A simple and exactly solvable model for a semiflexible polymer chain interacting with a surface

P. K. Mishra, S. Kumar and Y. Singh

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

We use the lattice model of directed walks to investigate the conformational as well as the adsorption properties of a semiflexible homopolymer chain immersed in a good solvent in two and three dimensions. To account for the stiffness in the chain we have introduced energy barrier for each bend in the walk and have calculated the persistent length as a function of this energy. For the adsorption on an impenetrable surface perpendicular to the preferred direction of the walk we have solved the model exactly and have found the critical value of the surface attractions for the adsorption in both two and three dimensions. We have also enumerated all the possible walks on square and cubic lattices for the number of steps $N \leq 30$ for two-dimensions and $N \leq 20$ for three dimensions and have used ratio method for extrapolation. The transition located using this method is in excellent agreement with the results found from the analytical method.

PACS numbers: 64.60.-i,68.35.Rh,05.50.+q

I. INTRODUCTION

Biopolymers are known to exhibit under different environments a variety of persistent lengths ranging from being much smaller than the overall length of the polymer, to being comparable to the chain length \cite{1}. When the persistent length associated with the polymer is much smaller than the overall length of the chain, the polymer is said to be flexible. On the other hand, when the persistent length is comparable to the chain length, the polymer is said to be rigid. When the persistent length falls in between the two extremes, the chain
is said to be semiflexible. The conformational properties of such chains have attracted considerable attention in recent years because of experimental developments in which it has become possible to pull and stretch single molecule to measure elastic properties. Such studies reveal a wealth of information about the conformational behavior of semiflexible polymers that are of clear biological importance.

An impenetrable surface is known to affect the conformational properties of polymers in a significant way. This is due to a subtle competition between the gain of internal energy and a corresponding loss of entropy at the surface. Since the flexibility of the chain affects this competition, a semiflexible chain is expected to show different adsorption behavior compared to that of a flexible polymer chain. A stiff chain is known to get adsorbed easily compared to a flexible chain.

A simple way to account the stiffness of a semiflexible chain is to constrain the angle between the successive segments to be fixed. The value of the angle depends on the local stiffness of the chain. This prescription leads to the freely rotating chain model. In the continuum limit the freely rotating chain becomes the so-called wormlike chain (WLC). In these models the persistent length \( l_p \) is defined as a characteristic length for tangent-tangent correlation function \( \langle t(s)t(s') \rangle \sim \exp(-\frac{|s-s'|}{l_p}) \). The tangent vector \( t(s) \) is defined as \( \frac{\partial r(s)}{\partial t} \), where \( r(s) \) is parametrized in terms of the arc length \( s \) of the chain.

Though the worm-like chain model of Kratky and Porod has been used extensively to study the conformational properties and surface adsorption of a semiflexible chain, it cannot mimic exactly the dimensional behavior of the real chains. In this paper we use the lattice model of directed walk and introduce stiffness in the chain by associating energy with every bend of the walk and calculate the bulk and adsorption properties of the chain as a function of stiffness of the chain.

The paper is organized as follows: In Sec. II we describe the lattice model of directed walk and investigate the bulk properties. We calculate the value of persistent length as a function of energy associated with the bend. In Sec. III we discuss the surface adsorption of
a semiflexible chain represented by a directed walk on a plane perpendicular to the preferred
direction of the walk. We also use the exact enumeration technique to locate the adsorption
desorption transition and compare the result with those found exactly. This allows us to
comment upon the accuracy of the method of exact enumerations.

II. A LATTICE MODEL FOR THE SEMIFLEXIBLE CHAIN

We consider a model of a self-avoiding directed walk on a lattice \([9]\). Though the
directedness of a walk amounts to some degree of stiffness as all directions of the space is
not treated equally, stiffness in the chain is introduced by associating energy barrier with
every turn of the walk. Though the model is very restrictive in the sense that the bend can
be either 90° or no bend at all, The model can be solved analytically and therefore gives
the exact values of conformational and adsorption properties of a semiflexible chain. We
consider two specific cases of directed walks: If the walker is allowed to take steps along
\(\pm y\)-axis (in two-dimensions) and only along +\(x\)-axis the walk is said to be partially directed-
self-avoiding walk (\(PDSA W\)). On the other hand, if the walker is allowed only along +\(y\)
and +\(x\) directions then the walk is said to be fully directed-self-avoiding walk (\(FDSA W\)).
In the case of three dimensions (3\(D\)), a \(PDSA W\) is one in which walker is allowed along \(\pm y\)-
direction but only along +\(x\) and +\(z\) directions while in the \(FDSA W\) the walker is allowed
to move only along +\(x\), +\(y\) and +\(z\) directions.

A stiffness weight \(k = \exp(-\beta \epsilon_b)\) where \(\beta = (k_B T)^{-1}\) is inverse of the temperature and
\(\epsilon_b(>0)\) is the energy associated with each turn. For \(k = 1\) or \(\epsilon_b = 0\) the chain is said to be
flexible and for \(0 < k < 1\) or \(0 < \epsilon_b < \infty\) the chain is said to be semiflexible. When \(\epsilon_b \to \infty\)
or \(k \to 0\), the chain becomes a rigid rod.

The partition function of such a chain can be written as
\[
Z(x, k) = \sum_{N=0}^{N=\infty} \sum_{\text{all walks of } N \text{ steps}} x^N k^{N_b}
\]
(1)

Here \(N_b\) is the total number of bends in a walk of \(N\) steps and \(x\) is the step fugacity.
A. Conformational properties of the chain in Two-Dimensions

(i) The case of $PDSAW$:

In $2D$, the generating function for $PDSAW$ has two components; one along the direct-edness ($i.e. +x$-axis) and other perpendicular to it ($i.e. \pm y$-axis) as shown in Fig.1. The recursion relation for these two components of generating function are [9]:

\[ X = x + x(X + 2kY) \]

\[ Y = x + x(kX + Y) \]

\[ Z_{p.d.}(x, k) = X + 2Y = \frac{(4k - 3)x^2 + 3x}{1 - 2x + x^2 - 2x^2k^2} \]

The critical point for polymerization of an infinite chain is found from the relation

Fig. 1: The diagrammatic representation of the recursion relations Eqs. (2) and (3), for $PDSAW$. The thick arrows $X$ and $Y$ denote all possible walks with the initial step along $+x$ and $\pm y$ directions respectively.
This leads to the critical value of the step fugacity for a given value of \( k \) as \( x_c = \frac{1}{1 + \sqrt{2k}} \).

**Fig. 2:** The variation of step fugacity \( x_c \) with \( \beta \varepsilon_b \).

The stiffness in the chain increases the value of fugacity for polymerization. This dependence is shown in Fig. (2) by long-dashed line in which we plot \( x_c \) as a function of \( \beta \varepsilon_b \).

We define the persistent length as the average distance between two successive bends of the walk, *i.e.*

\[
l_p = \langle L \rangle / \langle N_b \rangle \tag{8}
\]

Where \( L = \langle N \rangle a \), \( a \) being the lattice parameter.

For the *PDSAW* in 2D we find

\[
l_p = \frac{3 + \frac{2\sqrt{2}}{\sqrt{2} + \exp(\beta \varepsilon_b)}}{4 + 3\sqrt{2}} \tag{9}
\]

The dependency of \( l_p \) on \( \beta \varepsilon_b \) is shown in Fig. (3) by a long-dashed line.
The value of $l_p$ increases exponentially with the bend energy at a given temperature.

(ii) The case of $FDSA W$:

In this case the polymer is directed along $+x$ and $+y$ direction; leading to the following recursion relations for the generating functions,

$$X = x + x(X + kY) \quad (10)$$

$$Y = x + x(kX + Y) \quad (11)$$

Solving these equations we get the following value for the partition function $Z_{f.d.}^{2d}$:

$$Z_{f.d.}^{2d} = X + Y = \frac{2x}{1 - (1 + k)x} \quad (12)$$

The critical value of step fugacity is found to be $x_c = \frac{1}{1+k}$. The variation of $x_c$ with $\beta \epsilon_b$ is shown in Fig. (2) by solid line.

The value of persistent length in this case attains a simple relation, i.e.

$$l_p = 1 + e^{\beta \epsilon_b} \quad (13)$$

The variation of $l_p$ with the bending energy is shown in Fig. (3) by a solid line.
B. Conformational properties of the chain in Three-Dimensions

(i) The case of **PDSAW**:

In the case of **PDSAW** the polymer chain is directed in two-directions. The recursion relations for generating functions are

\[ X = x + x(X + 2kY + kZ) \]  \hspace{1cm} (14)

\[ Y = x + x(kX + Y + kZ) \]  \hspace{1cm} (15)

\[ Z = x + x(kX + 2kY + Z) \]  \hspace{1cm} (16)

Solving these equations we get the values of \( X, \ Y, \ Z \) and the partition function as

\[ X = Z = \frac{x + (2k - 1)x^2}{(1 + k - 4k^2)x^2 - (k + 2)x + 1} \]  \hspace{1cm} (17)

\[ Y = \frac{x + (k - 1)x^2}{(1 + k - 4k^2)x^2 - (k + 2)x + 1} \]  \hspace{1cm} (18)

\[ Z^{3d}_{p.d.} = X + 2Y + Z = \frac{(6k - 4)x^2 + 4x}{(1 + k - 4k^2)x^2 - (k + 2)x + 1} \]  \hspace{1cm} (19)

That is at \( x_c = \frac{k + 2 - \sqrt{17k}}{2(k + 1 - 4k^2)} \), the \( Z^{3d}_{p.d.} \) will diverge. In this case the dependence of the fugacity for polymerization on the stiffness is more involved compared to the case in 2D. The variation of \( x_c \) with \( \beta \epsilon_b \) is shown in Fig. (2) by the dashed line. For persistent length we find

\[ l_p = \frac{[85 + 19\sqrt{17} - (102 + 26\sqrt{17})exp(\beta \epsilon_b) + (34 + 8\sqrt{17})exp(2\beta \epsilon_b)]2[exp(2\beta \epsilon_b) + exp(\beta \epsilon_b) - 4]}{(1 - \sqrt{17} + 2exp(\beta \epsilon_b))[204 + 52\sqrt{17} - (272 + 64\sqrt{17})exp(\beta \epsilon_b)] + (85 + 21\sqrt{17})exp(2\beta \epsilon_b)} \]  \hspace{1cm} (20)

The value of \( l_p \) as a function of \( \beta \epsilon_b \) is plotted in Fig. (3) by the dashed line.
(ii) The case of FDSA

In this case the polymer is directed along all the three directions i.e. along $+x$, $+y$ and $+z$ directions. We can write following recursion relations

$$X = x + x(X + kY + kZ) \quad (21)$$

$$Y = x + x(kX + Y + kZ) \quad (22)$$

$$Z = x + x(kX + kY + Z) \quad (23)$$

The solution of these equations leads to

$$X = Y = Z = \frac{x}{1 - (1 + 2k)x} \quad (24)$$

Thus the partition function of the system can be written as

$$Z_{f.d.}^{3d} = X + Y + Z = \frac{3x}{1 - (1 + 2k)x} \quad (25)$$

The critical value of the step fugacity is $x_c = \frac{1}{1 + 2k}$. The variation of step fugacity with bending energy $\beta \epsilon_b$ is shown in Fig. (2) by a dot-dashed line. In this case $l_p$ is found to be

$$l_p = 1 + \frac{1}{2} \exp(\beta \epsilon_b) \quad (26)$$

The value of $l_p$ as a function of $\beta \epsilon_b$ is plotted in Fig. (3) by a dot-dashed line.

In all the cases discussed above the persistent length shows exponential dependence on the bending energy.

III. SURFACE ADSORPTIONS

In the case of directed model we have two distinct surfaces; one parallel and the other perpendicular to the directedness of the walk. The adsorption of polymer on a surface parallel to the preferred direction of the walk has been studied in case of 2D using the
transfer matrix method [9]. The features associated with the adsorption were found to be same as in the isotropic case except that the critical value of surface attraction for adsorption is higher. The surface perpendicular to the direction of walk may give different features as the walk once leaves the surface it can not return to it due to restriction on the walk. Here we report the result found analytically for the adsorption of directed semiflexible chain on a surface perpendicular to the directedness of the chain both in two and three dimensions.

A. Adsorption of a directed semiflexible chain on a surface perpendicular to the
directedness of the chain in two-dimensions

(i) The case of PDSAW:

In case of two-dimensions, surface is a line represented by \( x = 0 \). Let \( S \) be the component of generating function along the surface and \( X \) the component perpendicular to the surface as shown in Fig. (4). Following the method outlined above we can write surface component as

\[
S = s + s(s + kX) + s^2(s + kX) + s^3(s + kX) + \ldots
\]  

(27)

where \( s = \omega x \), and \( \omega = \exp(-\beta \epsilon_s) \) being the weight associated with each step along the wall.

Fig. 4; The diagrammatic representation of the recursion relation (28). Each walk of the polymer chain starts from O. In this diagram \( X \) and \( S \) denotes all possible walks with initial step along the \(+x\) and along the wall respectively.
For $\omega = 1$ Eq. (27) reduces to Eq. (5).

The partition function in presence of surface for \textit{PDSAW} is found to be

$$Z_{sp.d.}^{2d}(k, \omega, x) = X + 2S$$  \hspace{1cm} (28)

Combining with Eq. (4) we find

$$Z_{sp.d.}^{2d} = \frac{2sx^2(1 - 2k) + 2s(1 - 2x) + (2sk + 1 - s)[x + (2k - 1)x^2]}{(1 - s)(1 - 2x + x^2 - 2k^2x^2)}$$  \hspace{1cm} (29)

The critical value of adsorption transition is found from the relation

$$(1 - s)(1 - 2x + x^2 - 2k^2x^2) = 0$$  \hspace{1cm} (30)

This leads to $\omega_c = \frac{1}{x_c} = \sqrt{2k} + 1$, which reduces to $\omega_c = \sqrt{2} + 1$ \footnote{4} for the flexible polymer chain. The variation of $\omega_c$ with $\beta \epsilon_b$ is shown in Fig. (5) by a long dashed line.

\textbf{Fig. 5;} The exact value of $\omega_c$ for different values of $\beta \epsilon_b$. The lines in this figure correspond to analytical results however the dots on the lines correspond to the value obtained from exact enumeration method in $2D$ and the cross used to denote the $\omega_c$ value for $3D$ partially directed case.

(ii)\textbf{The case of FDSA W:}

It is straight forward to show that for \textit{FDSA W} the partition function in the presence of surface is
\[ S = s + s(s + kX) + s^2(s + kX) + s^3(s + kX) + \ldots \] (31)

Using value of \( X \) from Eq. (12) we get
\[ Z^{2d}_s = X + S = \frac{s(1 - (1 + k)x) + x(sk - s + 1)}{(1 - s)(1 - (1 + k)x)} \] (32)

Which gives adsorption transition point at \( \omega_c = 1 + k \). The variation of \( \omega_c \) with \( \beta \epsilon_b \) is shown in Fig. (5) by a solid line.

**B. Adsorption of a semiflexible directed chain on a surface perpendicular to one out of the two preferred direction of the chain in three dimensions**

(i) **The case of PDSAW:**

The analysis given above can be generalized in 3 dimensions where surface dimension is two i.e. \( x - y \) plane at \( z = 0 \). In the case of PDSAW as mentioned above the choice of the walker is restricted to the \(+x\)-axis, \( \pm y\)-axis and \(+z\)-axis. Let \( S_x \) and \( S_y \) is the component of the total partition function \( Z^{3d}_s \) along \(+x\) and \( \pm y \) axis respectively, however component perpendicular to the wall along \( +z \) axis remains same as defined by Eq. (17). We can, therefore write
\[ S_x = \frac{s - s^2 + 2s^2k + Z(2k^2s^2 + sk - s^2k)}{1 - 2s + s^2 - 2s^2k^2} \] (s < 1) (33)
\[ S_y = \frac{s - s^2 + s^2k + Z(k^2s^2 + sk - s^2k)}{1 - 2s + s^2 - 2s^2k^2} \] (34)

The expression for the partition function in this case found from the relation
\[ Z_{s.p.d.}^{3d} = S_x + 2S_y + Z \] (35)

Substituting the value of \( S_x, S_y \) and \( Z \) we find
\[ Z_{s.p.d.}^{3d}(k, \omega, x) = \frac{x(1 - x + 2kx)U + s(3 - 3s + 4sk)V}{(1 - 2s + s^2 - 2s^2k^2)[(1 + k - 4k^2)x^2 - (k + 2)x + 1]} \] (36)

Where \( U \) and \( V \) are,
\begin{equation}
U = 1 - 2s + 3sk + s^2 - 3s^2k + 2s^2k^2 \tag{37}
\end{equation}

\begin{equation}
V = 1 - 2x - kx + x^2 + kx^2 - 4k^2x^2 \tag{38}
\end{equation}

The two singularities appearing in eqn.(37) give the critical value of \(x_c = \frac{k+2-\sqrt{17}k}{2(1+k-4k^2)}\) and \(\omega_c = \frac{2(1+k-4k^2)}{(1+\sqrt{2}k)(k+2-\sqrt{17}k)}\). For flexible polymer chain (i.e. \(k = 1\) or \(\epsilon_b = 0\)) it gives \(x_c = \frac{-3+\sqrt{17}}{4}\) and \(\omega_c = 1.47524\).

(ii) **The case of FDSA\textsc{W}:**

For \textsc{FDSA\textsc{W}}, the partition function can be easily be evaluated. Here we write the final form of the partition function as

\begin{equation}
Z_{s}^{3d}(k, \omega, x) = S_x + S_y + Z = \frac{(2s + x - 3sx - 3sxk)}{(1 - s - sk)(1 - (2k + 1)x)} \tag{39}
\end{equation}

The two singularities appearing in Eq. (39) gives the critical value of \(x_c = \frac{1}{2k+1}\) and \(\omega_c = \frac{2k+1}{k+1}\).

The variation of \(\omega_c\) with \(\beta\epsilon_b\) are given in Fig. (5) for \textsc{PDSA\textsc{W}} and \textsc{FDSA\textsc{W}} by a dashed and dot-dashed lines respectively.

**IV. RESULT FROM EXACT ENUMERATION METHOD**

Since the analytical approach is limited to very few cases, one often has to resort to numerical methods, such as Monte Carlo simulations or a lattice model using extrapolation of exact series expansion (referred to as exact enumeration method). The later method has been found to give satisfactory results as it takes into account the corrections to scaling. To achieve the same accuracy by the Monte Carlo method, a chain of about two orders of magnitude larger than in the exact enumeration method has to be considered [10].

We have enumerated all possible walks of length \(N \leq 30\) on square lattice and of length \(N \leq 20\) on cubic lattice. The canonical partition function is written as

\begin{equation}
Z_N(k, \omega) = \sum_{N_x} \sum_{N_b} C_N(N_x, N_b) \omega^{N_x} k^{N_b} \tag{40}
\end{equation}
Here $N_s$ is the number of steps on the surfaces. The reduced free energy per monomer is found from the relation

$$G(k, \omega) = \lim_{N \to \infty} \frac{1}{N} \log Z_N(k, \omega)$$

(41)

The limit $N \to \infty$ is found by using the ratio method \[11\] for extrapolation.

The transition point for adsorption-desorption is found from the maximum of $\frac{\partial^2 G(k, \omega)}{\partial \epsilon_s^2}$ ($= \frac{\partial <N_s>}{\partial \epsilon_s}$). The transition points found from this method are shown in Fig. (5) by dots and cross. The results found from this method are in very good agreement with those found exactly in above sections. This result indicates that as for as locating the adsorption-desorption transition of a long flexible as well as semiflexible chains immersed in a good solvents are concerned the method of exact enumeration can give reliable results.

V. CONCLUSION

In spite of the sever restriction imposed on the angle of bending of the chain, the lattice models may provide interesting results for the conformational and surface adsorption properties of a semiflexible chain. Introducing directedness in the walk allowed us to solve the model exactly in both two and three dimensions. We have calculated the step fugacity for polymerization of an infinite chain and the persistent length as a function of bending energy associated with bending. We have also been able to obtain to the critical value for adsorption of a directed chain on a surface perpendicular to the preferred direction of the walk analytically in both two and three dimensions. The dependence of this critical value of surface attraction on the stiffness of the chain have been evaluated.

We have also examined the accuracy of the method of exact enumeration in locating the adsorption-desorption transition and have found that the method give values that are in excellent agreement with the exact values.
Acknowledgements

This work has been financially supported by the Department of Science and Technology, New Delhi, INDIA.

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