Conformational properties of a semiflexible polymer chain: Exact results on a Hexagonal lattice

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Abstract: We have investigated conformational properties of a linear semiflexible homopolymer chain in the bulk and in the presence of an attractive impenetrable surface using lattice models. Since, it is understood that the essential physics associated with the conformational behavior of such polymer chain can be derived from a model of a self avoiding walk (SAW) or directed self avoiding walk (DSAW) on a suitable lattice. Therefore, DSAW models have been solved analytically to study the structural phase transitions in the polymer on a two dimensional hexagonal lattice. We have found that the persistent length of the polymer is independent of bending energy of the chain and its value is unity for directed walk models for hexagonal lattice. Result obtained in presence of an attractive impenetrable surface shows that adsorption of a stiffer polymer chain takes place at a smaller value of surface attraction than the flexible polymer.

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Key words: Homopolymer, adsorption, exact results

1. Introduction

Polymer physics is an important branch of condensed matter systems. Depending upon the stiffness (stiffness weight $k = e^{-\frac{\varepsilon_b}{k_B T}}$ 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) of polymer chain, the chain can have persistent length that may vary from a very small value in comparison to length of the chain to a value equal to its actual length. In former case polymer is known as flexible polymer ($k \to 1$ or $\varepsilon_b \to 0$) and in later case stiff polymer ($k \to 0$ or $\varepsilon_b \to \infty$). However, if stiffness of the polymer chain is in between stiff and flexible chain ($0 < k < 1$ or $0 < \varepsilon_b < \infty$), polymer is known as semiflexible polymer. Biopolymers (e. g. DNA, protein) are known to be semiflexible polymer chain. The conformational properties of such chains have attracted considerable attention in past few 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 chains.

The essential physics associated with the behavior of a semiflexible polymer chain in the bulk and in presence of an attractive impenetrable surface can be derived from a model of SAW or DSAW on a suitable lattice (Privman and Svrakic, 1989; Mishra *et al.*, 2003). Conformational properties of the polymer are strongly modified when it is near an attractive impenetrable surface (Eisenriegler, 1993; Singh *et al.* 1999; 2000 and references therein). An impenetrable surface introduces constrain on the polymer and therefore reduces its entropy. On the other hand, presence of an attractive impenetrable surface is responsible for competition between gain in internal energy to the polymer from surface attraction and corresponding loss of its entropy due to constrain imposed by impenetrable surface. This subtle competition may lead to the co-existence of different regimes and multicritical behavior in the phase diagram of such system.

The conformational properties of a flexible polymer in the bulk and in presence of an attractive impenetrable surface have been studied using renormalization group methods (Derrida, 1981; Kremer, 1983; Diehl, 1986; Bouchaud and Vannimenus, 1989) transfer matrix methods (Privman *et al.,* 1988a; Privman and Frisch, 1988b and Privman and Svrakic, 1989), exact enumeration method (Foster *et al.*, 1992; Singh *et al.*, 1999 and 2000) and Monte Carlo methods (Grassberger and Hegger, 1995). Similar studies on hexagonal lattice for flexible chain have also been reported (Forcrand, *et al.*, 1986; Batchelor and Yung, cond-mat/9410082; cond-mat/9507010 and Richard *et al.,* cond-mat/0406027). Since, stiffness of the polymer chain controls its bending and therefore modifies its conformational properties. In the past few years much attention have been paid to study conformational properties of semiflexible polymer on square and cubic lattice using SAW and DSAW models (Privman and Svrakic, 1989; Mishra *et al.*, 2003 and references therein). In the case of a square lattice, a walker can walk on the lattice with and without bend. However, this is not the case for hexagonal lattice and walker has to bend once for each step movement. Therefore, we expect different conformational properties of semiflexible polymer on a hexagonal lattice. This is to be noted that the universal features of a surface interacting polymer and qualitative nature of phase diagram will remain independent of the type of lattice chosen to model the polymer.

The analytical solutions for semiflexible polymer are limited to WLC (worm like chain) and DSAW models (Kratky and

Porod, 1949; Privman and Svrakic, 1989; Mishra *et al.*, 2003 and Giri *et al.* 2003). The WLC model has been used extensively to study conformational properties of semiflexible polymer chain and it can not mimic exactly the dimensional behavior of polymer chain (Semjon, 2001). On the other hand DSAW models are analytically solvable and simple to report quantitative behavior.

2. Model and methods

We consider a model of DSAW on a two dimensional hexagonal lattice. The directedness will introduce stiffness in the walk because all directions in space are not treated equally. In this sense model is restrictive but analytically solvable, therefore gives exact value of conformational properties and transition points. In the hexagonal lattice case walker has to bend once for movement of each new step on the lattice and angle of bending is same for all the bends of the chain. The possible three cases of directedness of the walk on a hexagonal lattice can be defined with help of the direction of movement of the walker on a unit cell of the lattice (as shown in Fig. 1A).
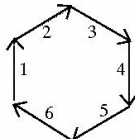

Fig. (1A): All the possible directions along which a walker can take steps on a hexagonal lattice have been shown and steps are named by 1, 2, 3, 4, 5 and 6.

All the possible directions of movement of walker can be named by 1, 2, 3, 4, 5 and 6 on a unit cell of the lattice. If walker is allowed to take step along all the above mentioned five directions excluding direction along step 6, such a model is named as partially directed self avoiding walk model of type one (PDSAW-I). In another case, when steps like 5 and 6 are not allowed on the hexagonal lattice, we name such model as PDSAW model of type two or PDSAW-II. However, if steps along 4, 5 and 6 are not allowed such a model corresponds to fully directed self avoiding walk (FDSAW) model. In the FDSAW model, walker moves nearly along a line and therefore not of our interest.

The grand canonical partition function of the semiflexible polymer chain can be written as,

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

Where, N_b is the number of bends in a walk of N monomers, x is the step fugacity associated with each monomer of the chain and k is its stiffness. We define X as the sum of Boltzmann weight of all the walks whose first step is along step 1 (or step 4) and Y shows sum of Boltzmann weight of all the walks with first step along any of the steps 2, 3, 5 and 6.

2. 1(a) PDSAW (I) model

The generating function for PDSAW (I) model can be written (as shown graphically in Fig. 1B) and solved to evaluate partition function, $Z_1(x,k)$ of the chain as follows.
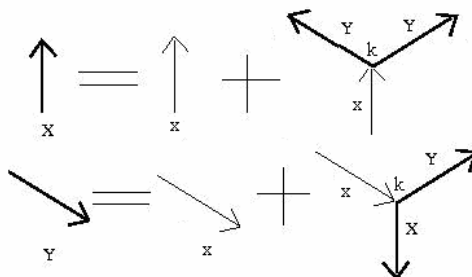

Fig. (1B): The recursion relations for PDSAW (I) model are shown diagrammatically. Sum of Boltzmann weight of all walks whose first step is along step 1 (or step 4) is shown by X. Similarly, Y shows sum of Boltzmann weight of all walks whose first step is along any one out of the steps 2, 3, 5 and 6. Step fugacity of each step is represented by x and k is stiffness associated with each bend of the chain.

Since walker is allowed to take steps on a hexagon lattice along all the possible directions excluding only along step 6. This allows us to write recursion relations for components of generating functions according to Fig. (1B) as,

$$X = x + kx(Y + Y) \qquad (2)$$

$$Y = x + kx(X + Y) \qquad (3)$$

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

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

Therefore, partition function $Z_1(x,k)$ for PDSAW (I) model can be written as,

$$Z_1(x,k) = X + Y = \frac{2x + 2kx^2}{1 - kx - 2k^2x^2} \qquad (5)$$

The partition function $Z_1(x,k)$ of chain diverges for,

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

From eq. (6) we obtain critical value of step fugacity for polymerization of an infinitely long polymer chain and it can be written in terms of stiffness as $x_c = 1/2k$ or in terms of bending energy of the chain, $x_c = (1/2)\exp(\beta\varepsilon_b)$. The dependency of step fugacity on bending energy for PDSAW (I) model is shown in Fig. (2) by star. The persistent length defined by Mishra *et al.*, (2003) can be calculated for PDSAW (I) model and its value is found to be independent of bending energy of the chain. The value of persistent length of the chain is found to be unity.

2. 1(b) PDSAW (II) model

In the PDSAW (II) model the walker is not allowed to walk along the direction of step 5 and 6. Generating function for such chain can be written in terms of following recursion relations,

$$X = x + kxY \qquad (7)$$

$$Y = x + kx(X + Y) \qquad (8)$$

We find value of X and Y by solving eqs. (7) and (8),

$$X = \frac{x}{1 - kx - k^2x^2} \qquad (9)$$

$$Y = \frac{x + kx^2}{1 - kx - k^2x^2} \qquad (10)$$

Thus, partition function $Z_2(x,k)$ for PDSAW (II) model is,

$$Z_2(x,k) = X + Y = \frac{2x + kx^2}{1 - kx - k^2x^2} \qquad (11)$$

The critical value of step fugacity for an infinitely long chain can be obtained from singularity of $Z_2(x,k)$, i. e.,

$$1 - kx - k^2x^2 = 0 \qquad (12)$$

In this case step fugacity in terms of stiffness is written as $x_c = (\sqrt{5} - 1)/(2k)$ and its variation with bending energy of the chain is shown in Fig. (2) by plus. The value of persistent length of the polymer chain is unity for this model.
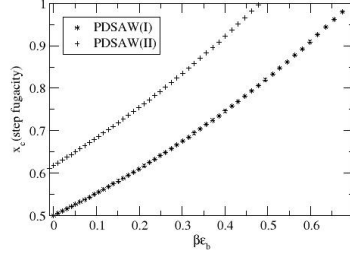
Fig. (2) Shows variation of critical value of step fugacity for polymerization of an infinitely long semiflexible polymer chain with its bending energy for PDSAW (I) and (II) models.

2.2 Adsorption on an attractive, impenetrable and curved surface

In a case when polymer chain is interacting with an attractive impenetrable surface, the surface contributes an excess energy $\varepsilon_s (\varepsilon_s < 0)$ for each step of the walk lying on the surface. This 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 chain and therefore, reduces its entropy. The chain may move away from surface to increase its entropy and desorbed state will prevail. However, if polymer and surface attraction wins over the loss of entropy of the chain, most of the part of chain gets 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 adsorption energy. The phenomenon of adsorption-desorption transition finds applications in lubrication, adhesion and surface protection.

2.2 (a) PDSAW (I) model

In the lattice models of polymer near at attractive surface using square lattice, the surface can be flat. However, in the case of a hexagonal lattice shape of surface is like a saw tooth wave. Therefore, we expect different feature in the adsorption desorption behavior of a semiflexible polymer chain. In this section we report the results found from analytical calculation for the adsorption of a directed semiflexible polymer chain on a curved surface. Let S be the component of generating function along the surface and X is the component perpendicular to the surface. Following the method outlined above, we can write generating function for surface interacting chain as written in eq. (13),

Surface component of recursion relation for PDSAW (I) model can be written using Fig. (3) as,

$$S = s(1 + s + sX) + s^3(1 + s + sX) + s^5(1 + s + sX)...... \qquad (s < 1) \quad (13)$$

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

$$S = \frac{s}{1-s} + \frac{s^2 X}{1-s^2} \qquad\qquad (s < 1) \quad (14)$$
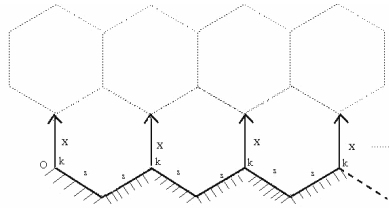

Fig. (3) Recursion relation for a semiflexible polymer chain interacting with an attractive impenetrable surface is shown diagrammatically. All the walks starts from O and S represents sum of Boltzmann weight of all the walks whose first step is on the surface. X is the component of generating function perpendicular to the surface.

The partition function, $Z_1^s(k, \omega, x)$ of a surface interacting semiflexible chain is written as,

$$Z_1^s(k, \omega, x) = S + X \qquad\qquad (s < 1) \quad (15)$$

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

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$$Z_1^s(k,\omega,x) = \frac{x + kx^2 + s(1+s)(1-kx-2k^2x^2)}{(1-s^2)(1-kx-2k^2x^2)} \qquad (s<1) \quad (16)$$

The singularities of partition function $Z_1^s(k,\omega,x)$ suggest that the value of $\omega_c = 2\exp(-\beta\varepsilon_s)$. The variation of ω_c with bending energy of the chain is shown in Fig. (4) by star.

2.2 (b) PDSAW (II) model

The component of generating function along surface has same relation as we have obtained for PDSAW (I) model and partition function of the chain for this model $Z_2^s(k,\omega,x)$ differs from PDSAW (I) model only due to different value of X. We have used value of X from eq. (9). Thus, we have partition function in this case turns out to be,

$$Z_2^s(k,\omega,x) = S + X \qquad (s<1) \quad (17)$$

$$Z_2^s(k,\omega,x) = \frac{x + s(1+s)(1-kx-k^2x^2)}{(1-s^2)(1-kx-k^2x^2)} \qquad (s<1) \quad (18)$$

From singularity of the partition function $Z_2^s(k,\omega,x)$, we obtain critical value of ω for adsorption of a semiflexible chain and it can be written in terms of bending energy as $\omega_c = \{2/(\sqrt{5}-1)\}\exp(-\beta\varepsilon_s)$ for PDSAW (II) model. The variation of ω_c with bending energy of the chain is shown by plus symbol in Fig. (4) for PDSAW (II) model.
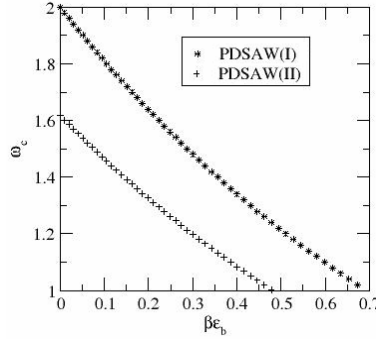

Fig. (4) The variation of critical value of ω has been shown for adsorption of a semiflexible chain on the surface with bending energy for PDSAW (I) and (II) models.

2.3 Result and discussion

The directed self avoiding walk models on a hexagonal lattice have been solved analytically and exact value of step fugacity for polymerization of an infinitely long semiflexible polymer chain have been reported. The critical value of step fugacity for a flexible chain is found to be 0.5 for PDSAW (I) and 0.618033 for PDSAW (II) model. There is a difference between walks on a square lattice than a hexagonal lattice. In the case of former lattice walker can move with and without bend. However, in the later lattice the walker has to bend once to move each step on a hexagonal lattice. The value of persistent length found for PDSAW (I) and (II) models is unity and therefore independent of bending energy of the chain. This is obvious from definition of persistent length as defined by Mishra *et al.* (2003). Persistent length is the average length of polymer chain between its two successive bends and on a hexagonal lattice walker has to move one step between its two successive bends. Therefore, we are unable to predict dependency of persistent length on the bending energy of the chain in our present investigation.

We have been able to obtain critical value of surface adsorption of a semiflexible polymer chain and its value for flexible chain is $\omega_c = 2.0$ for PDSAW (I) and $1.6180..$ for PDSAW (II) model. Our study also showed that the adsorption of a stiffer chain takes place at a smaller value of ω_c than a flexible chain.

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