immersed in a good solvent on a curved (one dimensional) impenetrable surface. To calculate adsorption properties of the copolymer chain on a curved impenetrable surface, we have considered two dimensional hexagonal lattice. Such study is useful in examining the question whether the copolymers differ from homopolymers with respect to their critical behaviour near an impenetrable surface. We have considered semiflexible sequential copolymer chain composed of two type of monomers (A & B) and model the copolymer chain as a directed self avoiding walk on the lattice. Such copolymer model serve as a paradigmatic model of actually disordered macromolecules (for example, proteins). For adsorption of semiflexible sequential copolymer chain on an impenetrable flat and curved surface perpendicular to the preferred direction of the walks of the copolymer chain, directed walk model has been solved analytically and exact critical value of the surface attraction for
the adsorption of the copolymer chain has been evaluated.

The paper is organized as follows: In Sec. 2 lattice model of directed self avoiding walk has been described for the semiflexible sequential copolymer chain in two dimensions on a hexagonal lattice. Directed self avoiding walk models of the copolymer chain has been solved analytically for the adsorption of the chain on an impenetrable curved surface. Finally, in Sec. 3 we discuss the results obtained.

2 Model and method

A lattice model of directed self-avoiding walk [12] has been used to study adsorption-desorption phase transition behaviour of a sequential copolymer chain under good solvent condition on a curved impenetrable surface. The directed walk models are restrictive in the sense that angle of bending has a unique value that is $60^\circ$ for each bend. In addition to it, directedness of the walk amounts to some degree of stiffness in the copolymer chain because all directions of the space are not treated equally. However, directed self avoiding walk model can be solved analytically and therefore gives exact value of adsorption transition point of the chain.

For two dimensional hexagonal lattice, we have consider directedness of the copolymer chain that can be defined with the help of direction of movement of the walker on the unit cell of the lattice as follows: There are six possible directions of movement of the walker and steps along these directions can be named by 1, 2, 3, 4, 5 and 6 (as shown in Fig. 1). Time direction is along step 6. If walker is allowed to take steps along all the possible directions excluding only directions along step 2, 3 & 4.

The stiffness in the sequential copolymer chain has been introduced by associating an energy barrier for each bend in the walk of copolymer chain. The stiffness weight $k = \exp(-\beta \epsilon_b)$ where $\beta = (k_B T)^{-1}$ is inverse of the temperature and $\epsilon_b(> 0)$ is the energy associated with each bend of the walk of copolymer chain. For $k = 1$ or $\epsilon_b = 0$ the copolymer chain is said to be flexible and for $0 < k < 1$ or $0 < \epsilon_b < \infty$ the copolymer chain is said to be semiflexible. However, when $\epsilon_b \to \infty$ or $k \to 0$, the copolymer chain has a rigid rod like shape.

The partition function of a semiflexible sequential copolymer chain made of two type of monomers (A & B) can be written as,
Figure 1: All the possible directions of movement of the walker on a two dimensional hexagonal lattice has been named by 1, 2, 3, 4, 5 and 6.

\[
Z(k, x_1, x_2) = \sum_{N=0}^{N=\infty} \sum_{\text{all walks of } N \text{ steps}} x_1^{N/2} x_2^{N/2} k^{N_b} \quad (1)
\]

where, \( N_b \) is the total number of bends in a walk of \( N \) steps (monomers), \( x_1 \) and \( x_2 \) is the step fugacity of each of the A and B type monomers respectively. For the sake of mathematical simplicity we assume here onwards \( x_1 = x_2 = x \). Method of analysis discussed in this paper can be easily extended to the case \( x_1 \neq x_2 \).

2.1 Polymer chain in the bulk: Directed self avoiding walk model on a two dimensional hexagonal lattice

\( Y(k, x) \) is sum of Boltzmann weight of all the walks having first step along step 1 or step 5 while \( X(k, x) \) is sum of Boltzmann weight of all the walks having first step along step 6. One end of the chain grafted at \( O \), as shown in figure (2). The components of partition function for copolymer chain in the bulk can be written as (as shown in figure 2B),

\[
Y(k, x) = x + kx^2 + 2k^2x^2Y \quad (2)
\]

and,

\[
X(k, x) = x + 2xkY \quad (3)
\]
solving Eqs. (2 & 3), we have,

\[ Y(k, x) = -\frac{x + x^2k}{1 + 2k^2x^2} \quad (4) \]

\[ X(k, x) = -\frac{x + 2kx^2}{1 + 2k^2x^2} \quad (5) \]

With \( O \) as starting point where chain is grafted, so that partition function of the chain \( G(k, x) \) can be written as,

\[ G(k, x) = 2Y(k, x) = -\frac{2(x + x^2k)}{1 + 2k^2x^2} \quad (6) \]

from singularity of the partition function \( G(k, x) \), we have \( x_c = \frac{1}{\sqrt{2k}} \), required for polymer polymerization of an infinitely long linear polymer chain.

Figure 2: In this figure surface interacting copolymer chain is shown for directed self avoiding walk model on the hexagonal lattice. Walks of the chain starts from at \( O \) from curved surface. \( S(k, \omega_1, \omega_2, x) \) is the surface component of the partition function of the polymer chain.

### 2.2 Adsorption on a curved surface: Directed self avoiding walk model on a two dimensional hexagonal lattice

Adsorption of the copolymer chain has been studied on a two dimensional hexagonal lattice to investigate adsorption desorption phase transition behaviour of a semiflexible sequential copolymer chain on a curved surface. In the case of a two dimensional hexagonal lattice, surface is an impenetrable
line and its shape is like a saw tooth wave [14]. Therefore, adsorbed parts of the copolymer chain have bends and in this case components of partition function of the copolymer chain having first monomer grafted to the surface of A type can be written following the method outlined above as,

$$S(k, \omega_1, \omega_2, x) = s_1(1 + ks_2 + k^2s_2Y) + s_1^2s_2k^2(1 + ks_2 + k^2s_2Y) + \ldots$$ (7)

$S(k, \omega_1, \omega_2, x)$ and $Y(k, x)$ are the components of the partition function on the surface and perpendicular to the surface respectively.

$$S(k, \omega_1, \omega_2, x) = \frac{s_1(1 + ks_2 + k^2s_2Y)}{1 - s_1s_2k^2} \quad (s_1s_2k^2 < 1) \quad (8)$$

The partition function of surface interacting copolymer chain can be written for the sequential copolymer chain for two dimensional hexagonal lattice as follows:

The component of the partition function perpendicular to the plane of the surface is [14],

$$Y(k, x) = -\frac{x + kx^2}{-1 + 2x^2k^2}$$ (9)

so that,

$$G_s(k, \omega_1, \omega_2, x) = S(k, \omega_1, \omega_2, x) + Y(k, x)$$ (10)

$$G_s(k, \omega_1, \omega_2, x) = \frac{f(k, \omega_1, \omega_2, x)}{(-1 + k^2s_1s_2)(-1 + 2k^2x^2)} \quad (s_1s_2k^2 < 1) \quad (11)$$

In this case, singularities of the partition function give, $\omega_{c_1} = \frac{2}{\omega_{c_2}}$.

Variation of $\omega_{c_1}$ for various value of $\omega_{c_2}$ is shown in Fig. (3) for two dimensional hexagonal lattice. When we substitute $\omega_{c_1} = \omega_{c_2} = \omega_c$, we are able to obtain critical value of monomer surface attraction required for adsorption of homopolymer chain on a curved impenetrable surface. It is to be noted that $\omega_{c_1}$ required for adsorption of copolymer chain on a curved impenetrable surface is independent of bending energy of the copolymer chain.

3 Result and discussion

Lattice model of directed self avoiding walk has been solved using generating function method for adsorption of a semiflexible sequential copolymer chain on a curved surface. We have used two dimensional hexagonal lattice to
model the copolymer chain and to investigate adsorption properties of the copolymer chain on an impenetrable curved surface. The copolymer chain is made of two type of monomers (A & B) and A type monomer has attractive interaction with the surface while B type monomer can have attractive, repulsive or no interaction with the surface. Our study revealed that for curved impenetrable surface, critical value of monomer surface attraction required for the copolymer chain adsorption is independent of bending energy of the chain [14].

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