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A semiflexible alternating copolymer chain adsorption on a flat and a fluctuating surface

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Abstract

A lattice model of a directed self-avoiding walk is used to investigate adsorption properties of a semiflexible alternating copolymer chain on an impenetrable flat and fluctuating surface in two (square, hexagonal and rectangular lattice) and three dimensions (cubic lattice). In the cubic lattice case the surface is two-dimensional impenetrable flat and in two dimensions the surface is a fluctuating impenetrable line (hexagonal lattice) and also flat impenetrable line (square and rectangular lattice). Walks of the copolymer chains are directed perpendicular to the plane of the surface and at a suitable value of monomer surface attraction, the copolymer chain gets adsorbed on the surface. To calculate the exact value of the monomer surface attraction, the directed walk model has been solved analytically using the generating function method to discuss results when one type of monomer of the copolymer chain has attractive, repulsive or no interaction with the surface. Results obtained in the flat surface case show that, for a stiffer copolymer chain, adsorption transition occurs at a smaller value of monomer surface attraction than a flexible copolymer chain while in the case of a fluctuating surface, the adsorption transition point is independent of bending energy of the copolymer chain. These features are similar to that of a semiflexible homopolymer chain adsorption.

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 a *protein* molecule is made of a 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. So, *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 biomolecules to measure its elastic properties [1, 2]. These studies reveal a wealth of information about the conformational behaviour of biopolymers and therefore of biological importance. In addition to it, the 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 [3–8], and references quoted therein. However, analytical methods for adsorption of a copolymer chain with self-avoidance effect are limited to directed-walk-like models. In the past few years alternating copolymer adsorption has also received attention [9] due to the location of its adsorption transition point and calculation of crossover exponent. Adsorption of the copolymer chain merits somewhat differently from the homopolymer chain in a sense that different types of monomers of the copolymer chain need not have attractive interaction with the surface.

A lattice model of self-avoiding walks and directed self-avoiding walks has been used extensively to derive the essential physics associated with the behaviour of a surface interacting polymer chain in a good solvent in two and three dimensions [9–12]. If the surface is attractive, it contributes

an energy ϵ_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 ϵ_s . The transition between adsorbed and desorbed regimes is marked by a critical value of adsorption energy or ω_c . One may define the crossover exponent ϕ 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 the directed self-avoiding walk model, introduced by Privman *et al* [12] for homopolymer chains, to study the adsorption–desorption phase transition behaviour of the semiflexible alternating copolymer chain immersed in a good solvent on a flat (one-dimensional and two-dimensional) and fluctuating (one-dimensional) impenetrable surface. To calculate adsorption properties of the copolymer chain on a fluctuating impenetrable surface, we have considered a two-dimensional hexagonal lattice while square and rectangular lattices have also been considered for the sake of completion. In the case of the square and rectangular lattices, the surface is one-dimensional and flat. However, in three-dimensional space we have considered a cubic lattice with a flat two-dimensional impenetrable surface to compare the results obtained in two and three dimensions. Such a 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 a semiflexible alternating copolymer chain composed of two type of monomers (A and B) arranged along the chain length in a sequence A–B–A–B–A–B ... and model the copolymer chain as a directed self-avoiding walk on the lattice. Such a copolymer model serves as a paradigmatic model of actually disordered macromolecules (for example, *proteins*). For adsorption of a semiflexible alternating copolymer chain on an impenetrable flat and fluctuating surface perpendicular to the preferred direction of the walks of the copolymer chain, the directed walk model has been solved analytically and the exact critical value of the surface attraction for the adsorption of the copolymer chain has been evaluated.

This paper is organized as follows. In section 2 the lattice model of a directed self-avoiding walk has been described for the semiflexible alternating copolymer chain in two dimensions on a hexagonal, square and rectangular lattice while in three dimensions for cubic lattice. Partially directed and fully directed self-avoiding walk models of the copolymer chain have been solved analytically for the adsorption of the chain on an impenetrable fluctuating and impenetrable flat surface perpendicular to the preferred direction of the walks of the copolymer chain. Finally, in section 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

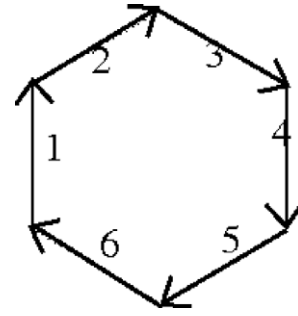


Figure 1. All the possible directions of movement of the walker on a two-dimensional hexagonal lattice have been named by 1, 2, 3, 4, 5 and 6.

of a alternating copolymer chain under good solvent conditions on a flat and a fluctuating impenetrable surface. The directed walk models are restrictive in the sense that the angle of bending has a unique value that is 90° or no bend (for square, rectangular and cubic lattices) while in the case of a hexagonal lattice the value of the bending angle is 60° 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, the directed self-avoiding walk model can be solved analytically and therefore gives an exact value of the adsorption transition point of the chain.

We consider the following two cases of directedness of the copolymer chain for square, rectangular and cubic lattices: in case (i) the partially directed self-avoiding walk (PDSAW) model, a walker is allowed to walk along $\pm y$ and $+x$ directions for the square and rectangular lattice case while in the cubic lattice case a walker walks along $\pm y$, $+x$ and $+z$ directions. In case (ii) the fully directed self-avoiding walk (FDSAW) model, the walker is allowed to take steps along the $+x$, $+y$ directions in the square and rectangular lattice case while along $+x$, $+y$ and $+z$ directions for the case of a cubic lattice. For a two-dimensional hexagonal lattice, we have considered three cases of directedness of the copolymer chain, and these cases can be defined with the help of the 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 figure 1). If the walker is allowed to take steps along all the possible directions excluding only directions along step 4, such a directed walk model for a hexagonal lattice is named a PDSAW(I) model. In another case in which steps like 4 and 5 are not allowed for a walker on the hexagonal lattice, it corresponds to a PDSAW(II) model while the FDSAW model corresponds to the case in which a walker is allowed to walk along steps 1, 2 and 3 on the hexagonal lattice. The stiffness in the alternating copolymer chain has been introduced by associating an energy barrier for each bend in the walk of the copolymer chain. The stiffness weight $k = \exp(-\beta\epsilon_b)$, where $\beta = (k_B T)^{-1}$ is the inverse of the temperature and $\epsilon_b(>0)$ is the energy associated with each bend of the walk of the 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 $\epsilon_b \rightarrow \infty$ or $k \rightarrow 0$, the copolymer chain has a rigid rod-like shape.

The partition function of a semiflexible alternating copolymer chain made of two types of monomers (A and B) can be written as

$$G(k, g_1, g_2) = \sum_{N=0}^{N=\infty} \sum_{\text{all walks of } N \text{ steps}} g_1^{N/2} g_2^{N/2} k^{N_b} \quad (1)$$

where N_b is the total number of bends in a walk of N steps (monomers), and g_1 and g_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 $g_1 = g_2 = g$. The method of analysis discussed in this paper can be easily extended to the case $g_1 \neq g_2$.

It is possible to consider two distinct surfaces, one parallel and the other perpendicular to the directedness of the walks of the copolymer chain. In the case of homopolymer chain adsorption on an attractive impenetrable surface, it has been found that the features associated with the adsorption were the same in both surface orientations; only the critical value of surface attraction differs for the two surface orientations. This fact is also true for isotropic and directed walk models of the homopolymer chain adsorption [13].

2.1. Directed self-avoiding walk model on a cubic lattice

We consider an impenetrable surface i.e. a x - y plane located at $z = 0$, the first monomer of the copolymer chain is grafted to the surface and the walker can walk along $+x$, $\pm y$ and $+z$ directions on the cubic lattice for the PDSA model (as shown schematically in figure 2). Since an alternating copolymer chain is made of two type monomers (A and B) therefore if the first monomer of the copolymer chain grafted to the surface is of A type, the component of the partition function of the copolymer chain with the first step along the $+x$ direction is written as S_{1x} (sum of the Boltzmann weight of all the walks with the first step on the surface and along the $+x$ direction) and similarly, if the first step is along any one out of the $\pm y$ directions, we have S_{1y} . However, if the B type monomer is the first monomer of the copolymer chain and it is grafted on the surface, then, if the first monomer of the polymer chain is along the $+x$ direction, the component of the partition function is written as S_{2x} but S_{2y} is the component of the partition function with the first monomer of B type and the first step of the walk of the copolymer chain is along any one out of the $\pm y$ directions. The component of the partition function perpendicular to the plane of the surface is written as Z .

(i) *Partially directed self-avoiding walk model.* The partition function of the surface interacting copolymer chain can be calculated using the method of analysis discussed by Mishra *et al* [13] and components of the partition function are graphically shown in figure 3. The components of the partition function $G_{PD-C}(k, \omega_1, \omega_2, g)$ of the copolymer chain interacting with the surface having a first monomer of A type can, therefore, be written as follows:

$$S_{1x}^{PD-C}(k, \omega_1, \omega_2, g) = s_1 + s_1(s_2 + 2kS_{2y}^{PD-C} + kZ^{PD-C}) + s_1s_2(s_1 + 2kS_{1y}^{PD-C} + kZ^{PD-C}) + \dots \quad (2)$$

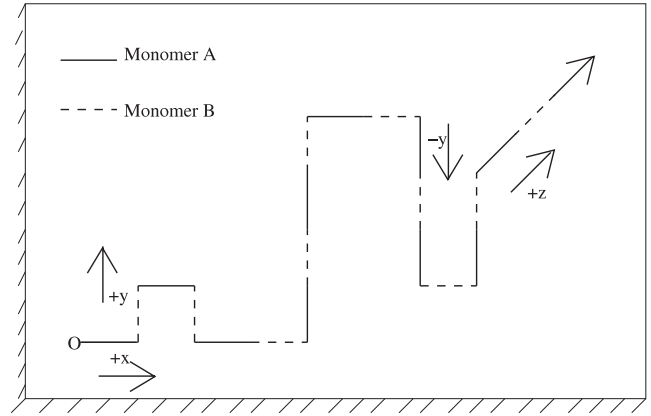


Figure 2. In this figure we have schematically shown a walk of an alternating copolymer chain interacting with an impenetrable surface located at $z = 0$ and one end of the chain is grafted at O. The walk of the chain is partially directed in three dimensions, i.e. walker is allowed to walk along $+x$, $\pm y$ and $+z$ directions.

where $s_1(=\omega_1g)$ is the Boltzmann weight of the interaction energy of the A type monomer with the surface and similarly $s_2(=\omega_2g)$ is that of the B type monomer. For $s_1s_2 < 1$, we have

$$S_{1x}^{PD-C}(k, \omega_1, \omega_2, g) = s_1 + \frac{s_1(s_2 + 2kS_{2y}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} + \frac{s_1s_2(s_1 + 2kS_{1y}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} \quad (3)$$

the component along the y axis:

$$S_{1y}^{PD-C}(k, \omega_1, \omega_2, g) = s_1 + s_1(s_2 + kS_{2x}^{PD-C} + kZ^{PD-C}) + s_1s_2(s_1 + kS_{1x}^{PD-C} + kZ^{PD-C}) + \dots \quad (4)$$

for $s_1s_2 < 1$:

$$S_{1y}^{PD-C}(k, \omega_1, \omega_2, g) = s_1 + \frac{s_1(s_2 + 2kS_{2x}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} + \frac{s_1s_2(s_1 + 2kS_{1x}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} \quad (5)$$

and components of the partition function with the first monomer of B type are

$$S_{2x}^{PD-C}(k, \omega_1, \omega_2, g) = s_2 + s_2(s_1 + 2kS_{1y}^{PD-C} + kZ^{PD-C}) + s_2s_1(s_2 + 2kS_{2x}^{PD-C} + kZ^{PD-C}) + \dots \quad (6)$$

which can be rewritten for $s_1s_2 < 1$:

$$S_{2x}^{PD-C}(k, \omega_1, \omega_2, g) = s_2 + \frac{s_2(s_1 + 2kS_{1y}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} + \frac{s_1s_2(s_2 + 2kS_{2y}^{PD-C} + kZ^{PD-C})}{1 - s_1s_2} \quad (7)$$

also

$$S_{2y}^{PD-C}(k, \omega_1, \omega_2, g) = s_2 + s_2(s_1 + kS_{1x}^{PD-C} + kZ^{PD-C}) + s_2s_1(s_2 + kS_{2x}^{PD-C} + kZ^{PD-C}) + \dots \quad (8)$$

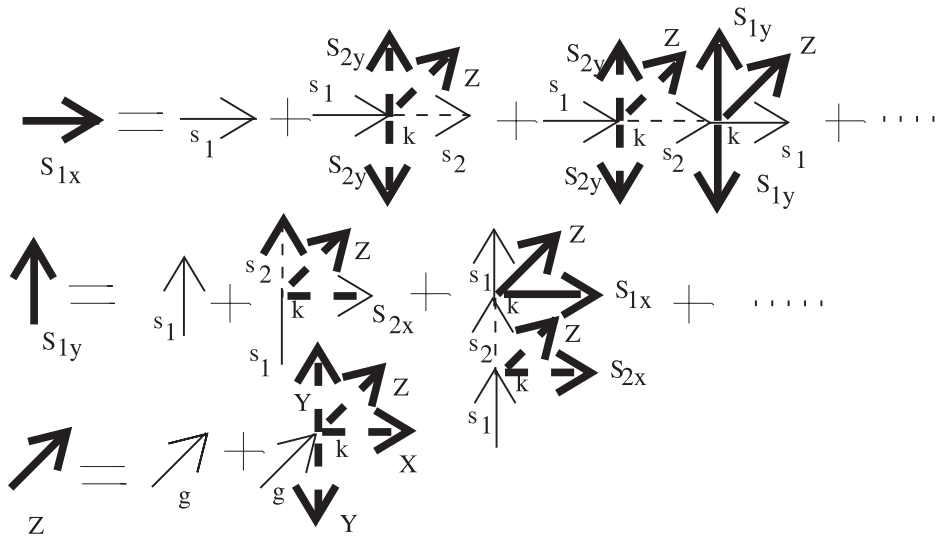


Figure 3. The generating functions for a partially directed self-avoiding walk on a three-dimensional cubic lattice is shown diagrammatically. X , Y and Z represent the sum of the Boltzmann weight of all the walks of a copolymer chain having the first step along $+x$, $\pm y$, $+z$ directions respectively while S_{1x} , S_{1y} show the sum of the Boltzmann weight of all the walks with the first monomer of the chain of A type and this step on the surface is along $+x$, $+y$ directions respectively and S_{2x} , S_{2y} is the sum of the weights of all the walks when the first monomer of the chain is B type and this step is on the surface along $+x$, $+y$ directions respectively.

when $s_1 s_2 < 1$:

$$S_{2y}^{\text{PD-C}}(k, \omega_1, \omega_2, g) = s_2 + \frac{s_2(s_1 + k S_{1x}^{\text{PD-C}} + k Z^{\text{PD-C}})}{1 - s_1 s_2} + \frac{s_2 s_1 (s_2 + k S_{2x}^{\text{PD-C}} + k Z^{\text{PD-C}})}{1 - s_1 s_2}. \quad (9)$$

Using figure 3, we write the component of the partition function perpendicular to the plane of the surface as [13]

$$Z^{\text{PD-C}}(k, g) = g + g(k X^{\text{PD-C}} + 2k Y^{\text{PD-C}} + Z^{\text{PD-C}}) \quad (10)$$

where $X^{\text{PD-C}}(k, g) = S_{1x}^{\text{PD-C}}(k, \omega_1 = \omega_2 = 1, g) = S_{2x}^{\text{PD-C}}(k, \omega_1 = \omega_2 = 1, g)$ and $Y^{\text{PD-C}}(k, g) = S_{1y}^{\text{PD-C}}(k, \omega_1 = \omega_2 = 1, g) = S_{2y}^{\text{PD-C}}(k, \omega_1 = \omega_2 = 1, g)$. In other words, we have an expression for $X^{\text{PD-C}}(k, g)$ and $Y^{\text{PD-C}}(k, g)$:

$$X^{\text{PD-C}}(k, g) = g + \frac{g}{1-g}(g + 2k Y^{\text{PD-C}} + k Z^{\text{PD-C}}) \quad (11)$$

$$Y^{\text{PD-C}}(k, g) = g + \frac{g}{1-g}(g + k X^{\text{PD-C}} + k Z^{\text{PD-C}}). \quad (12)$$

On solving equations (10)–(12) we obtain the component of the partition function perpendicular to the plane of the surface as [13]

$$Z^{\text{PD-C}}(k, g) = -\frac{g + (2k - 1)g^2}{(-1 - k + 4k^2)g^2 + (k + 2)g - 1}. \quad (13)$$

On solving equations (3), (5), (7) and (9) and using the value of $Z^{\text{PD-C}}$ from equation (13), we get the value of $S_{1x}^{\text{PD-C}}$ and $S_{1y}^{\text{PD-C}}$ [14]:

$$S_{1x}^{\text{PD-C}}(k, \omega_1, \omega_2, g) = \frac{s_1(-1 + u_1 s_2 + u_2 s_1 s_2^2)(-1 + 2g + (-1 + 2k^2)g^2)}{(1 - 2s_1 s_2(1 + 2k^2) + s_1^2 s_2^2(1 - 2k^2)^2)u_3} \quad (s_1 s_2 < 1) \quad (14)$$

where u_1 , u_2 and u_3 are

$$u_1 = -1 + s_1 + 2k^2 s_1 - 2k(1 + 2s_1)$$

$$u_2 = 1 - 2k - 2k^2 + 4k^3$$

$$u_3 = (-1 - k + 4k^2)g^2 + (k + 2)g - 1$$

and

$$S_{1y}^{\text{PD-C}}(k, \omega_1, \omega_2, g) = \frac{(-s_1 + s_1 s_2 u_4 + u_5 s_1 s_2^2)(-1 + 2g + (-1 + 2k^2)g^2)}{(1 - 2s_1 s_2(1 + 2k^2) + s_1^2 s_2^2(1 - 2k^2)^2)u_3} \quad (s_1 s_2 < 1) \quad (15)$$

where

$$u_4 = -1 + s_1 + 2k^2 s_1 - k(1 + 2s_1)$$

$$u_5 = 1 - k - 2k^2 + 2k^3.$$

Thus, the partition function of the copolymer chain having the first monomer of A type and grafted to the surface can be written as [14]

$$G_{\text{PD-C}}(k, \omega_1, \omega_2, g) = S_{1x}^{\text{PD-C}} + 2S_{1y}^{\text{PD-C}} + Z^{\text{PD-C}} \quad (s_1 s_2 < 1) \quad (16)$$

where

$$G_{\text{PD-C}}(k, \omega_1, \omega_2, g) = \frac{(u_6 + u_7 + s_1^2 s_2(-24k^5 s_2 g^2 + (-1 + g)u_8 + u_9))}{(1 - 2s_1 s_2(1 + 2k^2) + s_1^2 s_2^2(1 - 2k^2)^2)u_3} \quad (17)$$

here

$$u_6 = g(-1 + g - 2kg) + s_1(-3 + 6g + (-3 + 6k^2)g^2)$$

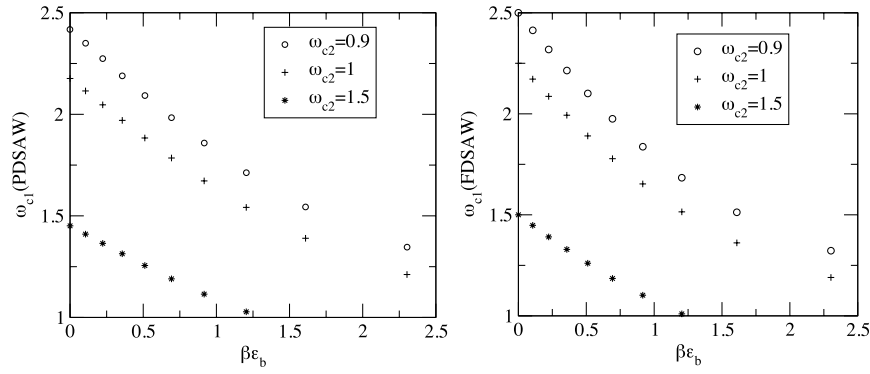


Figure 4. This figure compares the values of ω_{c1} for different values of $\beta\epsilon_b$ for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to one of the preferred directions of the copolymer chain for PDSAW and FDSAW models on a cubic lattice for values of $\omega_{c2} = 0.9, 1$ and 1.5 .

$$u_7 = s_1 s_2 (-3 + 8g - 5g^2 + 16k^3 g^2 + 2k^2 g(2+g) + k(-4+8g))$$

$$u_8 = -3 - 3s_2 + 3g + 4s_2 g$$

$$u_9 = 8k^3 u_{10} + 4k^4 g u_{11} - 2k u_{12} - 2k^2 u_{13}$$

$$u_{10} = s_2 - 2s_2 g + 2g^2 + 3s_2 g^2$$

$$u_{11} = -3g + s_2(-1 + 4g)$$

$$u_{12} = 4(-1 + k)^2 + s_2(2 - 4g + 3g^2)$$

and

$$u_{13} = -3 + 6g + s_2(3 - 8g + 8g^2).$$

Singularities appearing in equation (17) give the critical value of $g_c = \frac{k+2-\sqrt{17k}}{2(1+k-4k^2)}$ [13] and $\omega_{c1} = \frac{4(1+k-4k^2)^2}{(1+\sqrt{2k})^2(k+2-\sqrt{17k})^2\omega_{c2}}$ [14]. On substitution of $\omega_{c1} = \omega_{c2} = \omega_c$, we are able to obtain ω_c required for adsorption of a semiflexible homopolymer chain for 3D-PDSAW, as reported by Mishra *et al* [13].

We consider the value of ω_{c2} equal to one, greater than one (say, 1.5) and less than one (say, 0.9), depending on the fact that the B type monomer is having no interaction, attractive or repulsive interaction with the surface and obtain ω_{c1} required for adsorption of the copolymer chain on the surface. Variation of ω_{c1} is shown for different values of $\beta\epsilon_b$ for three values of ω_{c2} in figure 4.

(ii) *Fully directed self-avoiding walk model.* The partition function $G_{FD-C}(k, \omega_1, \omega_2, g)$ for this case can be easily evaluated following the method used for the 3D-PDSAW model, discussed above. We write components of the partition function $G_{FD-C}(k, \omega_1, \omega_2, g)$ of a semiflexible alternating copolymer chain having the first monomer of A type as

$$S_{1x}^{FD-C}(k, \omega_1, \omega_2, g) = s_1 + s_1(s_2 + kS_{2y}^{FD-C} + kZ^{FD-C}) + s_1 s_2 (s_1 + kS_{1y}^{FD-C} + kZ^{FD-C}) + \dots \quad (18)$$

for $s_1 s_2 < 1$:

$$S_{1x}^{FD-C}(k, \omega_1, \omega_2, g) = s_1 + \frac{s_1(s_2 + kS_{2y}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} + \frac{s_1 s_2 (s_1 + kS_{1y}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} \quad (19)$$

other component:

$$S_{1y}^{FD-C}(k, \omega_1, \omega_2, g) = s_1 + s_1(s_2 + kS_{2x}^{FD-C} + kZ^{FD-C}) + s_1 s_2 (s_1 + kS_{1x}^{FD-C} + kZ^{FD-C}) + \dots \quad (20)$$

when $s_1 s_2 < 1$:

$$S_{1y}^{FD-C}(k, \omega_1, \omega_2, g) = s_1 + \frac{s_1(s_2 + kS_{2x}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} + \frac{s_1 s_2 (s_1 + kS_{1x}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} \quad (21)$$

and components of the partition function with a monomer grafted on the surface of B type are

$$S_{2x}^{FD-C}(k, \omega_1, \omega_2, g) = s_2 + s_2(s_1 + kS_{1y}^{FD-C} + kZ^{FD-C}) + s_2 s_1 (s_2 + kS_{2y}^{FD-C} + kZ^{FD-C}) + \dots \quad (22)$$

when $s_1 s_2 < 1$:

$$S_{2x}^{FD-C}(k, \omega_1, \omega_2, g) = s_2 + \frac{s_2(s_1 + kS_{1y}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} + \frac{s_2 s_1 (s_2 + kS_{2y}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} \quad (23)$$

also

$$S_{2y}^{FD-C}(k, \omega_1, \omega_2, g) = s_2 + s_2(s_1 + kS_{1x}^{FD-C} + kZ^{FD-C}) + s_2 s_1 (s_2 + kS_{2x}^{FD-C} + kZ^{FD-C}) + \dots \quad (24)$$

here too, $s_1 s_2 < 1$, so that

$$S_{2y}^{FD-C}(k, \omega_1, \omega_2, g) = s_2 + \frac{s_2(s_1 + kS_{1x}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} + \frac{s_2 s_1 (s_2 + kS_{2x}^{FD-C} + kZ^{FD-C})}{1 - s_1 s_2} \quad (25)$$

The component of the partition function perpendicular to the plane of the surface for this case can be written using the method discussed for the PDSAW model as [13]

$$Z^{FD-C}(k, g) = g + g(kX^{FD-C} + 2kY^{FD-C} + Z^{FD-C}) \quad (26)$$

where $X^{\text{FD-C}}(k, g) = S_{1x}^{\text{FD-C}}(k, \omega_1 = \omega_2 = 1, g) = S_{2y}^{\text{FD-C}}(k, \omega_1 = \omega_2 = 1, g)$ and $Y^{\text{FD-C}}(k, g) = S_{1y}^{\text{FD-C}}(k, \omega_1 = \omega_2 = 1, g) = S_{2x}^{\text{FD-C}}(k, \omega_1 = \omega_2 = 1, g)$. In this case, we have an expression for $X^{\text{FD-C}}(k, g)$ and $Y^{\text{FD-C}}(k, g)$ that can be written as

$$X^{\text{FD-C}}(k, g) = g + \frac{g}{1-g}(g + kY^{\text{FD-C}} + kZ^{\text{FD-C}}) \quad (27)$$

$$Y^{\text{FD-C}}(k, g) = g + \frac{g}{1-g}(g + kX^{\text{FD-C}} + kZ^{\text{FD-C}}). \quad (28)$$

On solving equations (26)–(28) we obtain the component of the partition function perpendicular to the plane of the surface as [13]

$$Z^{\text{FD-C}}(k, g) = -\frac{g}{-1 + g(1 + 2k)}. \quad (29)$$

On solving equations (19), (21), (23) and (25) and substituting the value of $Z^{\text{FD-C}}$ from equation (29) we get the following values of $S_{1x}^{\text{FD-C}}$ and $S_{1y}^{\text{FD-C}}$ [14], ($s_1s_2 < 1$):

$$S_{1x}^{\text{FD-C}}(k, \omega_1, \omega_2, g) = S_{1y}^{\text{FD-C}}(k, \omega_1, \omega_2, g) = -\frac{s_1(1 + s_2 + ks_2)(-1 + g + kg)}{(-1 + (1 + k)^2s_1s_2)(-1 + g + 2kg)} \quad (30)$$

$$G_{\text{FD-C}}(k, \omega_1, \omega_2, g) = S_{1x}^{\text{FD-C}} + S_{1y}^{\text{FD-C}} + Z^{\text{FD-C}} \quad (31)$$

so that

$$G_{\text{FD-C}}(k, \omega_1, \omega_2, g) = \frac{g - s_1u_{14}}{(-1 + (1 + k)^2s_1s_2)(-1 + g + 2kg)} \quad (s_1s_2 < 1) \quad (32)$$

where

$$u_{14} = 2(-1 + g + kg) + (1 + k)s_2(-2 + 3(1 + k)g).$$

Singularities of the partition function, in this case give the critical value of $g_c = \frac{1}{2k+1}$ [13] and $\omega_{c1} = \frac{(2k+1)^2}{\omega_{c2}(k+1)^2}$ [14]. Assuming ω_{c2} equal to one, greater than one (say, 1.5, an attractive interaction of B type monomers with the surface) and less than one (say, 0.9, a repulsive interaction of B type monomers with the surface), we obtained $\omega_{c1} \geq 1$ so that the adsorption of a copolymer chain may take place on the surface. Variation of ω_{c1} with bending energy of the copolymer chain is shown in figure 4 for the FDSA model on a cubic lattice. In this case too, on substitution of $\omega_{c1} = \omega_{c2} = \omega_c$, we are able to reproduce the value of ω_c required for adsorption of the semiflexible homopolymer chain, as reported by Mishra *et al* [13] for the FDSA model on the cubic lattice.

2.2. Adsorption on a fluctuating 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 alternating copolymer chain on a fluctuating surface. In the case of a two-dimensional hexagonal lattice, the surface is an impenetrable line and its shape is like a sawtooth wave [15] (as shown in figure 5 schematically). Therefore, adsorbed parts of

the copolymer chain have bends and in this case components of the partition function of the copolymer chain having the first monomer grafted to the surface of A type can be written following the method outlined above and using figure 5(B) as

$$S^{\text{H}}(k, \omega_1, \omega_2, g) = s_1(1 + ks_2 + k^2s_2Y^{\text{H}}) + s_1^2s_2k^2(1 + ks_2 + k^2s_2Y^{\text{H}}) + \dots \quad (33)$$

where $Y^{\text{H}}(k, g)$ is the component of the partition function perpendicular to the plane of the surface:

$$S^{\text{H}}(k, \omega_1, \omega_2, g) = \frac{s_1(1 + ks_2 + k^2s_2Y^{\text{H}})}{1 - s_1s_2k^2} \quad (s_1s_2 < 1). \quad (34)$$

The components of the partition function of a surface interacting copolymer chain can be written for the above-mentioned three cases of directedness of the walks of the alternating copolymer chain for a two-dimensional hexagonal lattice as follows.

(i) *Partially directed self-avoiding walk (I) model.* For this model the component of the partition function perpendicular to the plane of the surface can be calculated following the method discussed above. We write the expression of $X^{\text{PD1-H}}$ by substituting $\omega_1 = \omega_2 = 1$ in equation (34), such that

$$X^{\text{PD1-H}}(k, g) = \frac{g(1 + kg + k^2gY^{\text{H}})}{1 - g^2k^2} \quad (35)$$

and $Y^{\text{PD1-H}}$ can be written using figure 5(A) as [15]

$$Y^{\text{PD1-H}}(k, g) = g + 2kg^2 + 2k^2g^2(X^{\text{PD1-H}} + Y^{\text{PD1-H}}) \quad (36)$$

and solving equations (35) and (36) to obtain the component of the partition function perpendicular to the plane of surface as [15]

$$Y^{\text{PD1-H}}(k, g) = -\frac{g(1 + 2gk + g^2k^2)}{-1 + 3g^2k^2} \quad (37)$$

therefore, the partition function for this model can be written as (provided, $s_1s_2 < 1$)

$$G_{\text{PD1-H}}(k, \omega_1, \omega_2, g) = \frac{g(1+kg)^2 + s_1(2+2ks_2+k^2(s_2-6g)g - 4k^3s_2g^2 + k^4s_2g^3)}{(-1 + k^2s_1s_2)(-1 + 3k^2g^2)}. \quad (38)$$

Singularities of the partition give $\omega_{c1} = \frac{3}{\omega_{c2}}$.

(ii) *Partially directed self-avoiding walk (II) model.* Following the method used for the PDSA(I) model we have obtained the component of the partition function perpendicular to the plane of the surface and for this case, the component of the partition function perpendicular to the plane of the surface is [15]

$$Y^{\text{PD2-H}}(k, g) = -\frac{g(1 + gk)}{-1 + gk + g^2k^2} \quad (39)$$

so that the partition function is

$$G_{\text{PD2-H}}(k, \omega_1, \omega_2, g) = \frac{g(1 + kg) - s_1(1 + ks_2)(-1 + kg + k^2g^2)}{(-1 + k^2s_1s_2)(-1 + gk + g^2k^2)} \quad (s_1s_2 < 1). \quad (40)$$

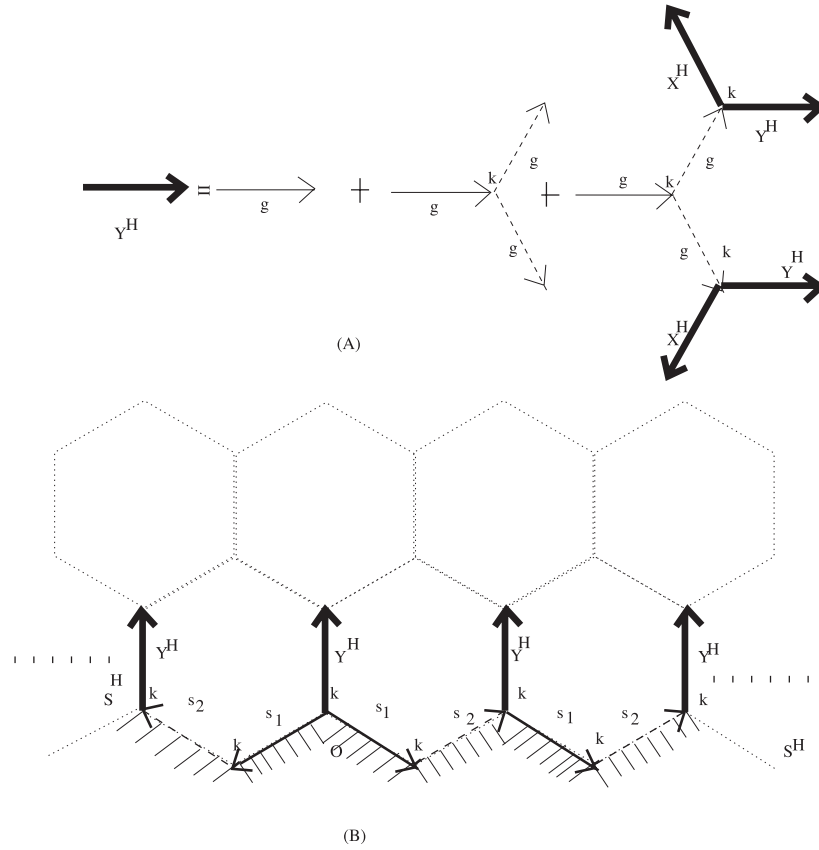


Figure 5. A surface interacting alternating copolymer chain is shown schematically for the PDSAW(I) model on a hexagonal lattice. One end of the polymer chain is grafted on the fluctuating impenetrable surface at O, S^H is the component of the partition function along the surface and Y^H is the component perpendicular to the plane of the surface.

In this case, singularities of the partition function give $\omega_{c1} = \frac{4}{(\sqrt{5}-1)^2 \omega_{c2}}$.

(iii) *Fully directed self-avoiding walk model.* For this model, we have the component of the partition function perpendicular to the plane of the surface is Y^{FD-H} [15], which can be obtained following the method discussed above for the PDSAW(I) model:

$$Y^{FD-H}(k, g) = -\frac{g(1 + gk)}{-1 + 2g^2k^2} \quad (41)$$

Therefore, the partition function is

$$G_{FD-H}(k, \omega_1, \omega_2, g) = \frac{g(1 + kg) - s_1(1 + ks_2)(-1 + 2k^2g^2)}{(-1 + k^2s_1s_2)(-1 + 2k^2g^2)} \quad (s_1s_2 < 1). \quad (42)$$

From singularities of the partition function of the copolymer chain, we write the critical value of the monomer surface attraction required for A type monomers as $\omega_{c1} = \frac{2}{\omega_{c2}}$ for the adsorption of the copolymer chain on the surface.

Variation of ω_{c1} for various values of ω_{c2} is shown in figure 6 for PDSAW(I), PDSAW(II) and FDSAW models for a two-dimensional hexagonal lattice. When we substitute $\omega_{c1} = \omega_{c2} = \omega_c$, we are able to obtain the critical value of the monomer surface attraction required for adsorption of a homopolymer chain on a fluctuating impenetrable surface [15].

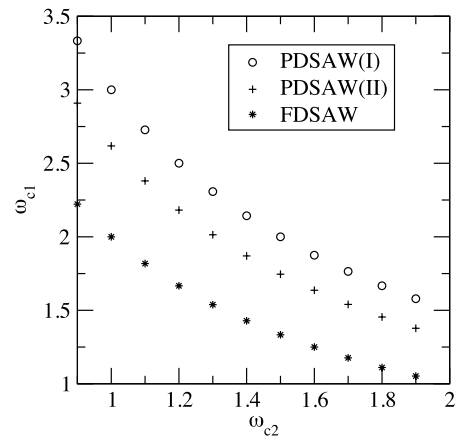


Figure 6. In this figure we have shown the values of ω_{c1} for different values of ω_{c2} for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to the preferred direction of the copolymer chain for PDSAW(I), PDSAW(II) and FDSAW models on a two-dimensional hexagonal lattice.

It is to be noted that ω_{c1} required for adsorption of a copolymer chain on a fluctuating impenetrable surface is independent of the bending energy of the copolymer chain. These features are similar to homopolymer adsorption on a fluctuating impenetrable surface [15].

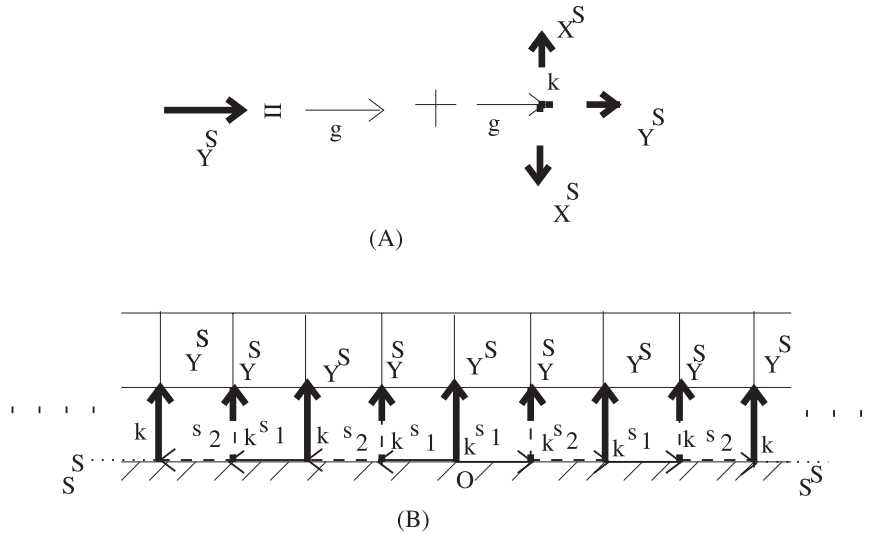


Figure 7. A surface interacting copolymer chain on a square lattice is shown schematically and the generating function for the perpendicular component of the partition function for the PDSAW model is also shown in this figure graphically.

2.3. Directed self-avoiding walk model on a square lattice

In the case of a square lattice, the surface is a line, located at $y = 0$ (as shown graphically in figure 7) and the A type monomer of the copolymer chain is grafted to the surface. In this case too, walks of the copolymer chains are directed perpendicular to the plane of the surface.

The surface component of the partition function of the copolymer chain with the first monomer grafted on the surface of A type can be written using figure 7(B) as

$$S^S(k, \omega_1, \omega_2, g) = s_1(1 + kY^S) + s_1s_2(1 + kY^S) + s_1^2s_2(1 + kY^S) + s_1^2s_2^2(1 + kY^S) + \dots \quad (43)$$

where $Y^S(k, g)$ is the component of the partition function perpendicular to the plane of the surface and the component along the surface is rewritten as

$$S^S(k, \omega_1, \omega_2, g) = \frac{s_1(1 + s_2)(1 + kY^S)}{1 - s_1s_2} \quad (s_1s_2 < 1). \quad (44)$$

(i) *Partially directed self-avoiding walk model.* In this case we obtain X^{PD-S} by substituting $\omega_1 = \omega_2 = 1$ in equation (44) and the perpendicular component of the partition function has been written according to figure 7(A) as [13]

$$X^{PD-S}(k, g) = \frac{g(1 + kY^{PD-S})}{1 - g} \quad (45)$$

and

$$Y^{PD-S}(k, g) = g + g(2kX^{PD-S} + Y^{PD-S}). \quad (46)$$

On solving equations (45) and (46) we obtain the component of the partition function perpendicular to the plane of the surface as [13]

$$Y^{PD-S}(k, g) = \frac{g + (2k - 1)g^2}{1 - 2g + g^2 - 2g^2k^2} \quad (47)$$

Thus, the partition function for this case is

$$G_{PD-S}(k, \omega_1, \omega_2, g) = \frac{g(1 + (-1 + 2k)g + s_1u_{15})}{(-1 + s_1s_2)(-1 + 2g + (-1 + 2k^2)g^2)} \quad (s_1s_2 < 1) \quad (48)$$

where

$$u_{15} = (-2(-1 + g)(1 + (-1 + k)g) + s_2(2 + (-5 + 2k)g + (3 - 4k)g^2)).$$

Singularities of the partition function for this case give $\omega_{c1} = \frac{(\sqrt{2k+1})^2}{\omega_{c2}}$.

(ii) *Fully directed self-avoiding walk model.* For this case we write the final form of the component of the partition function perpendicular to the plane of the surface using the method described for the PDSAW model on a square lattice as [13]

$$Y^{FD-S}(k, g) = \frac{g}{1 - (1 + k)g} \quad (49)$$

and therefore the partition function is

$$G_{FD-S}(k, \omega_1, \omega_2, g) = \frac{g + s_1(1 + s_2 - g - 2s_2g)}{(-1 + s_1s_2)(-1 + g + kg)} \quad (s_1s_2 < 1). \quad (50)$$

Singularities of the partition function give $\omega_{c1} = \frac{(k+1)^2}{\omega_{c2}}$. On substitution of $\omega_{c1} = \omega_{c2} = \omega_c$ in equations (48) and (50), we are able to reproduce ω_c required for adsorption of a semiflexible homopolymer chain in two dimensions [13]. Variation of ω_{c1} with bending energy of the copolymer chain is shown in figure 8 for PDSAW and FDSAW models on the square lattice.

2.4. Directed self-avoiding walk model on a two-dimensional rectangular lattice

We consider a two-dimensional rectangular lattice, which is derived from a two-dimensional hexagonal lattice (as shown in

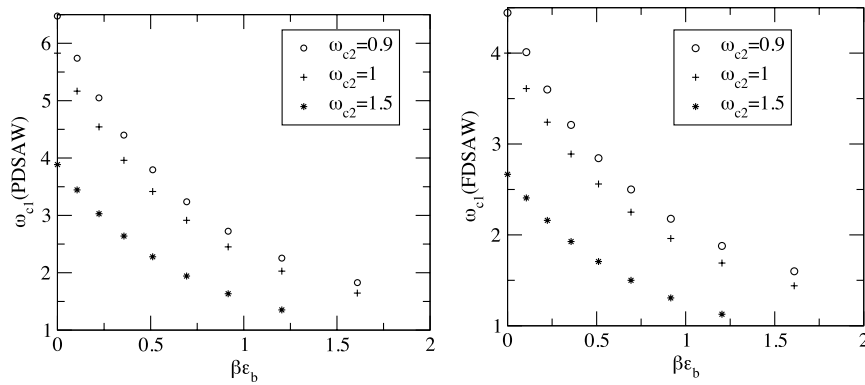


Figure 8. We compare the values of ω_{c1} for different values of $\beta\epsilon_b$ for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to the preferred direction of the copolymer chain for PDSAW and FDSAW models on a square lattice for three values of $\omega_{c2} = 0.9, 1$ and 1.5 .

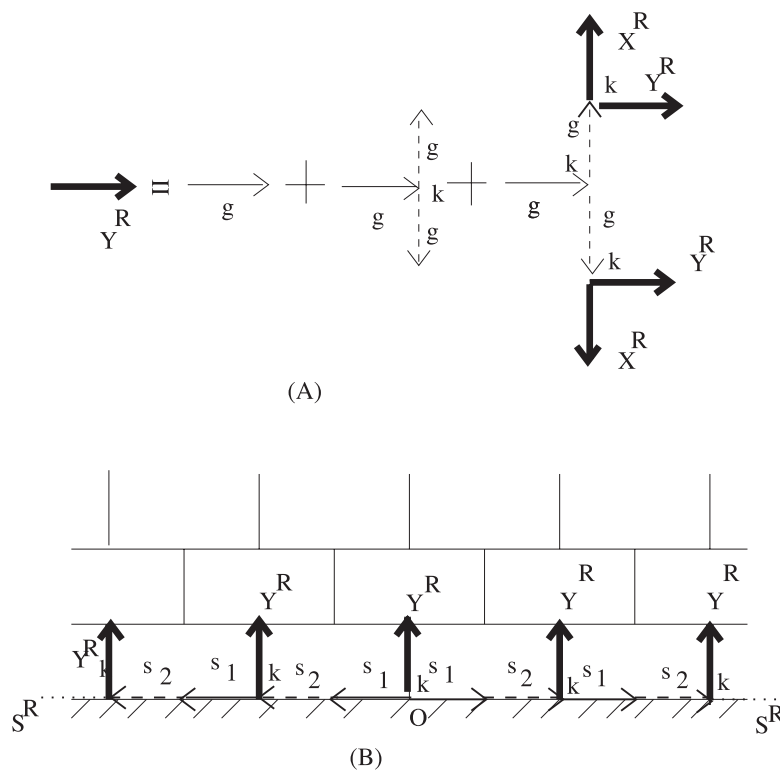


Figure 9. A surface interacting copolymer chain on a two-dimensional rectangular lattice is shown graphically and the generating function for the perpendicular component of the partition function is also shown in this figure graphically for the PDSAW model on the rectangular lattice.

figure 9). In this case too, the surface is an impenetrable line located at $y = 0$ and walks of the copolymer chain are directed perpendicular to the plane of the surface. Therefore, the component of the partition function along the surface for the copolymer chain having the first monomer of A type and that monomer is grafted on the surface is written using figure 9(B) as

$$S^R(k, \omega_1, \omega_2, g) = s_1(1 + s_2 + ks_2Y^R) + s_1^2s_2(1 + s_2 + ks_2Y^R) + \dots \quad (51)$$

where $Y^R(k, g)$ is the component of the partition function perpendicular to the plane of the surface, the above equation

can be rewritten as

$$S^R(k, \omega_1, \omega_2, g) = \frac{s_1(1 + s_2 + s_2kY^R)}{1 - s_1s_2} \quad (s_1s_2 < 1). \quad (52)$$

(i) *Partially directed self-avoiding walk model.* For the PDSAW model on the rectangular lattice, the generating function for the component of the partition function perpendicular to the plane of the surface is written using figure 9(A) as [16]

$$Y^{PD-R}(k, g) = g + 2g^2k + 2g^2k(X^{PD-R} + kY^{PD-R}) \quad (53)$$

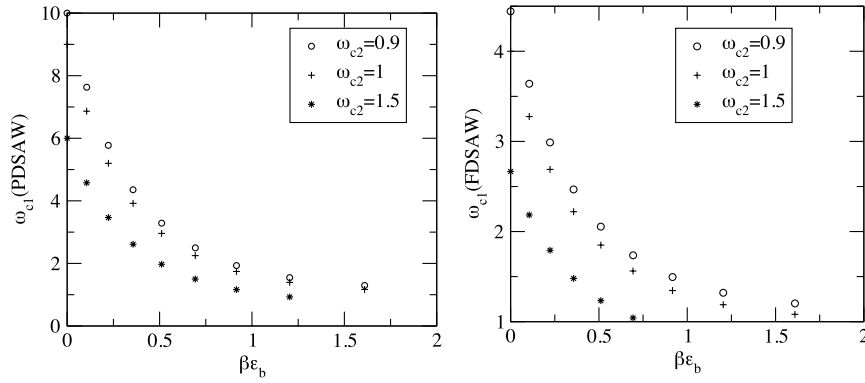


Figure 10. This figure compares the values of ω_{c1} for different values of $\beta\epsilon_b$ for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to the preferred direction of the walks of a copolymer chain for PDSAW and FDSAW models on a two-dimensional rectangular lattice for the values of $\omega_{c2} = 0.9, 1$ and 1.5 .

where $X^{\text{PD-R}}(k, g) = S^{\text{R}}(k, \omega_1 = \omega_2 = 1, g)$. In other words we can write $X^{\text{PD-R}}(k, g)$ by substituting $\omega_1 = \omega_2 = 1$ in equation (52):

$$X^{\text{PD-R}}(k, g) = \frac{g(1 + g + gkY^{\text{PD-R}})}{1 - g^2}. \quad (54)$$

On solving equations (53) and (54) we get

$$Y^{\text{PD-R}}(k, g) = -\frac{g + 2g^2k - g^3 + 2g^3k}{-1 + g^2 + 2g^2k^2} \quad (55)$$

Therefore, the partition function is

$$G_{\text{PD-R}}(k, \omega_1, \omega_2, g) = \frac{g(1 + g)(1 + (-1 + 2k)g + s_1(u_{16} + s_2u_{17}))}{(-1 + s_1s_2)(-1 + (1 + 2k^2)g^2)} \quad (56)$$

$(s_1s_2 < 1)$

where

$$u_{16} = -2(-1 + (1 + 2k^2)g^2)$$

and

$$u_{17} = 2 + (-1 + 2k)g - 2(1 + k)g^2 + (1 - 2k)^2g^3.$$

From singularities of the partition function we have $\omega_{c1} = \frac{(2k^2+1)^2}{\omega_{c2}}$.

(ii) *Fully directed self-avoiding walk model.* For the fully directed walk model on the rectangular lattice, we have $Y^{\text{FD-R}}(k, g)$ as [16] that we have obtained using the method discussed above:

$$Y^{\text{FD-R}}(k, g) = -\frac{g + g^2k - g^3 + g^3k}{-1 + g^2 + g^2k^2} \quad (57)$$

and the partition function:

$$G_{\text{FD-R}}(k, \omega_1, \omega_2, g) = \frac{g(1 + g)(1 + (-1 + k)g + s_1(u_{18} + s_2u_{19}))}{(-1 + s_1s_2)(-1 + (1 + k^2)g^2)} \quad (58)$$

$(s_1s_2 < 1)$

where

$$u_{18} = 1 - (1 + k^2)g^2$$

and

$$u_{19} = 1 + (-1 + k)g - (1 + k)g^2 + (-1 + k)^2g^3.$$

In this case, singularities of the partition function give $\omega_{c1} = \frac{(k^2+1)^2}{\omega_{c2}}$. Variation of ω_{c1} with bending energy of the copolymer chain for a few values of ω_{c2} is shown in figure 10. For the case of directed walk models on the rectangular lattice, when we substitute $\omega_{c1} = \omega_{c2} = \omega_c$ in the partition function, we are able to reproduce the critical value of the monomer surface attraction required for the adsorption of a semiflexible homopolymer chain on the rectangular lattice [16].

3. Result and discussion

The lattice model of a directed self-avoiding walk has been solved using the generating function method for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to the preferred direction of the walks of the copolymer chain. We have used a three-dimensional (cubic) lattice and two-dimensional (hexagonal, square and rectangular) lattice to model the copolymer chain and to investigate adsorption properties of the copolymer chain on an impenetrable flat surface (two-dimensional and one-dimensional) and impenetrable fluctuating surface (one-dimensional). The copolymer chain is made of two types of monomers (A and B) and the A type monomer has an attractive interaction with the surface while the B type monomer can have attractive, repulsive or no interaction with the surface. Our study showed that adsorption on the flat surface of a stiffer copolymer chain takes place at a smaller value of the monomer surface attraction when compared to that of a flexible copolymer chain.

We have compared the values of ω_{c1} (as shown in figure 11 for $\omega_{c2} = 1$) required for adsorption of an alternating copolymer chain for square, rectangular and cubic lattice cases where the surface is flat and impenetrable. We have found in all these lattice case that a stiffer chain adsorption occurs at a

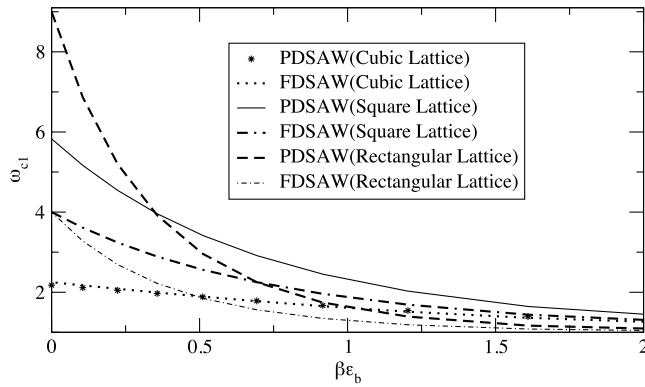


Figure 11. This figure compares the values of ω_{c1} for different values of $\beta\epsilon_b$ for adsorption of a semiflexible alternating copolymer chain on a surface perpendicular to the preferred direction of the walks of a copolymer chain for PDSAW and FDSAW models on a cubic, square and rectangular lattice for the values of $\omega_{c2} = 1$.

smaller value of monomer surface attraction than the flexible chain. However, in the case of a fluctuating impenetrable surface, the critical value of monomer surface attraction required for the copolymer chain adsorption is independent of the bending energy of the chain. These features of adsorption on an impenetrable flat and fluctuating surface are similar to the semiflexible homopolymer adsorption [13–16].

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