Thermodynamics of a confined macromolecule: An analytical approach

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Abstract: We consider a fully directed self-avoiding walk model on a cubic lattice to mimic the conformations of an infinitely long flexible polymer chain and also to mimic confirmations of a short flexible chain under confined conditions. The confinement conditions is achieved using two parallel impenetrable plates. The confined chain is under good solvent conditions and we revisit this problem to solve the real (self avoiding) polymer's model for any length of the chain and also for any given separation in between the confining plates. The equilibrium statistics of the confined polymer chain are derived using analytical approach of the generating function technique. The force of the confinement, the surface tension and the monomer density profile of the confined chain are obtained analytically. We propose that the methods of calculation are suitable to understand thermodynamics of an arbitrary length confined polymer chain under other possible conditions of the confinement.

1. Introduction: A lattice model of a self-avoiding walk (SAW) has been widely used for the past a few decades to understand the conformational statistics of a confined short polymer chain under various geometries, and the lattice models were also used to understand the equilibrium statistics of a polymer chain in the bulk [1-3]. Therefore, there are a variety of interesting results on thermo-dynamical aspect of a short and an infinitely long flexible polymer chain in the bulk, and also for a short and an infinitely long polymer chain under various geometries [4-7]. Such studies revealed a wealth of information regarding scaling behavior/universal properties and phase transitions in the polymer macromolecules. These reports gave us understanding of the steric stabilization of the polymer dispersions, colloidal solutions, thin films, and such studies were relevant for surface coatings and sensors [3,5,7-9].

Though, there are a couple of facts that are not well understood regarding an infinitely long as well as a short polymer chain for their three-dimensional confined geometries, *e. g.*, variations of thermo-dynamical properties (force of the confinement, entropic surface tension, monomer density profile, etc.) of a confined self-avoiding flexible polymer chain; and hence it requires an investigation to understood a few such aspects which we shall discuss for three-dimensional confinement**s** here.

We have chosen a directed walk model [3] for a self-avoiding polymer chain to understand the thermo-dynamical properties of an infinitely long flexible chain. Also, we report results for a short flexible polymer chain to understand the thermodynamics of the chain under the proposed confined geometry. The confinement condition is achieved around the polymer chain using a pair of impenetrable flat plates (as shown in figure 1); the plate's

separation is measured in a unit of a monomer length. Thus, the separation of the confining plates is varied from one monomer length to the size of the polymer chain.

2. Model and method: We use theory of critical phenomenon to understand the Physics of a single polymer chain merely because a linear polymer chain is a critical object [3,5,7]. Therefore, there are several reports on the thermodynamics of a single polymer chain. These reports on the statistics of the single polymer chain and chain's statistics so obtained correspond to a condition that the chain is under very dilute solution [1,3,7,10-13]. We confine our discussion to the model of a fully directed walk of a confined flexible polymer chain.
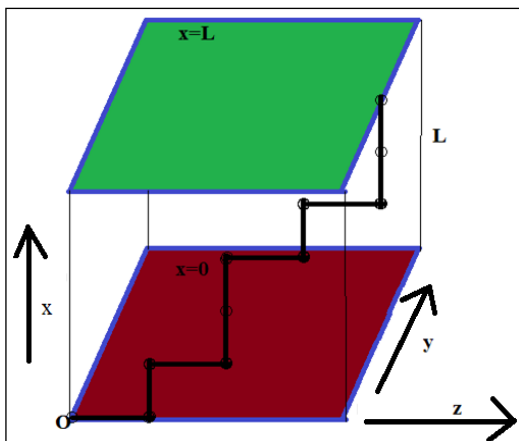

Figure 1: An N monomers long confined flexible polymer chain is shown in figure 1. A pair of impenetrable parallel plates confine the self-avoiding/real polymer chain. The lower plate is located at $x = 0$, and the upper plate is located at $x = L$; one end of the polymer chain is grafted at a point O on the lower plate, i.e., on the plate located at $x = 0$.

It is also to be highlighted that there are several reports on the adsorption-desorption phase transitions of a confined chain and there are reports on conformational statistics of a confined polymer chain under various geometries; the author tried his best to refer to some of the results for the sake of literature survey on the issue of confined polymer chain under specific geometries.

2.1 Fully Directed Self Avoiding Walk (FDSAW) Model: A lattice model of the fully directed self-avoiding walk [3] is widely used to understand the thermodynamics of an infinitely long polymer chain under various geometries. Since a directed walk model is solvable analytically; therefore, we have exact results on single-chain statistics using a directed walk model. It is well known that the qualitative nature of the phase diagram for a directed walk model is the same as to that of its isotropic version [10]. It is assumed that the first impenetrable plate is placed at $x = 0$ and another impenetrable parallel plate is placed at $x = L$, where the value of $L = 1, 2, 3, ..., \infty$; and the parameter L is measured in the unit of a monomer length; and the confined real/self-avoiding polymer chain is schematically shown in figure 1. A condition of $L \geq N$ corresponds to a polymer chain in the bulk.

In the case of a fully directed walk model in three dimensions, it is known also that the walker is allowed to take steps only along $+x$, $+y$, and $+z$ directions in between two parallel plates, and along $+x$ direction walker can take the maximum L $(\leq N)$ steps while the walker can take any number of steps (N) along remaining other two directions, *i.e.*, along $+y$ and $+z$ directions. We have conformations (C_N^L) of **an** N monomers long polymer chain in between two parallel plates, where one end of the chain is grafted at the corner (O) of the lower plate $(x = 0)$. Thus, we have a condition of the confinement provided $L<N$. A general expression of the grand canonical partition function for an infinitely long confined self-avoiding flexible chain is written as:

$$G(g,z) = \sum_{N=1}^{\infty} \sum_{All\ walks\ of\ N\ monomers} g^P z^{N-P}$$
(1)

A symbol g refers to the step fugacity of the walker along a direction parallel to the plane of the confining plates. At the same time, z is the step fugacity perpendicular to the plane of the confining plates. There are P monomers of the chain lying in the plane of the parallel plates, and remaining $(N-P)$ monomers are located perpendicular to the plane of the plates for an N

monomers long confined polymer chain.

3. Results: A lattice model is often used to obtain an equilibrium statistics of an infinitely long confined flexible polymer chain and a short-confined polymer chain [3,5,7]. We obtained the exact results on the conformational statistics of a flexible self-avoiding polymer chain for its confinement using two parallel impenetrable plates; the analytical calculations are **given** below for a short-confined chain and an infinitely long confined flexible polymer chain, separately.

3A. The equilibrium statistics of a confined Self Avoiding flexible polymer chain using Grand Canonical Ensemble (GCE) approach: An exact expression of the grand canonical partition function for an infinitely long confined flexible polymer chain is obtained for different possible values of the plate **separation (L)**; and also, for the bulk case, the partition function of the chain may be written as ($N \geq 1$ and $L < N$),

$$G(g,z) = \sum_{P=1}^{N \to \infty} [(2g)^P +$$
$$\sum_{K(\leq P)=1}^{L(\leq P) \to \infty} z^K \{ \frac{\Pi_{Q=1}^{K}(P-Q+1)}{K!} (2g)^{P-K} \}]$$
(2)

We were able to recover an expression for the grand canonical partition function of the chain for the bulk case [10] by substituting $z = g$ (when $L \geq N$ and $N \to \infty$) in equation 2. The first term on the right-hand side of equation 2 corresponds to the conformations of the chain lying on the lower plate (*i.e.,* at $x = 0$). A simple form of the expression for the grand canonical partition function for the bulk case (*i.e.,* for an infinite separation between the parallel plates and the chain length infinity) may be written as:

$$G(g,z,L=\infty) = \frac{z+2g}{1-z-2g}$$
(3)

The partition function of an infinitely long polymer chain is obtained for a finite separation (L) in between the confining plates. Accordingly, we calculate the thermo-dynamical properties of the confined chain. It is well known that the critical value of the step fugacity is 0.5 for a finite separation (L) in between parallel plates, and the critical value of the step fugacity is 0.33 for $L \geq N$ and $N \to \infty$.

We use canonical ensemble formalism to obtain an exact number (C_N^L) of a real flexible polymer chain conformation, and accordingly, the **equilibrium** statistics of the chain are **obtained** for a case when a pair of impenetrable parallel plate confines the polymer chain; an exact number of the conformations is written as follows for a case when $L < N$,

$$C_N^L = 2^N + \sum_{L=1}^{N-1} 2^{N-L} \frac{N(N-1)(N-2)\ldots\ldots(N+1-L)}{L!}$$
(4)

We have many conformations (C_N^B) of a chain for a case when this short flexible chain is in the bulk ($L \geq N$), and the number of the conformations for the bulk ($L \geq N$) case is written as:

$$C_N^B = \sum_{i=1}^{N-1} C_i^L + 1 = 3^N$$
(5)

3B. Equilibrium statistics of a confined Self Avoiding flexible polymer chain using Canonical Ensemble approach: An effect of the confinement is shown in figure 2, where a fraction of the polymerized (C_N^L) and a fraction of non-polymerized (1- C_N^L) short polymer chain conformations are demonstrated for a set of values of the plates separation (L); and the chain length is an N **monomers**. We have divided the terms C_N^L and (1- C_N^L) by 3^N to obtain the said fraction of the polymerized and non-polymerized chain conformations, respectively.

We have calculated the force [1,2,9] of the confinement ($f_N{}^L$) acting on a short polymer chain of an N monomers due to parallel plates, and the force is acting perpendicular to the plane of the plates while the separation in between the plate is L. While calculating the force, the free energy of the self-avoiding polymer chain is written in a unit of the thermal
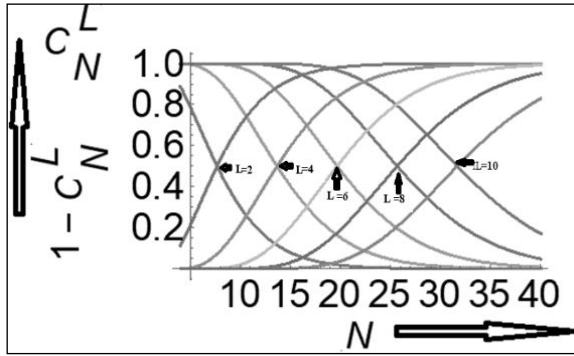

Figure 2: We have shown in figure 2, an average number of the polymer chain's conformations (1-CNL)/3N which were not polymerized due to a pair of an impenetrable plate's confinement. The curves for CNL/3N and (1-CNL)/3N intersect at the 50% value of the

energy as $E(=-k_B TLog[C_N{}^L])$, and thermal energy ($k_B T$) we have taken unity. Therefore, a graph between $f_N{}^L$ versus L and for an N monomers length chain is shown using figure 3(a). The following equation gives the force of the confinement **as**:

$$f_N^L \cong -Log[2] + \frac{\partial\{\frac{Log\,\prod_{L=1}^{L}(N-L+1)}{L!}\}}{\partial L}$$

(6)

The above equation (*i.e.,* equation 6) is simplified to the following relation to seeing that $f_N{}^L = -Log[2]-Log[L/N]$. Thus, the force bears logarithmic singularity provided $L<N$, $L\geq1$, and N→∞ for an infinitely long chain.

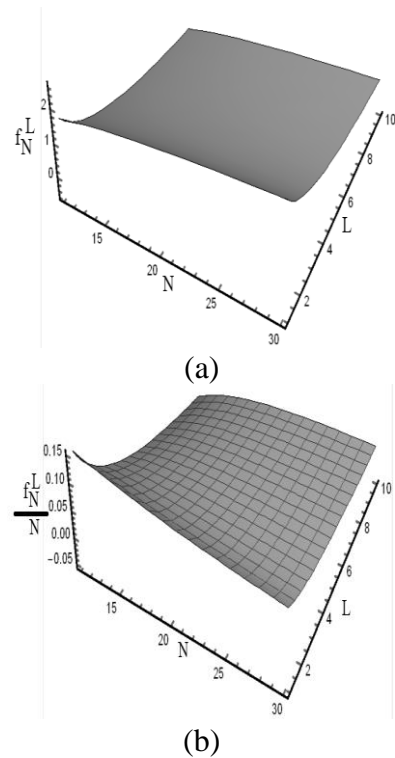$$f_N^L \cong Log[\frac{N}{2L}]$$

(7)

(a)

(b)

Figure 3: The force of the confinement which is acting perpendicular to the plane of the plates, and its nature of variation for a few sets of (N, L) has been shown in this figure 3(A) for a short chain of length an N monomers and we increase the separation in-between plates (L=2, 4, 6, 8 and 10) in a unit of monomer length. Figure 3(B) shows nature of variation of the confining force per monomer of the confined chain for set of N, L values.

The entropic surface tension (σ_N^L) of a short-chain and an infinitely long confined real polymer chain solution may be obtained using the following relation:

$$\sigma_N^L = \frac{\delta(E)}{\delta A}$$

(8)

Where $E(=-k_B TLog[C_N{}^L])$ is the Helmholtz free energy of a short polymer chain under confined geometry; and, again, we have taken the value of the thermal energy ($k_B T$) equal to unity for the sake of mathematical simplicity. The maximum change in the area is $[(N-L+1)^2 - (N-L)^2]/2$ when the walker steps one unit along the *x*-direction, and the plate separation varies in the unit of one monomer length. For a confined chain, $L_{Max}=N$-1. It is to be noted

here that the surface tension for the present case has an entropic origin, and the value of the surface tension for a self-avoiding confined chain is written as:

$$\sigma_N^L = \frac{2\,Log\left[\dfrac{1}{2}\right]}{N-L} + \frac{2\,L\,Log\left[\dfrac{1}{N}\right]}{(N-L)^2} + \frac{2\,Log[L!]}{(N-L)^2}$$

(9)

The nature of variation of the entropic surface tension of a short polymer chain with confining plate separation is shown in figure 4.

We have also calculated the monomer number density (ρ_N^L) profile, **and a plot on the density profile for the confined flexible chain is shown in figure 5**; we have an exact expression for the number density of an N monomers long chain, and the density is written as follows:

$$\rho_N^L = [2^{N+1-L}]\frac{N(N-1)\ldots(N-L+1)}{L!(N-L)}$$

(10)
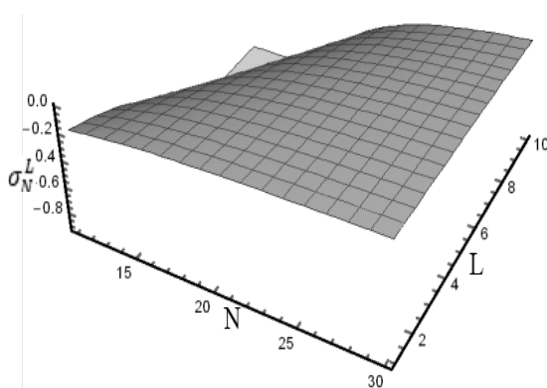

Figure 4: A plot on the entropic surface tension (σ_N^L) of a short polymer chain (N =11, 12, ..., 30 monomers) confined in between a pair of parallel plates is shown in this figure, and the plates are separated by a distance L (= 1, 2, ..., 10) monomers.

The monomer number density profile is shown in figure 5 for the confinement condition of a short flexible polymer chain for the given values of L. For L=0 and for a non-zero value of L, and for a confined chain ($L < N$), the monomer density profile is written as equation 10.
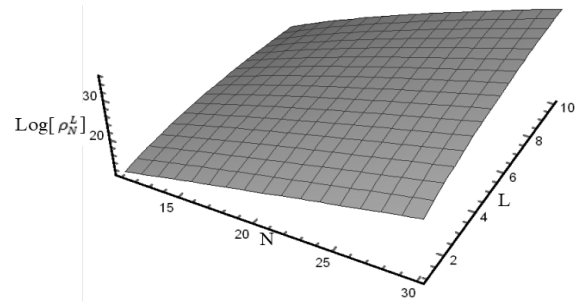

Figure 5: This figure shows the logarithmic value of the number density profile of a real flexible polymer chain. The length of the polymer chain (N) is varied from 11 to 30 monomers, and the separation (L) of the parallel plate is varied from 1 to 10 monomers.

4. Discussion: A lattice model of the fully directed self-avoiding walk is used to mimic the conformations of an infinitely long and a short confined flexible polymer chain, where the polymer chain is confined by a pair of impenetrable parallel plates (as shown schematically in figure 1). The confined regions **in** between a pair of parallel plates lead to different values of the step fugacity for the walker **along and perpendicular to** the plane of the confining plates. Therefore, along the plane of the plates, we have one value of step fugacity (*i.e., g*), and in a direction perpendicular to the plane of the confining plates, we have another value (*i.e., z*) of the step fugacity. We used the generating function method to solve the model analytically; and we obtained a general expression for the grand canonical partition function of an infinitely long self-avoiding flexible polymer chain for any given value of plate separation (L).

We have also obtained an exact expression of the canonical partition function for a short flexible self-avoiding polymer chain. The chain is made of an N monomers; the plate separation equals L monomers. We calculated an exact percentage of the polymer conformations which were not polymerized (suppressed) due to the confinement conditions imposed on the chain by the pair of parallel impenetrable plates. We derived expressions

for the force of the confinement, the entropic surface tension, and the monomer number density profile for a short-chain length of an N monomers and we derived a condition when an infinitely long chain is confined by the pair of plates for the plate separation L.

We have plotted $(C_N{}^L)/3^N$, *i.e.*, the number of a confined flexible polymer chain conformations of an N monomers long polymer chain along with the conformations, *i.e.*, $(1-C_N{}^L)/3^N$, which is suppressed due to the confinement, for different values of the plate separation (L); and we have shown the polymerized and suppressed fractions of the conformations in figure 2. It is seen from this figure that as we increase the length of the chain for a given value of the plate separation (L), the percentage of the polymerized chain's conformations decreases. Accordingly, the percentage of the non-polymerized/suppressed conformations increases due to the confinement. It is also found that the percentage of the polymerized conformations increases for a given length of the chain as the separation between the plates increases. The force of the confinement is a function of the chain length and the separation between the confining plates. It is found from analytical calculations that the force of confinement decreases logarithmically as we increase the plate separation for a given length of the confined chain. While the force of confinement increases logarithmically as we increase the length of the confined chain, provided the plate separation is retained constant. We have shown the nature of confining force which acts on a short polymer chain, in figure 3 for a set of N and L values.

The entropic surface energy per unit surface area (*i. e.* the entropic surface tension) for a confined flexible chain is shown in figure 4; it is seen that the surface tension of the confined chain increases for a given length of the chain as we increase the length of confinement, and it starts decreasing after a particular value of L. The surface tension of a confined chain also increases for a given value of L as we increase the number of monomers in the confined chain.

An actual dependency of the surface tension on N and L is shown in figure 4, and the mathematical form of the entropic surface tension is given by equation 9. Though we have a very dilute chain concentration, therefore, the entropic surface tension of a self-avoiding confined flexible polymer chain vanishes in the thermodynamic limit. The monomer number per unit areal extension of the confined flexible chain is shown in figure 5. It is seen from this figure that the monomer density increases as the length of the chain increases and L remains fixed, and also the monomer density increases as we increase L for a given length of the confined chain. The nature of the free energy curve for a confined short chain is also shown in figure 6 for the completeness. It is seen from figure 6 that in the thermodynamic limit, the free energy per monomer of the confined flexible chain is $Log[g_c(2D)]^{-1}$, where $g_c(2D) = 0.5$.

We have taken a factor $\alpha = (L/N)$ to report the confining force, the entropic surface tension, the monomer number density, and the free energy of a confined chain in terms of α (<1, for a confined chain); and accordingly, we have plotted these thermo-dynamical parameters in the thermodynamic limit in figure 7 for the sake of completeness. Therefore, we have these thermo-dynamical parameters that may be written in the thermo-dynamical limit ($N\rightarrow\infty$) as (i. e. for an infinitely long confined chain):

$$f_{N\rightarrow\infty}^L = -\log[2] - Log[\alpha]$$

(11)

$$\sigma_N^L * N = -\frac{2Log[2]}{(1-\alpha)} + \frac{2(Log[\alpha]-1)}{(1-\alpha)^2}$$

(12)

$$\frac{Log[\rho_N^L]}{N} = (1-\alpha)Log[2] + \alpha(1-Log[\alpha])$$

(13)

and finally, the free energy per monomer($\varepsilon=E_N{}^L/N$) of a confined chain is written as:

$$\varepsilon = -(1-\alpha)Log[2] + \alpha Log[\alpha] - \alpha$$
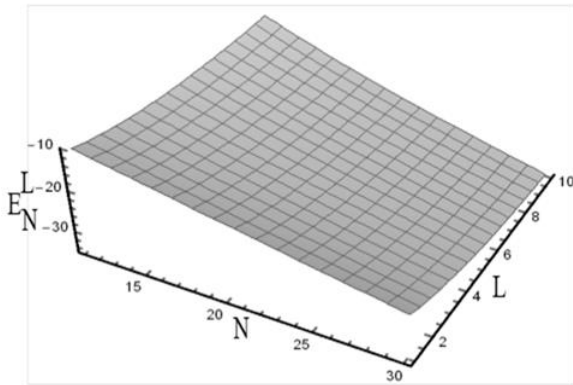
(14)

Figure 6: We have shown the free energy graph of a confined flexible polymer chain for the given values of *L* and *N* in this figure. The Helmholtz free energy is a function of *N* and *L*, and the free energy is approximated as $E_N{}^L \approx -NLog[2]+LLog[2]-LLog[N]+LLog[L]-L$. The thermal energy is set to unity for the sake of mathematical simplicity.

A method of calculations reported in this manuscript may be easily extended to calculate the thermodynamics of an infinitely long and a short self-avoiding polymer chain confined to a length L for other versions of the directed/isotropic walk models on different possible lattices. It is also to be noted from reports that the qualitative nature of the phase diagram obtained for an isotropic self-avoiding walk model is the same as that of the phase diagram of a directed walk model of the problem [10], and therefore, our findings may be relevant to understand the thermodynamics of a confined three-dimensional polymer chain.

Our calculations include entropy of the confined chain where those conformations were chosen, which are in the form of polymer bridges or polymer trains, though we have not considered the loop-like conformations; However, the entropy of the confined chain has a monotonous variation with *N* and or *L* for other versions (*i.e.,* isotropic or partially directed walk model of the confined chain) of the confined polymer models; therefore physical insight will remain same for the confined chain when one includes polymer

loop like conformations for such studies. It is also to be noted that in the presence of another confining plate (*i.e.,* a plate located at *x = L*), the entropy of the chain is reduced due to excluded volume interaction among the monomers of the confined chain. Hence, many chain conformations are suppressed for any value of L<N, *i.e.,* not polymerized.
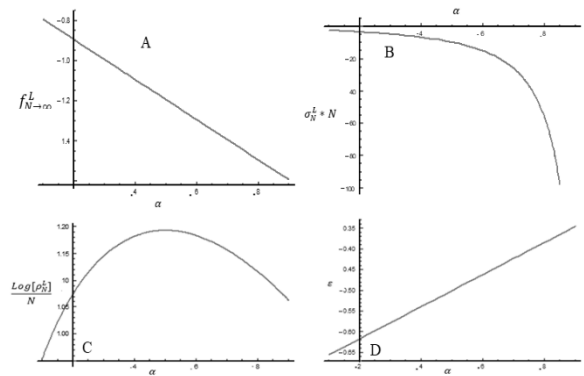

Figure 7: This figure no. 7A shows the force of the confinement acting on the chain as a function of α (as shown in the equation 11); the entropic surface tension of an *N* monomers long chain is shown in the figure (7B), and the equation 12; the logarithmic value of the monomer density per monomer is shown in the figure (7C), and the equation 13; and also, the free energy per monomer of the confined chain (ε) is shown in the figure (7D), and equation 14, as a function of α.

5. Challenges: There are limitations regarding visualizing a macromolecule in the restricted geometries, though we have reports on single macromolecule manipulations [11] and please also see the references quoted therein. Therefore, we can expect that it may be possible to track single macromolecule and measure its physical properties under the confined geometries soon.

6. Conclusion and Future Scope: The lattice model of a polymer chain has limitations, as the lattice model mimics discrete links of the monomers of a chain. Therefore, finite length fluctuations related physics of the system may have different results from real situations of the polymer Physics. Still, in the case of phase transitions, there are fluctuations of all length scales. Correlation length extends to the size of the confined chain length. Therefore, the phase

transitions which occur in the thermodynamic limit may not have any sensitivity regarding the finite and non-zero size of the monomers. Though there are studies based on continuum models of the polymer chain, it has been found that the Physics of polymer chain derived using continuum and discrete models have a qualitative similarity [1,3,5,11, 16].

Conflict of Interest: Authors declare No conflicts of interest.

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