Force of confinement on an infinitely long and linear semi-flexible homo-polymer chain: Exact results

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Abstract: We analyze nature of confinement of an infinitely long, linear semiflexible homo-polymer chain, when the chain is polymerized in between two geometrical constraints under good solvent condition in two dimensions. In two dimensions the constraint is a stair shaped impenetrable line and chain is confined by two (A&B) such surfaces. A lattice model of fully directed self avoiding walk is used to calculate the force of confinement exerted by the constraints on to the chain or force exerted by chain on the geometrical constraints. It has been found that variation of logarithm of the force with logarithm of constraints separation is linear.

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1 Introduction:

DNA & proteins like soft objects can be easily squeezed into the spaces that are much smaller than the natural size of the macro-molecule. For example, actin filaments in eukaryotic cell or protein encapsulated in Ecoli [1, 2] are the well known examples of confined bio-molecules that may serve as the basis for understanding molecular processes occurring in the living cells. The conformational properties of single bio-polymer have attracted considerable attention in recent years due to developments in the single molecule based experiments [3, 4, 5, 6, 7, 8] and also see, references quoted therein.

In this paper, we consider polymerization of an infinitely long and linear semiflexible homo-polymer chain in between two stair shaped geometrical constraints (A and B) with the help of directed walk model [9, 10] on a square lattice. The monomers of the chain have excluded volume interaction with each other. The solution of fully directed self avoiding walk (FDSA W) model was obtained [8] and used here for the discussion about the force of confinement. The separation between the geometrical constraints is increased by one unit of the monomer or step size. The force of confinement on the
chain due to constraints or on constraints due to polymer chain is evaluated and nature of its variation with constraints separation is illustrated.

The paper is organized as follows: In Section 2, a square lattice model of fully directed self avoiding walk is described, assuming polymerization of an infinitely long and linear semiflexible homo-polymer chain in between two geometrical constraints ($A$ and $B$), as shown in figure (1). In section 3, we have calculated the force of confinement that was exerted by the geometrical constraints on the polymer chain or the force that is exerted by chain on geometrical constraints. Finally, in Section 4, we summarize and discuss the results obtained.

Figure 1: A walk of an infinitely long and linear semiflexible homo-polymer chain is shown in between two geometrical constraints ($A$ & $B$). The separation ($n$) between the constraints had been defined as the maximum number of steps that a walker can successively move along any of the $+x$ and $+y$ directions. The value of $n$ is 5 for this figure.

2 Model

The Lattice model of fully directed self-avoiding walk [9, 10] on a square lattice is used to calculate free energy of an infinitely long linear semiflexible homo-polymer chain that can be polymerized in between two geometrical constraints. The walks of the polymer chain was generated on a square lattice, therefore, geometrical constraints are lines having shape like a stair.
The constraints are impenetrable. The walker is allowed to move in between
the geometrical constraints. Since we have used fully directed self avoiding
walk (FDSA W) model, therefore, walker is allowed to take steps only along
positive directions of $x$, and $y$ axes in between the constraints [8]. The
directed walk model is restrictive in the sense that the angle of bending
is 90° on a square lattice and directedness of the walk amounts to certain
degree of stiffness in the walks of the chain as all directions of the space are
not treated equally. Since, directed self avoiding walk model can be solved
analytically and, therefore, it gives exact value of free-energy of the polymer
chain.

![Graph](image)

Figure 2: This figure shows variation of force $f(n,k)$ exerted by geometrical
constraints on each monomer of the chain with separation ($n$) between the
constraints. The force-separation ($f(n,k) - n$) graph is shown for a flexible
chain ($k = 1$) and semiflexible chain ($k=0.4, 0.6$ and $0.8$). The force is
reported in the units of $10pN$ at room temperature $300K$ for monomer (step)
size $4.14\text{Å}$.

The walks of the chain starts from a point $O$, located on an impenetrable
surface and walker moves through out the space in between the two surface
(as we have shown schematically in figure (1) that a walk of the polymer
chain confined in between two surfaces for a value of separation $n (= 5)$ [8]).

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 temper-
angle, $\epsilon_b (> 0)$ 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 [8].

3 Method and results

The partition function of the semiflexible polymer chain confined in-between the geometrical constraints can be written as,

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

where, $N_b$ is the total number of bends in a walk of $N$ steps (monomers) and $g$ is the step fugacity of each monomer of the chain [8]. In this paper, we have used values of $g_c(n, k)$ obtained [8] for various values of separations between the constraints ($3 \leq n \leq 19$) to calculate free energy of the chain. The free energy so obtained is used to find the value of force exerted by confining constraints on each monomer of the chain or force on to the constraints due to each monomer of the chain.

The free energy per monomer of the confined semiflexible chain is obtained using well known formula,

$$A(n, k) = k_b T \ln(g_c(n, k))$$

The force of confinement per monomer $f(n, k)$ is evaluated for separation, $n$, between the constraints using the relation,

$$f(n, k) = -\frac{\partial A(n, k)}{\partial n} = \frac{A(n + 1, k) - A(n - 1, k)}{(n + 1) - (n - 1)}$$

The free energy of the chain is written in units of thermal energy $k_b T (=25.875\text{meV})$ per monomer at room temperature ($T=300K$). We have used value of step length (monomer size) $4.14$ Å. So that force can be expressed in the units of $10pN$. Since, the force of confinement is of the order $pN$ and, therefore, can be measured with the help of $AFM$. The values of $f(n, k)$ for few values of $n$ are shown in the figure 2 for a flexible chain ($k=1$) and semiflexible chain $k$ ($=0.4, 0.6$ and 0.8).

The nature of variation of the confining force per monomer $f(n, k)$ with constraints separation $n$ shows that curve is like a hyperbola ($f(n, k) \propto n$=constant). Therefore, log-log plot of $f(n, k) - n$ is a straight line for
a flexible \((k = 1)\) and semiflexible chain \(k = (0.4, 0.6 \text{ and } 0.8)\), as shown in figure 3. The slope of \(\ln(f(n,k)) - \ln(n)\) curve is varying gradually from \(-2.5788\) (for flexible chain) to \(-2.4266\) for a semiflexible chain \((k=0.4)\).

Finally, in figure 4, we have shown variation of \(\mu_c = \frac{1}{g_c(n,k)}\) to discuss contribution of stiffness \(k\) of the chain to the force of confinement \(f(n,k)\) in comparison to presence of geometrical constraints.

Figure 3: We have plotted logarithm of force \(f(n,k)\) on each monomer due to constraints with logarithm of separation \(n\) between the constraints for flexible \((k = 1)\) and semiflexible chain \((k=0.4, 0.6 \text{ and } 0.8)\) in this figure. The curve is linear for chosen values of \(k\).

4 Summary and conclusions

We have considered an infinitely long linear semiflexible homopolymer chain confined in between two \((A&B)\) impenetrable stair shaped geometrical constraints (or surfaces) under good solvent condition. We had used fully directed self avoiding walk model on a square lattice to model the situation [8] and value of \(g_c(n,k)\) is used to determine the free energy per monomer \((A(n,k))\) of the chain. The value of free energy is used to calculate the force of confinement \((f(n,k))\) exerted by each monomer on constraints or force of confinement experienced by each monomer due presence of constraints around it for values of spacing \((3 \leq n \leq 19)\).

The nature of variation of force \((f(n,k))\) with \(n\) is shown in the figure 2. The curve \(f(n,k)-(n)\) appears like a hyperbola. The log-log plot of \(f(n,k)\)
and \( n \) is a straight line unlike our previous findings [11]. The deviations from earlier reported results are due to restrictions imposed on the chain. The restrictions are geometrical constraints, stiffness of the chain and directedness of the chain. The slope of staright line (as shown in figure 3) varies gradually with the variation of stiffness of the chain. The curve is straight line for flexible chain and with increase of stiffness of the chain slope of curve decreases. There is large entropy \( \sim \mu_c(n,k)^N \) of a flexible chain and due to confinement the entropy is controlled. The entropy is increased in controlled manner with the increase of separation between the constraints and therefore, log-log plot of \( f(n,k)-n \) is a straight line.

When there is no constraint around the chain, the entropy of chain grows with monomer size as \( \sim 2^N \), however, for stiffer chain it grows as \( \sim (1+k)^N \). The value of \( k \) is less than 1 for stiffer chain. The constraints around the chain further reduces entropy and it grows with chain size as \( \sim (\mu_c)^N \) (where \( \mu_c < (1+k) \), i.e. \( \mu_c \) (bulk) as shown in figure 4).

It appears from our present results that log-log plot of \( f(n,k)-n \) may deviate from straight line for possible stiffer chain that can polymerize in between the constraints. This is due to fact that entropy of the stiffer chain is much smaller than the flexible chain and presence of constraints around the chain further reduces entropy of the stiffer chain. Therefore, entropy is radially reduced to small value and curve deviates from straight line.

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Figure 4: Critical value of effective co-ordination number of walker is shown for flexible ($k=1$) and semiflexible ($k=0.4, 0.6$ and $0.8$) chain in this figure, when the separation between the constraints varies from $4$ to $19$. In the bulk (when there is no geometrical constraints around the cahin) effective value of co-ordination number is $=1+k$, [12].

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