Directed self avoiding walk model of a semiflexible polymer chain on a rectangular lattice and a square lattice

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Abstract: Essential physics associated with the conformational behavior of a linear semiflexible homopolymer chain have been derived from a model of directed self avoiding walk (DSAW) on a two dimensional rectangular lattice. The DSAW model has been solved analytically to study the structural phase transitions in the polymer chain and exact values of conformational properties and transition points have been reported. We have analyzed the variation of critical value of step fugacity and persistent length with bending energy of the semiflexible polymer chain for a case when the chain is in the bulk. In presence of an attractive impenetrable surface, variation of critical value of monomer-surface attraction with bending energy of the polymer chain shows that adsorption of a stiff chain takes place at a smaller value of monomer surface attraction than a flexible chain. We have compared the results so obtained for a two dimensional rectangular lattice case to the corresponding results obtained using square lattice and found that qualitative nature of phase diagrams are similar in the case of both the lattices.

Key words: Rectangular lattice, square lattice, semiflexible polymer, linear chain, conformational properties.

1. Introduction

Biopolymers (e. g. DNA, protein) are known to be semiflexible polymer chains. The conformational properties of such chains have attracted considerable attention in recent years because of new developments in experimental techniques in which it has become possible to pull and stretch single Biopolymer to measure its elastic properties (Bustamante *et al.* 2000; Shivashankar *et al.* 1997). These studies will reveal a wealth of information about the conformational behavior of Biopolymers and of clear Biological importance.

The essential physics associated with the conformational behavior of a semiflexible polymer chain in the bulk and in presence of an attractive impenetrable surface can be derived in the lattice model from a model of self avoiding walk (SAW) or directed self avoiding walk (DSAW) on a suitable lattice (Privman and Svrakic, 1989; Mishra *et al.*, 2003, Giri *et al*., 2003; Mishra, 2009). The analytical solutions for semiflexible polymer chain are limited to DSAW models (Privman and Svrakic, 1989; Mishra *et al.*, 2003 and Mishra, 2009) and WLC (worm like chain) model (Kratky and Porod, 1949). The WLC model has been used extensively to study conformational properties of a semiflexible polymer chain and it can not mimic exactly the dimensional behavior of semiflexible polymer chain (Semjon, 2001). On the other hand DSAW models are analytically solvable, simple to report quantitative behavior and provides clear picture of the phase diagram of a semiflexible polymer chain in the bulk and in presence of an attractive impenetrable surface.

Lattice models are useful in analyzing the modifications in the conformational properties of the polymer chain when it is near an attractive impenetrable surface (Eisenriegler, 1993; Singh *et al.* 1999; 2000 and references therein). Since, impenetrable attractive surface introduces constrain on the polymer chain and therefore reduces its entropy and due to attractive interaction between monomer of the polymer chain and the surface, the polymer chain gains internal energy. A competition between the gain in internal energy and corresponding loss of entropy fo the polymer chain is responsible for adsorption-desorption transition. This phenomenon of adsorption-desorption transition finds applications in lubrication, adhesion and surface protection.

In the past few years much attention have been paid to the study of conformational properties of a linear semiflexible polymer chain on square and cubic lattices using SAW and DSAW models (Privman and Svrakic, 1989; Mishra *et al.*, 2003; Giri *et al.*, 2003 and references therein). Since, stiffness of the polymer chain controls bending of the chain and therefore modifies its conformational properties. This is to be noted that the universal features of a surface interacting polymer chain and qualitative nature of phase diagram will remain independent of the type of lattice (square, hexagonal or rectangular lattice in two dimension) chosen to model the polymer chain.

In the present communication we have extended the idea of DSAW model to a two dimensional rectangular lattice derived from a hexagonal lattice and solved the model analytically to study conformational changes in a linear semiflexible homopolymer chain in the bulk and in presence of an attractive impenetrable surface. The results so obtained have been compared with the corresponding results found using square lattice (Mishra *et al*., 2003) for the sake of completion.

2. Model and methods

We define stiffness weight $k = \exp(-\varepsilon_b / k_B T)$ where, $\varepsilon_b (>0)$ is the energy required to introduce one bend in the polymer chain, k_B is Boltzmann constant and T is temperature. If polymer chain is flexible ($k \to 1$ or $\varepsilon_b \to 0$), the persistent length is very small in comparison to actual length of the polymer chain and if the polymer chain is stiff ($k \to 0$ or $\varepsilon_b \to \infty$) the persistent length is of the order of the polymer chain length. However, if $0 < k < 1$ or $0 < \varepsilon_b < \infty$, the polymer chain is known as a semiflexible polymer.

In the case of directed self avoiding walk model on a two dimensional rectangular lattice all the directions in space are not treated equally by the walker therefore model introduces stiffness in the polymer chain and angle of bending of the polymer chain is 90^0 for all the bends therefore model is restrictive. However, directed self avoiding model is exactly solvable therefore gives exact value of conformational properties, transition points and clear picture of phase diagram. In a case, when polymer chain is directed along +y direction, i. e. walker can take steps along ±x and +y directions, corresponds to the case of partially directed self avoiding walk (PDSAW) model. Another case, in which walker is directed along +x as well as +y direction, i. e. walker can not walk along -x and -y directions, model is known as fully directed self avoiding walk (FDSAW) model. We have taken lattice parameter 2:1 along x:y directions respectively for the two dimensional rectangular lattice which is derived from a hexagonal lattice.

The grand canonical partition function of a semiflexible polymer chain in general can be written as,

$$Z(x,k) = \sum_{N=0}^{N=\infty} \sum_{All\ walks\ of\ N\ steps} x^N k^{N_b} \tag{1}$$

In Eq. (1) N_b is the number of bends in a walk of N monomers (steps), x is the step fugacity associated with each monomer of the polymer chain and k is stiffness of the chain. We define X as the sum of Boltzmann weight of all the walks whose first step is along any of the ±x directions and Y is sum of Boltzmann weight of all the walks with first step along +y direction.

2. 1(a) PDSAW model

The generating function for PDSAW model on a two dimensional rectangular lattice (derived from a hexagonal lattice) can be written (as shown graphically in Fig. 1B) and solved to evaluate partition function, $Z_{PD}(x,k)$ of the linear semiflexible homopolymer chain as follows.

Fig. (1A) Rectangular lattice derived from a hexagonal lattice.
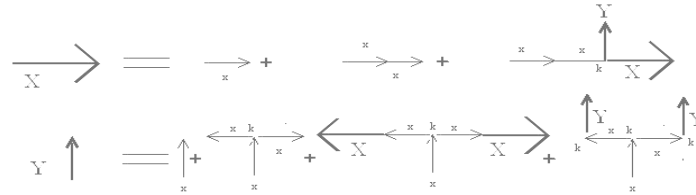

Fig. (1B) Recursion relations for PDSAW model are shown diagrammatically for a long linear semiflexible homopolymer chain on a rectangular lattice in two dimension. In the PDSAW model walks of the polymer chain are directed along +y direction. Step fugacity of each step is shown by x, k is stiffness associated with each bend of the polymer chain, X shows sum of Boltzmann weight of all the walks whose first is along any of the directions ±x and Y shows sum of Boltzmann weight of all the walks having first step along +y direction.

Components of recursion relations have been written according Fig. (1B) and solved for partition function $Z_{PD}(x,k)$ of the polymer chain as follows:

$$X = x + x^2 + x^2(X + kY) \tag{2}$$

$$Y = x + 2x^2k + 2x^2kX + 2x^2k^2Y \tag{3}$$

Eqs. (2) and (3) can be solved for X and Y,

$$X = \frac{x(-1 - x - x^2k + 2x^2k^2)}{-1 + x^2 + 2x^2k^2}; \qquad Y = -\frac{x + 2x^2k - x^3 + 2x^3k}{-1 + x^2 + 2x^2k^2} \qquad (4)$$

Therefore, partition function $Z_{PD}(x,k)$ for PDSAW model can be written as,

$$Z_{PD}(x,k) = 2X + Y = \frac{-(3x + 2x^2 + 2x^2k - x^3 + 4x^3k - 4x^3k^2)}{-1 + x^2 + 2x^2k^2} \qquad (5)$$

The partition function $Z_{PD}(x,k)$ of the polymer chain diverges for,

$$-1 + x^2 + 2x^2k^2 = 0 \qquad (6)$$

From Eq. (6) we obtain critical value of step fugacity for polymerization of an infinitely long linear semiflexible polymer chain and it can be written in terms of stiffness as $x_c = 1/(\sqrt{1 + 2k^2})$.

However, critical value of step fugacity for PDSAW model on a square lattice in terms of stiffness of the chain is written as $x_c = 1/(1 + \sqrt{2}k)$ (Mishra *et al.*, 2003). The dependency of step fugacity of a semiflexible polymer chain on its bending energy for PDSAW model is shown in Fig. (2) by up-triangle for a rectangular lattice and by star for a square lattice.

The persistent length (l_p) defined by Mishra *et al.*, (2003) can be calculated for PDSAW model of semiflexible polymer chain for the rectangular lattice and it can be written as $l_p = 1 + (1/2)k^{-2}$. Variation of persistent length with bending energy of the linear polymer chain for PDSAW model is shown in Fig. (3) by up-triangle for the rectangular lattice and by star for square lattice.

2. 1(b) FDSAW model

The recursion relations for generating functions of FDSAW model on a two dimensional rectangular lattice can be written according to the method outlined above and easily solved for calculation of partition function of the semiflexible polymer chain as follows:

$$X = x + x^2 + x^2(X + kY) \qquad (7)$$
$$Y = x + x^2k + x^2k(X + kY) \qquad (8)$$

On solving Eqs. (7) and (8) for X and Y, we find value of X and Y to calculate partition function $Z_{FD}(x,k)$ as follows,

$$X = \frac{x(-1 - x - x^2k + x^2k^2)}{-1 + x^2 + x^2k^2}; \quad Y = -\frac{x + x^2k - x^3 + x^3k}{-1 + x^2 + x^2k^2} \qquad (9)$$

Thus, partition function $Z_{FD}(x,k)$ for FDSAW model is,

$$Z_{FD}(x,k) = X + Y = -\frac{2x + x^2 + x^2k - x^3 + 2x^3k - x^3k^2}{-1 + x^2 + x^2k^2} \qquad (10)$$

The critical value of step fugacity for polymerization of an infinitely long linear semiflexible chain can be obtained from singularity of $Z_{FD}(x,k)$, i. e.,

$$-1 + x^2 + x^2k^2 = 0 \qquad (11)$$

Thus, in this case critical value of step fugacity $x_c = 1/\sqrt{1 + k^2}$, its variation with bending energy of the polymer chain is shown in Fig. (2) by down-triangle for rectangular lattice. For a square lattice $x_c[= 1/(1 + k)]$ (Mishra *et al.*, 2003) have been shown in Fig. (2) by plus symbol for FDSAW model to compare the results for different values of bending of the polymer chain.

The value of persistent length of the semiflexible polymer chain for FDSAW model on the rectangular lattice ($l_p = 1 + k^{-2}$) has been shown for different values of bending energy of the polymer chain in Fig (3) by down-triangle and by plus symbol for square lattice ($l_p = 1 + k^{-1}$) (Mishra *et al.*, 2003).
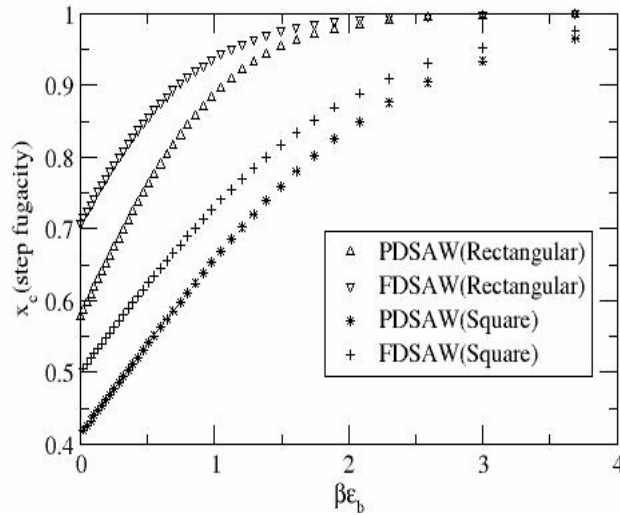
Fig. (2) Variation of critical value of step fugacity for polymerization of an infinitely long linear semiflexible polymer chain has been shown for various values of bending energy of the polymer chain for PDSAW and FDSAW models on a two dimensional rectangular lattice and square lattice.
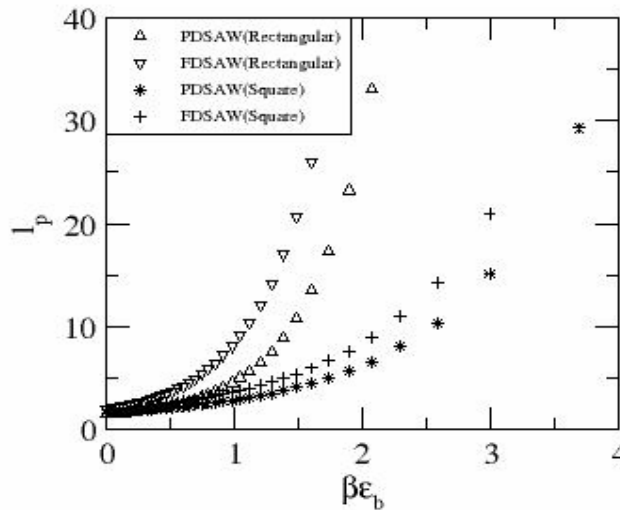

Fig. (3) Variation of persistent length of an infinitely long linear semiflexible polymer chain has been shown for various values of bending energy of the polymer chain for PDSAW and FDSAW models on a rectangular lattice and square lattice in two dimension.

2.2 Adsorption properties

In presence of an attractive impenetrable surface, conformational properties of the semiflexible polymer chain get modified due to constrain imposed by surface and attractive interaction of monomer of the chain with the surface. The attractive surface contributes an excess energy $\varepsilon_s(<0)$ for each step of the walk lying on the surface and thus leads to an increased probability, characterized by the Boltzmann weight $\omega(=e^{-\beta\varepsilon_s})$, of making a step on the surface. Impenetrable surface constrains the polymer chain and therefore, reduces its entropy. The polymer chain may move away from the surface to increase its entropy and desorbed state will prevail. However, if polymer chain and surface attraction wins over the loss of entropy of the chain due to constrain imposed on the polymer chain by the impenetrable attractive surface, most of the parts of chain get attached to the surface and adsorbed state will prevail. Thus, transition between adsorbed and desorbed regimes is marked by a critical value of ω or monomer surface attraction energy.

In this section, PDSAW and FDSAW models for a two dimensional rectangular lattice have been solved for an infinitely long linear semiflexible chain in the presence of an attractive impenetrable surface (i. e. a line y=0 for two dimensional space) and results obtained have been compared with corresponding results found using a square lattice.

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2.2 (a) PDSAW model

We report the results found from analytical calculation for the adsorption of a directed semiflexible polymer chain on a surface. For a two dimensional space surface is a line. Let S be the component of generating function along the surface. Following the method outlined above, we can write generating function for surface interacting chain, as written in eq. (12).

Surface component of recursion relation for PDSAW model can be written using Fig. (4) as,

$$S = s(1 + s + skY) + s^3(1 + s + skY) + s^5(1 + s + skY)...... \qquad (s<1) \quad (12)$$

Where, $s(= \omega x)$ is the weight associated with each step (monomer) lying on the surface. Above series can be summed for s < 1, such that,
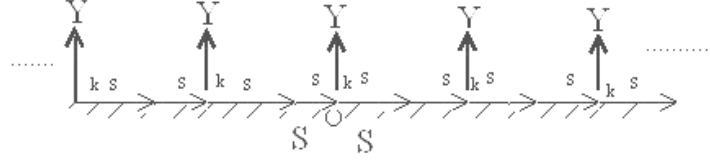

Fig. (4) Recursion relation for an infinitely long linear semiflexible polymer chain interacting with an attractive impenetrable surface is shown diagrammatically for a two dimensional rectangular lattice. Surface is a line and shown by y=0. All the walks starts from a point O lying on the surface and S represents sum of Boltzmann weight of all the walks whose first step is on the surface. Y is the component of generating function perpendicular to the surface.

The partition function, $Z^s_{PD}(k,\omega,x)$ of the surface interacting semiflexible polymer chain is written as,

$$Z^s_{PD}(k,\omega,x) = 2S + Y \qquad (s<1) \quad (13)$$

We have taken value of Y from eq. (4), thus,

$$Z^s_{PD}(k,\omega,x) = \frac{2s(1+s)(-1+x^2+2x^2k^2) - x(1-s^2+2s^2k)(1+2xk-x^2+2x^2k)}{(1-s^2)(-1+x^2+2x^2k^2)} \qquad (s<1) \quad (14)$$

For adsorption of an infinitely long linear semiflexible homopolymer chain on a surface perpendicular to the direction of directedness of walks has been found and its value in terms of stiffness can be written as $\omega_c = \sqrt{1+2k^2}$. This value of ω_c has been obtained from singularities of Eq. (14). The variation of ω_c for the semiflexible polymer chain with bending energy of the chain is shown in Fig. (5) by up-triangle for PDSAW model on a rectangular lattice. The value of $\omega_c = \sqrt{2k+1}$ (Mishra *et al.*, 2003) for square lattice in the case of PDSAW model and its variation is shown in Fig. (5) by star for different values of bending energy of the polymer chain.

2.2 (b) FDSAW model

In the case of FDSAW model the component of generating function along surface has same expression as we have obtained for PDSAW model. Therefore, partition function of the polymer chain for this model $Z^s_{FD}(k,\omega,x)$ can be written as,

$$Z^s_{FD}(k,\omega,x) = S + Y \qquad (s<1) \quad (15)$$

$$Z^s_{FD}(k,\omega,x) = \frac{s(1+s)(-1+x^2+x^2k^2) - x(1-s^2+s^2k)(1+xk-x^2+x^2k)}{(1-s^2)(-1+x^2+x^2k^2)} \qquad (s<1) \quad (16)$$

In above Eq. (15) we have used value of Y from Eq. (9). The singularities of $Z^s_{FD}(k,\omega,x)$ gives critical value of ω for adsorption of the semiflexible polymer chain as, $\omega_c = \sqrt{1+k^2}$ and its variation with bending energy of the semiflexible polymer chain is shown by down-triangle in Fig. (5) for FDSAW model on a rectangular lattice. However, in the case of a square lattice for FDSAW model $\omega_c = 1+k$ and its variation with bending energy of the polymer chain is shown in Fig. (5) by plus symbol.
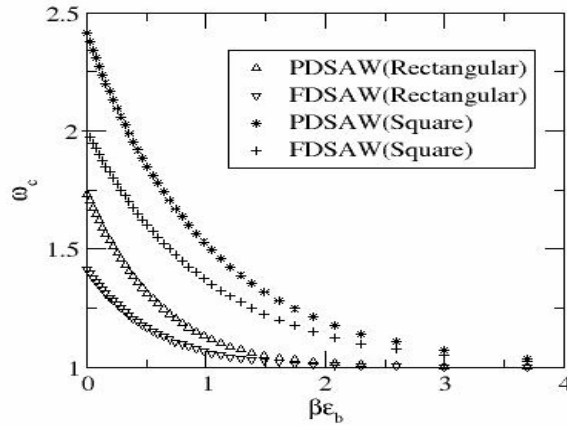
Fig. (5) The variation of ω_c for adsorption of an infinitely long linear semiflexible polymer chain on an attractive impenetrable surface has been shown with bending energy of the chain for PDSAW and FDSAW models on a two dimensional rectangular lattice and square lattice.

3. Result and discussion

We have solved PDSAW and FDSAW models for a linear semiflexible homopolymer chain on a two dimensional rectangular lattice and calculated exact value of step fugacity for polymerization of an infinitely long semiflexible chain. The variation of step fugacity and persistent length of the semiflexible polymer chain with its bending energy have been shown for directed walk models. The critical value of step fugacity for a flexible polymer chain is found to be 0.577.. and 0.707.. for PDSAW and FDSAW models respectively. Persistent length of a flexible chain has value 1.5 for PDSAW model and 2 for FDSAW model. We have been able to obtain critical value of ω for adsorption of an infinitely long linear semiflexible polymer chain on a surface perpendicular to the direction along which chain is directed. The critical value of ω for surface adsorption for a flexible chain is $\omega_c = 1.732$ in the case of PDSAW model and 1.414.. for FDSAW model on a two dimensional rectangular lattice. Our study also showed that the adsorption of a stiffer chain takes place at a smaller value of ω_c than a flexible chain (Sintes, 2001 and Mishra *et al.*, 2003). We have compared the results of critical value of step fugacity, persistent length and ω_c obtained for PDSAW and FDSAW models on rectangular lattice with their corresponding results obtained using a square lattice. In the case of square lattice surface is a line (x=0) and walks are directed perpendicular to the surface. It has been found that qualitative nature of phase diagrams are similar for the rectangular and square lattice for both PDSAW and FDSAW models.

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