

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 on a two dimensional hexagonal lattice have been solved analytically to study the structural phase transitions in the polymer. 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. Results obtained in presence of an attractive impenetrable surface show that adsorption of a stiffer polymer chains take place at a smaller value of surface attraction than the flexible polymer chains.

Key words: Homopolymer, adsorption, exact results

1. Introduction

Polymer physics is an important branch of condensed matter systems. A linear homopolymer chain is useful in understanding structural phase transitions in the polymer chain and provides simple way to calculate its conformational properties. The persistent length is a valuable conformational property of the polymer chain. When we compare persistent length of the chain with its actual length, we find that 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 to a value equal to its actual length. In former case polymer is known as flexible polymer ($k \rightarrow 1$ or $\varepsilon_b \rightarrow 0$) and in later case stiff polymer ($k \rightarrow 0$ or $\varepsilon_b \rightarrow \infty$). However, if stiffness of the polymer chain is in between stiff and flexible chain ($0 < k < 1$ or $0 < \varepsilon_b < \infty$), polymer chain is known as semiflexible polymer chain. 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.

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 chain and therefore reduces its entropy. On the other hand, presence of an attractive impenetrable surface is responsible for competition between gain of internal energy to the polymer chain 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 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 methods (Foster *et al.*, 1992; Singh *et al.*, 1999 and 2000) and Monte Carlo methods (Grassberger and Hegger, 1995). Few 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 chain 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 new 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 chain and qualitative nature of phase diagram will remain independent of the type of lattice chosen to model the polymer chain.

The analytical solutions for semiflexible polymer chains 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 and angle of bending is same for all the bends of the chain. In these sense model is restrictive but analytically solvable, therefore gives exact value of conformational properties and transition points. There are three cases of directedness of the walks on a hexagonal lattice that 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).

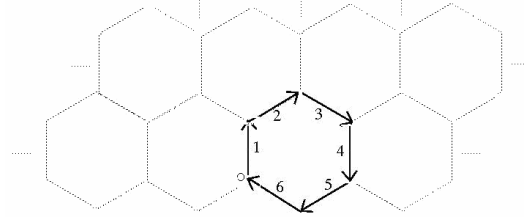


Fig. (1A): All the possible directions along which a walker can take steps on a hexagonal lattice have been shown and steps are named by 1, 2, 3, 4, 5 and 6. All walks start from O.

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 hexagonal lattice. If walker is allowed to take step along all the above mentioned five directions excluding only direction along step 4, such a model is named as partially directed self avoiding walk model of type one (PDSAW-I). In another case, when steps like 4 and 5 are not allowed on the hexagonal lattice, we name such a model as PDSAW model of type two or PDSAW-II. However, if steps along 4, 5 and 6 are not allowed on the lattice such a model corresponds to fully directed self avoiding walk (FDSAW) model.

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

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

Where, N_b is the number of bends in a walk of N monomers of the polymer chain, x is the step fugacity associated with each monomer of the 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 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

All walks of the chain starts from O (as shown in Fig. 1A). 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 polymer chain as follows.

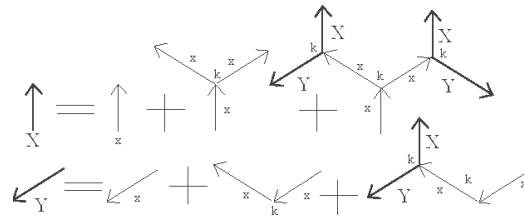


Fig. (1B): The recursion relations for PDSAW (I) model are shown diagrammatically. Sum of Boltzmann weight of all walks whose first step is along step 1 (or step 4) is shown by X. Similarly, Y shows sum of Boltzmann weight of all walks whose first step is along any one out of the steps 2, 3, 5 and 6. 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 4. This allows us to write recursion relations for components of generating functions according to Fig. (1B) as,

$$X = x + 2x^2k + 2x^2k^2(X + Y) \quad (2)$$

$$Y = x + x^2k + x^2k^2(X + Y) \quad (3)$$

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

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

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

$$Z_1(x, k) = X + 2Y = \frac{x(3 + 4xk - x^2k^2)}{1 - 3x^2k^2} \quad (5)$$

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

$$1 - 3x^2k^2 = 0 \quad (6)$$

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 $x_c = 1/(\sqrt{3}k)$ or in terms of bending energy of the chain, $x_c = (1/\sqrt{3})\exp(\beta\varepsilon_b)$. The dependency of step fugacity on bending energy of the chain 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, walker is not allowed to walk along the direction of steps 4 and 5. Generating function for such chains can be written in terms of following recursion relations,

$$X = x + 2x^2k + x^2k^2(2X + Y) \quad (7)$$

$$Y = x + x^2k + x^2k^2(X + Y) \quad (8)$$

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

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

Thus, partition function $Z_2(x, k)$ for PDSAW (II) model can be written as,

$$Z_2(x, k) = X + Y = \frac{2x + x^2k}{1 - xk - x^2k^2} \quad (10)$$

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

$$1 - xk - x^2k^2 = 0 \quad (11)$$

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 symbol. The value of persistent length of the polymer chain is unity for this model.

2. 1(c) FDSAW model

In this case walker walks along the directions of steps 1, 2 and 3 on the hexagonal lattice. The generating function can be written using methods used for calculating partition function of PDSAW models and partition function $Z_3(x, k)$ of FDSAW model can be written as,

$$Z_3(x, k) = \frac{2x(1 + xk)}{1 - 2x^2k^2} \quad (12)$$

Singularity of $Z_3(x, k)$ gives value of the step fugacity for polymerization of an infinitely long linear semiflexible chain as, $x_c = 1/(\sqrt{2}k)$. The variation of critical value of step fugacity of the chain is shown with bending energy of the chain by

cross symbol in Fig. (2) and persistent length of the chain has value unity for this model too.

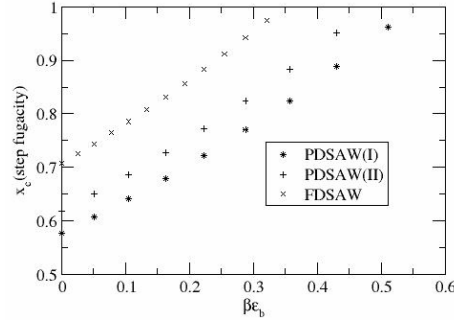


Fig. (2) Shows variation of critical value of step fugacity for polymerization of an infinitely long linear semiflexible polymer chain with its bending energy for PDSAW (I), PDSAW (II) and FDSAW models.

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 ϵ_s ($\epsilon_s < 0$) for each step of the walk lying on the surface. This leads to an increased probability characterized by the Boltzmann weight $\omega(= e^{-\beta\epsilon_s})$ of making a step on the surface. Impenetrable surface constrains the chain and therefore, reduces its entropy. The chain may move away from the 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 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 adsorption energy. The phenomenon of adsorption-desorption transition finds applications in lubrication, adhesion and surface protection.

In the case of two dimensional square lattice models of a linear polymer in presence of an attractive impenetrable surface, the surface is a straight line. However, in the case of a hexagonal lattice shape of surface is like a saw tooth wave. Therefore, we expect different features in the adsorption desorption behavior of a semiflexible polymer chain.

In two dimensional hexagonal lattice models surface is a curved line and adsorbed part of the chain will follow the curved shape of the surface. Adsorbed parts of the chain have bends. We ignore energy contribution to the chain due to bending of the adsorbed parts of the chain. In this section we report the results found from analytical calculation for the adsorption of a directed semiflexible linear homopolymer polymer chain on a curved surface.

2.2 (a) PDSAW (I) model

All the walks start from a point O lying on the 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 polymer chain, as written in eq. (13),

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

$$S = s(1 + s + skX) + s^3(1 + s + skX) + s^5(1 + s + skX) \dots (s < 1) \quad (13)$$

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,

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

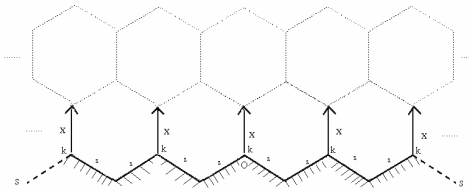


Fig. (3) Recursion relation for a semiflexible linear polymer chain interacting with an attractive impenetrable curved surface is shown diagrammatically. All the walks start from O and S represents sum of Boltzmann weight of all the walks whose first step is on the surface. X is the component of generating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

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

$$Z_1^s(k, \omega, x) = 2S + X \quad (s < 1) \quad (15)$$

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

$$Z_1^s(k, \omega, x) = \frac{2s(1+s)(1-3x^2k^2) + x(1+2xk+x^2k^2)(1-s^2+2s^2k)}{(1-s^2)(1-3x^2k^2)} \quad (s < 1) \quad (16)$$

The singularities of partition function $Z_1^s(k, \omega, x)$ suggest that the value of $\omega_c = \sqrt{3} \exp(-\beta\epsilon_s)$. 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 expression as we have obtained for PDSAW (I) model. Partition function $Z_2^s(k, \omega, x)$ of the chain for this model differs from its value for PDSAW (I) model due to different value of X and movement of walker that is not allowed along steps 4 and 5. Thus, we have partition function in this case turns out to be,

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

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

We have used value of X from eq. (9). From singularities of the partition function $Z_2^s(k, \omega, x)$, we obtain critical value of ω for adsorption of an infinitely long linear semiflexible homopolymer chain and its value can be written in terms of bending energy as $\omega_c = \{2/(\sqrt{5}-1)\} \exp(-\beta\epsilon_s)$ for PDSAW (II) model. Variation of ω_c with bending energy of the chain is shown by plus symbol in Fig. (4) for PDSAW (II) model.

2.2 (c) FDSAW model

Following the methods discussed in above sections for the cases in which chain is interacting with the surface, we can write partition function $Z_3^s(k, \omega, x)$ of the polymer chain interacting with the curved surface for FDSAW model as,

$$Z_3^s(k, \omega, x) = \frac{s(1+s)(2x^2k^2-1) + x(1+xk)(1-s^2+s^2k)}{(1-s^2)(2x^2k^2-1)}$$

In the case of FDSAW model we find value of $\omega_c = \sqrt{2} \exp(-\beta\epsilon_s)$ for adsorption of the linear semiflexible chain and showed its variation with bending energy of the chain by cross symbol in Fig. (4).

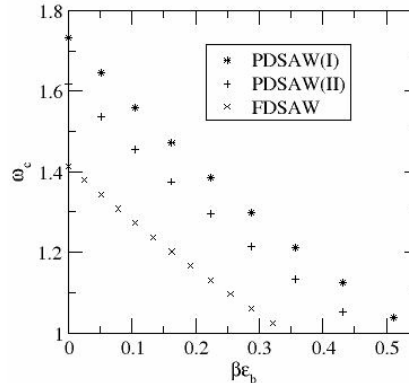


Fig. (4) Variation of critical values of ω have been shown for adsorption of an infinitely long linear semiflexible polymer chain on a curved surface with bending energy of the chain for PDSAW (I), PDSAW(II) and FDSAW models by star, plus and cross symbols respectively.

2.3 Results and discussion

The directed self avoiding walk models for a linear semiflexible homopolymer chain have been solved analytically on a hexagonal lattice and exact value of step fugacity for polymerization of an infinitely long linear semiflexible polymer chain have been reported. The critical value of step fugacity for a flexible chain is found to be 0.577.. for PDSAW (I), 0.618.. for PDSAW (II) and 0.707.. for FDSAW 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 case the walker has to bend once to move each new step on a hexagonal lattice. The value of persistent length found for PDSAW (I), PDSAW (II) and FDSAW models is unity and therefore independent of bending energy of the chain. Persistent length is the average length of the polymer chain between its two successive bends, as defined by Mishra *et al.* (2003) and on a hexagonal lattice walker has to move one step between its two successive bends. Therefore, the value of persistent length is unity and 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 value of ω_c for adsorption of a linear semiflexible polymer chain and its value for flexible chain is $\omega_c = 1.732$. . for PDSAW (I) model, 1.618 . . for PDSAW (II) model and 1.414.. for FDSAW 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. Finally, we would like to make a comment about critical value of ω for adsorption of the chain when adsorbed parts of the chain also contribute energy due to bending, to the chain. In this situation ω_c is independent of bending energy of the chain and has value 1.732, 1.618 and 1.414 for semiflexible polymer chains for PDSAW (I), PDSAW (II) and FDSAW models respectively.

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