Effect of geometrical constraint on conformational properties of a polymer chain

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In this article, we analyse the effect of geometrical constraint on the conformational properties of an infinitely long linear semiflexible polymer chain confined in-between two constraints under good solvent condition in two dimensions. The constraints are two impenetrable stair shaped surface and for two-dimensional space, the surface is a one-dimensional line. The semiflexibility of the chain is accounted by introducing a Boltzmann weight of bending energy required to produce each turn in the chain and good solvent condition was accounted by using self-avoiding walk model of the chain. We have calculated exact critical value of step fugacity required for polymerization of an infinitely long polymer chain confined in-between the constraints for different values of separation between the constraints for directed version of the model. We have also calculated possible maximum, minimum values of the persistent length for such chains and the maximum value of bending energy required for each turn in the chain for few values of separation between the constraints.

Keywords: polymer chain; semiflexible; constraint; exact results

1. Introduction

Biomolecules (DNA and proteins) live in the crowded, constrained regime. Such molecules are soft objects and therefore can be easily squeezed into the spaces that are much smaller than the natural size of the molecule in the bulk. For instance, actin filaments in eukaryotic cell [1] or protein encapsulated in Ecoli [2] found in nature are the examples of confined biomolecules that serves as the basis for understanding numerous phenomenon observed in the polymer technology, bio-technology and many other molecular processes occurring in the living cells. The conformational properties of a single biomolecule have attracted considerable attention in the recent years due to developments in the single molecule based observations and experiments [3–8]. Under confined geometrical condition, the excluded volume effect and effect of the geometrical constraint compete with entropy of the molecule. Therefore, geometrical constraint can modify the conformational properties of the molecules.

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The conformational properties of a linear flexible polymer molecule under good
solvent condition, confined to flat parallel walls (slit) have been studied for the past few
years; for instance, see, [9–15] and references quoted therein. Whittington and his
coworkers [12–15] used self-avoiding walk model to study behaviour of a surface
interacting flexible polymer chain confined between two parallel walls on a square lattice.
They calculated phase diagram of the polymer chain having attractive interaction with the
walls by solving the directed walk model exactly [12]. Rensburg et al. [15] through
numerical calculation using isotropic self-avoiding walk model showed that phase diagram
obtained for a surface interacting linear polymer chain confined in-between two parallel
walls has qualitatively similar phase diagram to that obtained by Brak et al. [12] for
directed walk model of the problem.

Theoretical understanding of a semiflexible polymer chain confined in a cylindrical
pore, rectangular shaped micro-channel, tube like narrow channel or other kinds of
confined regime is also discussed in the literature to analyse the effect of the confinement
on the conformational behaviour of the chain; see, for instance [16–23] and references
therein. However, in the present investigation, we have considered a linear semiflexible
homopolymer chain confined in-between one-dimensional stair shaped impenetrable
surface (geometrical constraint) under good solvent condition in two dimensions. For
two-dimensional space, the surface is a line and polymer chain is constrained by such a
surface.

To analyse the effect of the geometrical constraint on the conformational properties
of the semiflexible polymer, we have chosen fully directed self-avoiding walk model
(FDSAW) introduced by Privman et al. [24,25] and used generating function technique to
solve the model analytically. The results so obtained is used to discuss the behaviour of the
polymer chain in constrained geometry and also to compare the results obtained for
conformational properties of the polymer chain, when the chain is in bulk [26] and there is
no constraint near it.

The outline of this article is as follows: in Section 2, we describe the lattice model of
FDSAW and used it to model a semiflexible homopolymer chain confined in-between
constraints (stair shaped surface). We have solved the model analytically to calculate exact
critical value of step fugacity required for polymerization of an infinitely long linear
semiflexible polymer chain when the chain is confined in-between the constraints. We have
discussed the variation of minimum critical value of step fugacity (for flexible chain) with
separation between the constraints. We have also studied the variation of minimum and
maximum possible values of the persistent length of the flexible and stiff chains,
respectively, when it is confined in-between the constraints. Finally, in Section 3, we
discuss the results obtained.

2. Model and method
A model of FDSAW [24,25] on a square lattice has been used to calculate conformational
properties of a linear semiflexible homopolymer chain confined in-between two impenet-
trable stair shaped surface under good solvent condition (as shown schematically in
Figure 1). The directed walk model is restrictive in the sense that the angle of bending has
unique value, that is 90° (for the present case) and directedness of the walk amounts to
certain degree of stiffness in the walks of the chain because all directions of the space are not
treated equally. However, directed self-avoiding walk model can be solved analytically and
therefore it gives the exact value of the conformational properties of the polymer chain.
Since, we consider FDSAW model and therefore, the walker is allowed to take steps along $+x$, and $+y$ directions on a square lattice in-between the constraints.

The walks of the chain starts from a point $O$, located on an impenetrable surface and the walker moves throughout the space in-between the two surfaces (as we have shown schematically in Figure 1 i.e. a walk of the polymer chain confined in-between two surfaces for three different values of separation $(n)$ between the constraints along an axis three, four and five monomers (steps), respectively. The separation between the constraints have been defined on the basis of the fact of how many maximum number of steps a walker can successively move along any of the $+x$ or $+y$ directions.

The stiffness of the chain is accounted by associating a Boltzmann weight with bending energy for each turn in the walk of the polymer chain. The stiffness weight is $k = \exp(-\beta \epsilon_b)$; where $\beta = \frac{1}{k_b T}$ is inverse of the temperature, $\epsilon_b(>0)$ is the energy associated with each bend in the walk of the chain, $k_b$ is Boltzmann constant and $T$ is temperature). 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 polymer chain is said to be semiflexible. However, when $\epsilon_b \to \infty$ or $k \to 0$, the chain has shape like a rigid rod.

The partition function of a semiflexible polymer chain can be written as

$$Z(g, k) = \sum_{N=0}^{N=\infty} \sum_{\text{all walks of } N \text{ steps}} g^N k^{N_b}$$

(1)

where, $N_b$ is the total number of bends in a walk of $N$ steps (monomers), $g$ is the step fugacity of each monomer of the chain.

The partition function of an infinitely long linear semiflexible homopolymer chain confined in-between the constraints (as shown schematically in Figure 1A) can be calculated using the method of generating function technique. The components (as shown in Figure 2) of the partition function, $Z_3(k, g)$ (we have used here suffix three because

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**Figure 1.** This figure shows a walk of an infinitely long linear semiflexible polymer chain confined in-between two constraints (impenetrable stair-shaped surface). All walks of the chain starts from a point $O$ on the constraint. We have shown three different cases viz. (A), (B) and (C) having separation $(n)$ between the constraints along an axis three, four and five monomers (steps), respectively. The separation between the constraints have been defined on the basis of the fact of how many maximum number of steps a walker can successively move along any of the $+x$ or $+y$ directions.
in this case (i.e. Figure 1A) maximum step that a walker can move successively in one particular direction is three) of the chain can be written as

\[ X_1 = g + kgY_3 \]  

(2)

\[ X_2 = g + g(X_1 + kY_2) \]  

(3)

\[ X_3 = g + g(X_2 + kY_1) \]  

(4)

\[ Y_1 = g + kgX_3 \]  

(5)

\[ Y_2 = g + g(kX_2 + Y_1) \]  

(6)

and

\[ Y_3 = g + g(kX_1 + Y_2) \]  

(7)

On solving Equations (2)-(7), we get the expression for \( X_1(k, g) \) and \( Y_2(k, g) \). In obtaining the expression for \( X_1(k, g) \) and \( Y_2(k, g) \), we have solved a matrix of \( 2n \times 2n \) (\( n = 3 \), for present case i.e. Figure 1A). Thus, we have the exact expression of the partition function for the semiflexible polymer chain confined between the constraints (as shown in Figure 1A), which can be written as

\[ Z_3(k, g) = X_1(k, g) + Y_2(k, g) = \frac{-2g - g^2 - 2kg^3 + 2k^2g^3}{1 - kg - k^2g^2 - kg^3 + k^3g^3} \]  

(8)
From singularity of the partition function, \( Z_3(k, g) \), we obtain the critical value of step fugacity required for polymerization of an infinitely long linear semiflexible polymer chain in-between the constraints (as shown in Figure 1A).

The persistent length of the chain can be defined using tangent-tangent correlation function \( \langle t(s) \cdot t(s') \rangle \sim \exp(-|s-s'|/l_p) \) [27]. The tangent vector \( t(s) \) can be defined as \( \frac{\partial r(s)}{\partial t} \), here \( r(s) \) is parameterized in terms of arc length \( s \) of the polymer chain [27]. However, we have defined the persistent length \( l_p \), as the average length of the polymer chain between its two successive bends [26,28]. Thus, the persistent length is calculated by using following relation [26]

\[
l_p = \frac{\langle N \rangle a}{\langle N_h \rangle} = \left( g \frac{\partial \log Z_3(k,g)}{\partial g} \right) \left( \frac{\partial}{\partial k} \frac{\partial \log Z_3(k,g)}{\partial k} \right)
\]  

(9)

where, \( a \) is lattice parameter of the square lattice and we have chosen its value unity for mathematical sake.

The method discussed above can be used for different values of spacing (\( n \)) between the constraints and size of the matrix needed to solve in calculating partition of the chain confined in-between the constraints is \( 2n \times 2n \). We have calculated the exact expression of the partition function for \( n \) \((3 \leq n \leq 19)\).

We have plotted the maximum value of the persistent length \( (l_p)(\text{Max.}) = l_p(k=k_{\text{Min}}, g_c(k=k_{\text{Min}})) \) accessible to the stiff polymer chain confined in-between the constraints for different values of \( n \) \((3 \leq n \leq 19)\) in Figure 3 and found that maximum value of the persistent length scales linearly with \( n \) as, \( l_p = 0.66272 + 0.40723n \). The value of \( k_{\text{Min.}} \) is determined from singularity of the partition function \( Z_3(k, g) \) and it gives least possible value of stiffness weight or maximum value of bending energy of the chain for which an infinitely long linear semiflexible chain is polymerized in-between the constraints for a
given value of $n$. Since, stiffness weight of the chain is related with bending energy ($\epsilon_b$) as, $k = \exp(-\beta \epsilon_b)$, therefore, we have calculated the maximum value of bending energy accessible to the stiff chain confined in-between the constraints from minimum value of $k(= k_{\text{Min}})$ and plotted maximum value of bending energy with $n$ in Figure 3.

However, minimum value of the persistent length accessible to the confined chain and minimum critical value of the step fugacity accessible to the chain is shown for various values of $n$ ($3 \leq n \leq 19$) in Figure 4.

3. Result and discussion

We have considered an infinitely long linear semiflexible homopolymer chain confined in-between two impenetrable stair shaped surface (constraint) in two-dimensional space under good solvent condition. We have used FDSA model to study effect of geometrical constraint imposed on the polymer chain and solved the model analytically to calculate exact expression of the partition function for few values of separation ($n$) between the constraints $3 \leq n \leq 19$. We have found that maximum value of the persistent length scales linearly ($l_p = c + m \times n$, where $c = 0.67745$, $m = 0.40472$ and $n \to \infty$). Thus, the persistent length of a possible stiffer chain which can be polymerized in-between the constraints scales linearly with spacing ($n$) between the constraints. We have estimated value of $c$ and $m$ for spacing ($n \to \infty$) between constraints using linear extrapolation (as shown in Figure 5). We expect that exact maximum value of the persistent length will increase linearly for all values of $n(\geq 3)$.

We have also analysed variation of the maximum value of the bending energy of the polymer chain confined in-between the constraints and found that it increases with the increase of separation between the constraints for stiffer chains. The minimum value of the persistent length of a flexible polymer chain varies with separation between the constraints and appears to approach a value less than 2 for $n \to \infty$. However, critical value
of step fugacity \( g_c(\text{Min.}) = g_c(k = 1) \) required for polymerization of an infinitely long linear flexible polymer chain in-between the constraints approaches to 0.5 as \( n \to \infty \). The minimum critical value of step fugacity is 0.5 (i.e. for \( k = 1 \)) for a long linear polymer chain when chain is modelled as a FDSAW on a two-dimensional square lattice in absence of the constraints, i.e. \( g_c(k) = \frac{1}{1+k} \) [26]. Since, \( g_c(\text{Min.}) \) is critical value of step fugacity which is required for polymerization of an infinitely long linear flexible polymer chain on a two-dimensional square lattice for FDSAW model and hence remain un-affected due to geometrical constrain imposed by stair shaped surface as \( n \to \infty \).

However, minimum value of the persistent length is less than 2 for \( n \to \infty \), while the persistent length \( (l_p = 1 + k^{-1}) \) [26] has value 2 for a flexible polymer chain (i.e. for \( k = 1 \)) when there are no constraints near the chain. The persistent length is a local property, therefore, its value depends on the type of lattice (square, rectangular etc.) chosen to model the chain, space dimensionality and on the fact that polymer chain is ideal or self-avoiding type. We have found that the value of \( l_p(\text{Min.}) \) is less than 2 for \( n \to \infty \) and this value is different from 2, when there are no constraints near the chain, because for \( n \to \infty \) there is still one constraint near the chain confining to it or not allowing it to occupy space below the constraint at which the chain is grafted.

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