

# Directed Walk Models of Polymer Unzipping

*A dissertation submitted to Indian Institute of Science Education and Research,  
Mohali in partial fulfillment of the requirements for the B.S.- M.S. dual degree in  
Science*

by

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April, 2014

## Certificate of Examination

This is to certify that the dissertation titled "Directed Walk Model for Polymer Adsorption" submitted by Mr. Kapil Bharti (Reg. No. MS09069) for the partial fulfillment of B.S.–M.S. dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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## Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Rajeev Kapri at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Rajeev Kapri  
(Supervisor)

## Acknowledgment

I would like to express my gratitude to my dissertation guide Dr. Rajeev Kapri for his guidance, support, advice and for giving me enough freedom so that I could explore the problem as per my interest. I would also like to thank IISER Mohali for their support.

Finally, I am grateful to my friends and family for giving me all the non-technical support and of course sheer luck because of which I got the opportunity to explore application of mathematics in different areas of sciences.

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# Chapter 1

## Introduction

It is hard to imagine life without polymer because of their several uses. The term *polymer* is derived from a Greek word *poly* means 'many', and *meros* meaning 'parts'. Hereby, polymer is a large unit made up of small structural units, called *monomer* connected by a covalent bond [1]. They can have identical monomers (*homopolymer*) or it can be all different (*heteropolymer*). Polymer can be both found in nature or be produced artificially. Some of the well known polymers are natural rubber, cellulose etc., whereas plastic, nylon, to name a few, are synthetic polymers produced chemically by a process called *polymerization* [1].

Structurally, polymers can be linear, branched or has a network like structure. In a linear polymer the monomers are arranged in a linear fashion. For a branched polymer, there are side chains coming out as branches giving it a tree-like structure. However, by a polymer we shall mean a linear polymer.

During the past several decades, geometrical lattice models such as random walks etc., have played an important role in statistical mechanics such as study of polymer adsorption. Lattice models, in spite of their apparent simplicity, can be successfully used in the studies of real physical systems, to describe conformation and growth features. We focus on simple mostly two-dimensional lattice Models.

In order to make our models exactly solvable, we impose "microscopic" restrictions by disallowing certain steps in an unrestricted random walk. The resulting models are in many instances exactly solvable by methods including generating function. The idea is to solve exact solutions for Dyck and Motzkin paths.

Let us briefly discuss the properties of simple random walk before going to the directed

walk models.

## 1.1 Random Walk

This section focus on features of an unrestricted walk.

### 1.1.1 Simple Walk

The simplest example of a random walk is where the walker is confined to a straight line. In this case, the walker moves either in "right" or "left" direction with equal probability. Suppose the walker has taken  $N$  steps out of which,  $n$  are towards right and  $N - n$  are towards left direction. Assuming each step size to be  $l$ , the probability for such  $N$  step walk resembles to a Gaussian distribution [3]

$$P(N, d) \sim \exp\left(\frac{-x^2}{2l^2N}\right) \quad (1.1)$$

### 1.1.2 Elementary Calculation and Quantities of Interest

#### Average Displacement

Since the walker is moving with equal probability towards left and right directions, the average displacement of the walker from the origin is zero.

$$\langle x \rangle = 0. \quad (1.2)$$

#### Mean Square Displacement

The mean square displacement of the walker from the origin,  $\langle x^2 \rangle$  is given by [3]

$$\langle x^2 \rangle = Nl^2. \quad (1.3)$$

## 1.2 Polymer Adsorption

Polymers can be adsorbed spontaneously from solution onto surfaces if the interaction between the polymer and the surface is more stronger than that of the solvent with the surface. This phenomenon is of greater use in applications like lubrication, adhesion etc [7]. The adsorption process depends on the type of surface, on which the polymer is adsorbed. The surface can be penetrable (*soft wall*), or can be rigid (*hard wall*).

### 1.2.1 Adsorption-Desorption Transition

An adsorbed polymer can be desorbed from the surface simply by an increase in the temperature. At low temperatures, the polymer prefers to remain adsorbed on the surface to gain energy, however, at high temperatures, it stay away from the surface to gain entropy. This battle between the energy and the entropy ( to minimize the total free energy) result in an adsorption-desorption transition. The relevant quantities of interest is the critical temperature  $T_c$ , above which the polymer is desorbed from the surface [6, 7, 9, 10, 11, 12].

### 1.2.2 Unzipping Transition

An adsorbed polymer can also be removed from the surface by applying a pulling force at one end. This transition induced by a pulling force is known as unzipping transition. The polymer unzips from the surface if the pulling force exceeds a critical value [14, 15, 16, 17].

The thesis is organized as follows: In the next chapter, we study the directed walk models to understand unzipping of polymers. We consider fully directed walks of a polymer on a two- dimensional lattice and calculate quantity of interest associated with it. This include both soft-wall and hard-wall problems for both Dyck and Motzkin paths. The soft wall allows the polymer to cross through it while hard-wall restrict the polymer on the positive  $x$ -axis only.

In Appendix A and B, we give the solution for the unzipping of an adsorbed polymer for both Dyck and Motzkin paths, respectively. The attempt is to solve it exactly through generating function technique for both in the fixed distance, and the fixed force ensembles.

The force-distance isotherms for both Dyck and Motzkin paths are obtained by iterating the recursion relation using the exact transfer matrix technique. The details are given in Appendix C and D for Dyck and Motzkin paths respectively. The sample codes written in C programming language is also given.



## Chapter 2

# Directed Walk

In this chapter, we briefly review various possible directed walks and then consider the Fully Directed Self Avoidance Walk (FDSA) models to show their relevance in understanding polymer unzipping [2, 4, 5]. In sec. 2.1, we define directed walk. The exact solution is also discussed here. The various FDSA models, with their respective quantities of interests are defined in sec. 2.2. The results for various models are also discussed here. We draw our conclusion in sec. 2.3.

### 2.1 Definition

A directed walk in  $D = d + 1$  dimensions is a walk which grows in a preferred direction and can have transverse fluctuations in  $d$  dimensions. A discretized version of this is a directed random walk on a lattice and can be defined as follows: If we choose  $\vec{z}$  as a preferred direction, then for a Directed random walk, the projection of each step on  $\vec{z}$  is non-zero [19]. For example, in  $D = 1 + 1$ , a directed walk which takes steps only along the diagonal of a square lattice can be imitated as a directed walk. However, the number of configuration varies for different models. In a Dyck path, where there are only two possible steps at each lattice point, the total number of configuration for a  $N$  step polymer is  $2^N$ , while for a Motzkin path, where there are three possible steps at each lattice point, the total configuration turn outs to be  $3^N$ .

## 2.2 Model

### 2.2.1 Dyck Path

The systematic diagram of a polymer immersed in a medium with an attractive wall, with potential  $V_w(x)$ , at the diagonal of the square lattice ( $x = 0$ ) is shown in Fig. 2.1. The wall suppresses the transverse fluctuation of the polymer because the polymer gains energy every time it is on the wall. Depending on the ensemble one is working with, either a fixed force  $g$  can be applied at the end monomer (*fixed force ensemble*), or the distance  $x$  of the end monomer can be fixed from the wall (*fixed distance ensemble*). The starting end of the polymer is always anchored. Further, the following type of wall can be added as a constraint:

1. A hard-wall, which do not allow a polymer to cross through it,
2. A soft-wall which allows a polymer to cross.

This model has been studied earlier [19].

### Partition Function

In  $D = 1 + 1$ , the recursion relation, in the *fixed distance ensemble* is given by

$$Z_{N+1}(x) = \sum_{j=\pm 1} Z_N(x+j)[1 + (e^{\beta\epsilon} - 1)\delta_{x,0}] \quad (2.1)$$

where  $Z_N(x)$  is the partition function of a polymer of length  $N$  whose  $N$ th monomer is at a distance  $x$  from the wall,  $\beta = 1/k_b T$ . We take the Boltzmann constant  $k_b = 1$  [19].

The wall potential is of the form

$$V_w(x) = \begin{cases} -\epsilon \ (\epsilon > 0) & \text{for } x = 0, \\ 0 & \text{otherwise.} \end{cases} \quad (2.2)$$

The initial condition for the above recursion relation is

$$Z_0(x) = e^{\beta\epsilon}\delta_{x,0}. \quad (2.3)$$

The non crossing constraint of a polymer in a hard wall is taken care by the condition

$$Z_j(x) = 0, \forall \ x < 0, \quad (2.4)$$

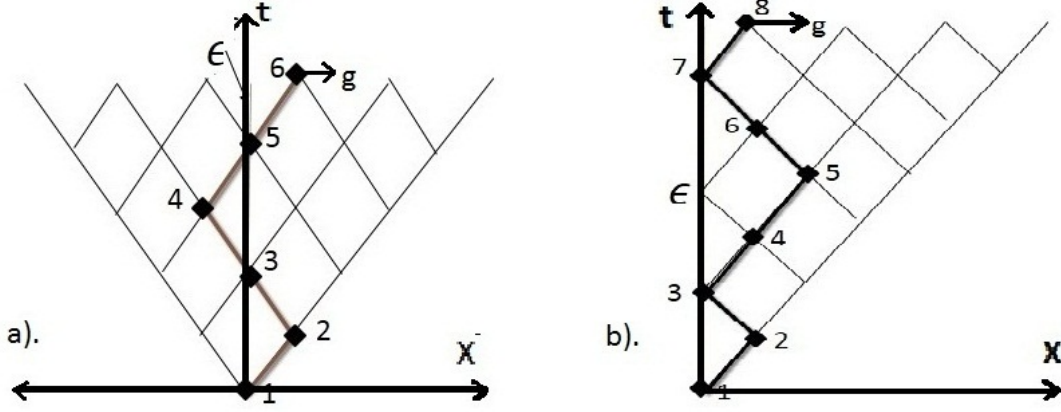


Figure 2.1: Schematic Diagram of a polymer in a medium with attractive wall. By construction, one direction along the polymer is special the wandering is along transverse  $d$  direction and therefore  $d + 1$  dimensional model. Here  $d=1$ . There is a line at  $x = 0$  (a wall or interface) that attracts the polymer. a). Soft Wall: polymer is allowed in the whole region. b). Hard Wall: polymer is not allowed in the region ( $x < 0$ ).

after each step  $j$ .

The canonical partition function in the *fixed force ensemble* with a fixed force  $g$  acting at one end, keeping the other end anchored at the diagonal of the square lattice ( $x = 0$ ) is then calculated by summing all allowed configurations of the walks on the lattice.

$$\mathbb{Z}_N(g) = \sum_x \mathbb{Z}_N(x) e^{\beta g x}, \quad (2.5)$$

where  $e^{\beta g x}$  is the Boltzmann weight added due to fixed force  $g$ . The thermodynamic properties in a given ensemble are obtained from the free energy,

$$F_N(T, x) = -T \log \mathbb{Z}_n(x), \quad \text{fixed-distance} \quad (2.6)$$

$$\Gamma_N(T, g) = -T \log \mathbb{Z}_n(g), \quad \text{fixed-force} \quad (2.7)$$

## Ensembles and Quantities of Interest

The process is studied in the following ensembles:

### A Fixed Force Ensemble:

In this ensemble a fixed force  $g$  is applied at the end monomer keeping the other end anchored at origin ( $x = 0$ ). In such transition, in order to keep the pulling force  $g$  constant, the distance between the wall and the end monomer of the polymer is allowed to fluctuate. Consequently, the quantities of interest is:

- *Average distance from the wall:* The average distance of the end monomer from the wall,  $\langle x \rangle$  when a fixed pulling force is applied is given by [19]:

$$\langle x \rangle = \frac{\sum_x x Z_N(x) e^{\beta g x}}{\sum_x Z_N(x) e^{\beta g x}} \quad (2.8)$$

**B Fixed Distance Ensemble:** In this ensemble, the distance between the wall and the end monomer,  $x$  is kept constant. In this case, the force  $g$  is the fluctuating variable.

- *Average Force:* The average force required to keep the distance between the wall and end monomer constant is given by:

$$\langle g(T, x) \rangle = \frac{\partial F(T, x)}{\partial x} \quad (2.9)$$

## Results

### A Phase Diagrams:

The recursion relation for the given canonical partition function can be solved exactly via generating function technique. The generating function Eq. (2.5) has the following three singularities:

$$z_1 = \frac{1}{2}, \quad (2.10)$$

$$z_2(\beta\epsilon) = \begin{cases} \frac{1}{2} \sqrt{1 - (1 - \exp(-\beta\epsilon))^2} & \text{for soft-wall} \\ \frac{1}{2} \sqrt{1 - (1 - 2 \exp(-\beta\epsilon))^2} & \text{for hard-wall} \end{cases} \quad (2.11)$$

and

$$z_3(\beta g) = \frac{1}{2 \cosh(\beta g)} \quad (2.12)$$

The phase of the polymer is given by the singularity which is closest to the origin and the phase transition takes place when two singularities cross. For low force,  $z_2$  is closest to the origin and polymer is in the zipped phase, while for high force,  $z_3$  becomes closest and the polymer is in the unzipped phase. The unzipping transition in the *fixed force ensemble* is given by the condition  $z_2 = z_3$  which gives the following analytical expressions in the force-temperature plane [19]

$$g_c(T) = 2T \cosh^{-1} \left[ \frac{1}{2} \left( \frac{1}{z_2(\beta \epsilon)} - 1 \right) \right], \quad (2.13)$$

where  $z_2(\beta \epsilon)$  for both the softwall and the hardwall cases are given by the above equation. The recursion relation can be solved exactly also in the fixed distance ensemble. The phase boundary is given by

$$g_c(T) = \begin{cases} T \log [2e^{\beta \epsilon} - 1] & \text{for soft-wall,} \\ T \log [e^{\beta \epsilon} - 1] & \text{for hard-wall.} \end{cases} \quad (2.14)$$

The phase diagrams are plotted in Fig.2.2. One can see that both the expressions give the same phase boundaries. The details of the calculations are given in Appendix A.

The absorption-desorption transition is given by the condition  $z_1 = z_2$  which gives the desorption temperature  $T_c = \frac{\epsilon}{\ln 2}$  for hard-wall and  $T_c = \infty$  for soft-wall. If we compare the phase boundary at very low temperature ( $T = 0$ ), the force required to unzip the polymer from the wall is same for both soft- wall and hard- wall. This implies the low temperature behaviour of polymer is same for both the walls i.e.  $g \propto \epsilon$  [19]. The polymer behaves differently with the increase in temperature. In the case of Hard-wall, the polymer can be unzipped simply by increasing the temperature. The transition temperature  $T_c = \frac{\epsilon}{\ln 2}$  corresponds to a pure *first -order transition*. However, in the case of soft wall, the transition in the force- temperature plane takes place at  $T_c = \infty$ , depicting that the force needed to unzip the polymer from the wall increases monotonically with the temperature.

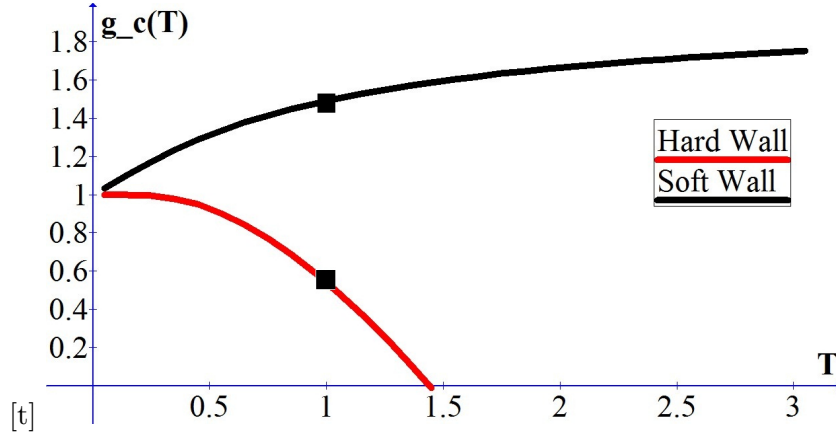


Figure 2.2:  $\langle g_c(T) \rangle$  Vs  $T$  phase diagram for both Hard and Soft Wall, following a Dyck path

### B Isotherms:

For the unzipping transition,  $\langle x \rangle / N$  Vs  $g$  (*fixed force ensemble*) or  $\langle g \rangle$  Vs  $x$  (*fixed distance ensemble*) are of interests. The isotherms for a polymer of length  $N=64$  at  $\epsilon = -1.0$  for a hard wall are shown in Fig. 2.3; for a soft wall shown in Fig. 2.4.

For finite  $N$ , they are obtained by iterating the recursion relation to calculate the partition function and then the extension or the force, depending on the ensemble used. The numerical procedure to calculate various thermodynamic quantities through the language of  $C$  is discussed in Appendix C. (Code A - *Soft Wall* and Code B - *Hard Wall*).

In the fixed distance ensemble, the distance between the end monomer of the polymer and the wall  $x$  is varied at a step 1. The quantity of interest, the average force required to maintain the distance  $x$  between the polymer and the wall, is calculated using finite differences in free energy. In the fixed force ensemble, the average separation  $\langle x \rangle$  between the polymer and wall at the site of application of force at a temperature  $T$ , is calculated by taking the finite difference of exact free energies as  $g$  is increased in steps of  $\Delta g = 0.001$ .

The  $\langle g \rangle$  Vs  $x$  isotherms in Fig. 2.3(a) and Fig. 2.4(a) signals a coexistence between the average force and the temperature  $T$  for a polymer of length  $N=64$ .

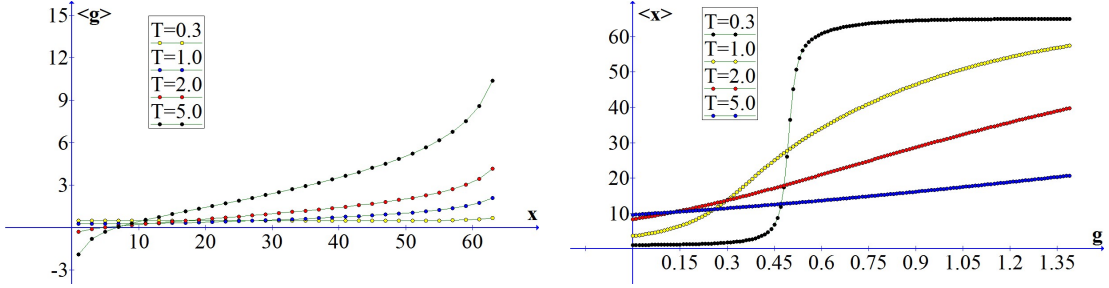


Figure 2.3: Isotherm in (a) fixed distance ensemble. (b) fixed force ensemble for the hard-wall case for a polymer of length  $N=64$  at  $\epsilon = -1.0$  for the Dyck path model

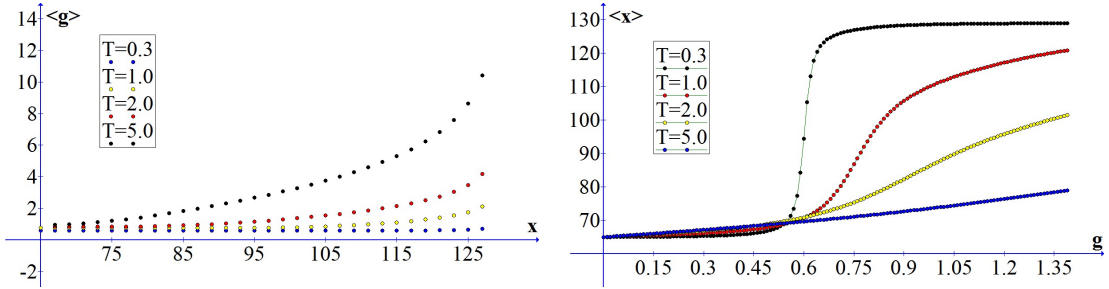


Figure 2.4: Isotherm in (a) fixed distance ensemble (b) fixed force ensemble for a soft wall, for a polymer of length  $N=64$  at  $\epsilon = -1.0$  following a Dyck path

At temperature above the critical temperature  $T_c$ , we need zero force to unzip the polymer. The attribute remains same when studying the dependence of  $T$  on the average separation between the wall and polymer,  $\langle x \rangle$ , for a polymer of length  $N=64$  given the fact the applied force is increased in steps of  $\Delta g = 0.001$ . The Fig. 2.3(b) and Fig. 2.4(b) shows that the average separation,  $\langle x \rangle$ , increase with the increase in temperature  $T$ . For small  $T$ , once the applied force  $g$  is slightly above the critical force, the average separation is proportional to  $N$ , but for large  $N$ , it is due to finite size effects.

The scaled separation between the polymer and the wall,  $x/N$ , versus the corresponding average force at  $T = 1.0$  for various length of polymers, for both soft wall and hard wall are shown in Fig. 2.5(a) and Fig. 2.6(a) respectively. The isotherms shows that a flat region for lower separation. The difference from the flat region for

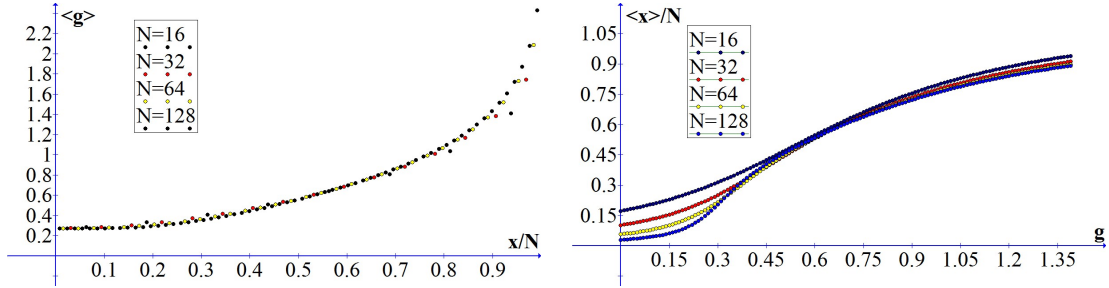


Figure 2.5: (a)  $\langle g \rangle$  Vs  $x/N$  and (b)  $\langle x \rangle / N$  Vs  $g$  isotherms at  $T = 1.0$  for various length of polymers for a hard wall following a Dyck path

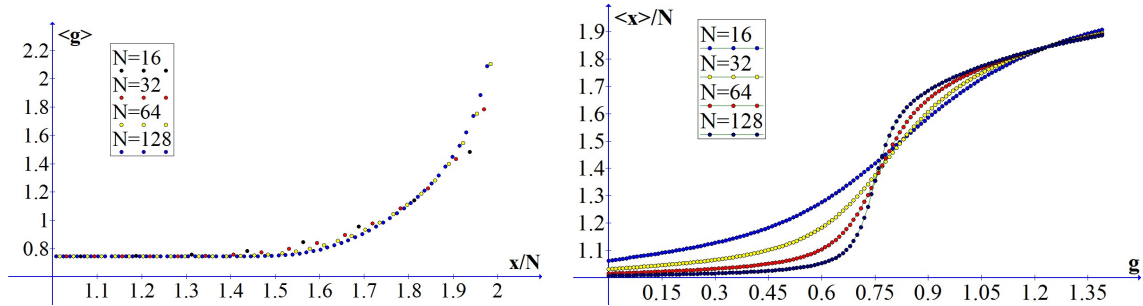


Figure 2.6: (a)  $\langle g \rangle$  Vs  $x/N$  and (b)  $\langle x \rangle / N$  Vs  $g$  isotherms at  $T = 1.0$  for various length of polymers, for a soft wall following a Dyck path

higher separation is due to the finite size effects.

The  $\langle x \rangle / N$  Vs  $g$  isotherms for the polymer of various length at  $T = 1.0$ , for a hard wall is shown in Fig. 2.5(b); for a soft wall in Fig. 2.6(b) The isotherms shows that for  $g$  below  $g_c$ , the polymer is adsorbed on the wall whereas for  $g$  slightly above  $g_c$ , the polymer is unzipped from the wall. The transition becomes sharp as the length of the polymer increases.

## 2.2.2 Motzkin Path

The idea of solving the Motzkin path is to visualise the change in the quantities of interest with the change in the number of configuration ( $3^N$  in the case of Motzkin path). The system is same, with an polymer immersed in a medium with attractive wall, with potential



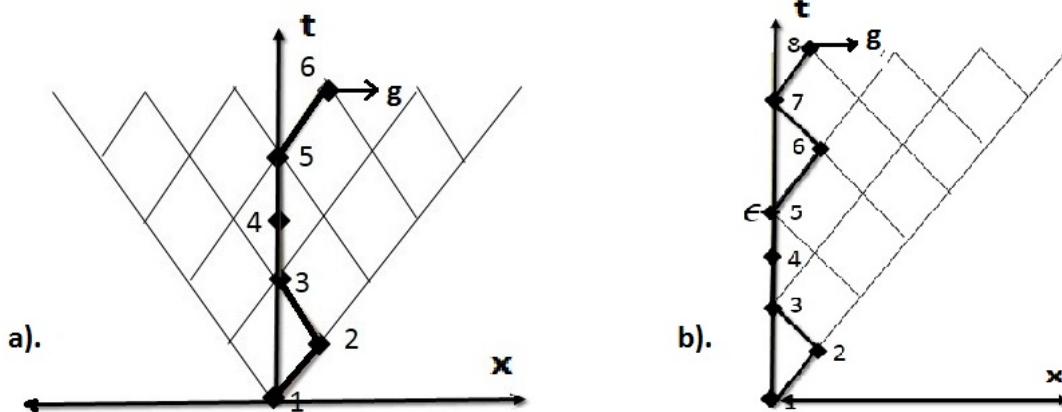


Figure 2.7: Schematic Diagram of a polymer in a medium with attractive wall for a Motzkin path. a). Soft Wall: polymer is allowed in the whole region. b). Hard Wall: polymer is not allowed in the region ( $x < 0$ ).

$V_m(x)$ , at the diagonal of square lattice ( $x = 0$ ) as shown in Fig. 2.7. The system is studied in both *fixed distance ensemble* and *fixed force ensemble* with constraints as above.

1. A hard wall, which do not allow a polymer to cross through it
2. A soft wall which allows a polymer to cross.

However, the change is in the iteration i.e. the number of lattice point approaching the final position. Unlike the Dyck path, the iteration in Motzkin path comes from  $\sum_{j=0,\pm 1} M_t(x)$ .

### Partition Function

The above recursion relation needs to be iterated with an initial condition:

$$M_0(x) = e^{\beta\epsilon} \delta_{x,0} \tag{2.15}$$

The non crossing constraint in a hard wall is taken care by:

$$M_j(x) = 0, \forall x < 0, \tag{2.16}$$

after each step  $j$ . The canonical partition function for a *fixed force ensemble* is then calculated with summing over all configurations

$$\Pi_N(g) = \sum_x M_N(x) e^{\beta g x}, \quad (2.17)$$

where  $e^{\beta g x}$  is the Boltzmann weight added due to a fixed force  $g$ . Further, the thermodynamic properties in a given ensemble are obtained from the free energy as above,

$$F_N(T, x) = -k_B T \log M_n(x), \quad \text{fixed distance} \quad (2.18)$$

$$\Gamma_N(T, g) = -k_B T \log \Pi_n(g), \quad \text{fixed force} \quad (2.19)$$

## Results

### A Phase Diagrams:

The recursion relation for the given canonical partition function is solved exactly. The generating function has the following singularities:

$$z_1 = \frac{1}{3} \quad (2.20)$$

$$z_2(\beta\epsilon) = \begin{cases} \frac{1}{3} \left[ e^{-2\beta\epsilon} \sqrt{e^{2\beta\epsilon}(-3 + e^{\beta\epsilon}(6 + e^{\beta\epsilon}) - 1)} \right] & \text{for soft-wall} \\ \frac{1}{2e^{\beta\epsilon}} \left[ \sqrt{(e^{\beta\epsilon} - 1)(e^{\beta\epsilon} + 3)} - (e^{\beta\epsilon} - 1) \right] & \text{for hard-wall} \end{cases} \quad (2.21)$$

$$z_3(\beta g) = \frac{1}{2 \cosh(\beta g) + 1} \quad (2.22)$$

The force-temperature phase boundary is given by equating  $z_2 = z_3$  which gives

$$g_c(T) = 2T \cosh^{-1} \left[ \frac{1}{2} \left( \frac{1}{z_2(\beta\epsilon)} - 1 \right) \right], \quad (2.23)$$

where  $z_2(\beta\epsilon)$  for both the softwall and the hardwall cases are given by the above equation. The recursion relation can be solved exactly also in the fixed distance ensemble. The details of calculations are is given in Appendix B.

Similar to the Dyck path model, the force-temperature plane bears resemblance as shown in Fig. 2.8 The absorption-desorption transition is given by the condition  $z_1 = z_2$  with a melting temperature  $T_c = \frac{\epsilon}{\ln 3/2} = 2.4663$  for hard-wall; and for the soft wall  $T_c = \infty$  as with the Dyck path. At low temperature, the polymer

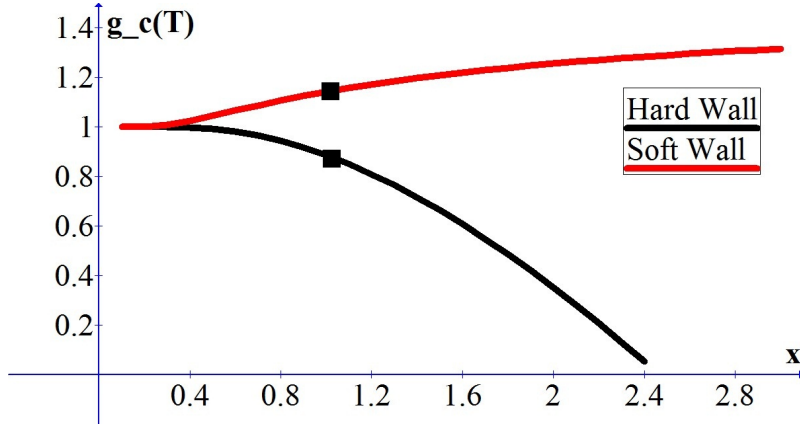


Figure 2.8:  $\langle g_c(T) \rangle$  Vs  $T$  phase diagram for both Hard and Soft Wall, following a Motzkin path

behaves similarly for both walls with  $g \propto \epsilon$ . However, as in the Dyck path, the polymer behaves differently with increase in temperature. For the hard wall, the force required to unzip the polymer in decreases monotonically with the increase in temperature. The transition is of *first-order* as in the case of Dyck path. However, for the soft wall it increases with increase in temperature.

## B Isotherms:

At a given temperature  $T$  and a force  $g$  the partition function for a polymer of length  $N$  can be obtained exactly by iterating the recursion relation. For the unzipping transition,  $\langle x \rangle / N$  Vs  $g$  (*fixed force ensemble*) or  $\langle g \rangle$  Vs  $x$  (*fixed distance ensemble*) are of interests, as studied in the Dyck path. However, the difference is in the number of configurations in the recursion relation. The isotherms for a polymer of length  $N=64$  at  $\epsilon = -1.0$  for a hard wall are shown in Fig. 2.9; for a soft wall shown in Fig. 2.10. The numerical procedure to calculate the quantities of interest is discussed in Appendix D.

The ensembles studied are identical to the ensembles discussed above. In the fixed distance ensemble, the distance between the end monomer of the polymer and the wall  $x$  is varied at a step 1. The average force required to maintain the distance  $x$  between the polymer and the wall, is then calculated using finite differences in free energy. In the fixed force ensemble, the average separation  $\langle x \rangle$  between the

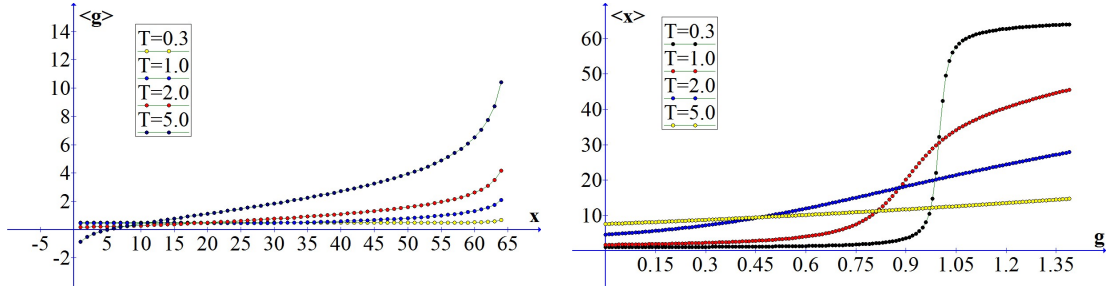


Figure 2.9: Isotherm in (a) fixed distance ensemble (b) fixed force ensemble for a hard wall, for a polymer of length  $N=64$  at  $\epsilon = -1.0$  for a Motzkin path

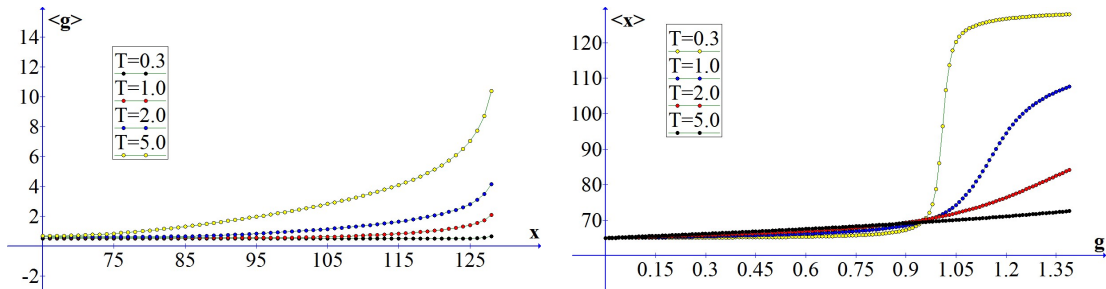


Figure 2.10: Isotherm in (a) fixed distance ensemble (b) fixed force ensemble for a soft wall, for a polymer of length  $N=64$  at  $\epsilon = -1.0$  for a Motzkin path

polymer and wall at the site of application of force at a temperature  $T$ , is calculated by taking the finite difference of exact free energies as  $g$  is increased in steps of  $\Delta g = 0.001$ .

The results bears resemblance. The  $\langle g \rangle$  Vs  $x$  isotherms in Fig. 2.9(a) and Fig. 2.10(a) signals the same coexistence between the average force and the temperature  $T$  for a polymer of length  $N=64$  as shown in Fig. 2.3(a) and Fig. 2.4(a) The average force, here again increases with decrease in temperature  $T$ . However, this is true for only *hard-wall*. For the *soft-wall*, the force increases as the temperature increases. The same happens when studying the dependence of  $T$  on the average separation between the wall and polymer,  $\langle x \rangle$ , for a polymer of length  $N=64$  when the applied force is increased in steps of  $\Delta g = 0.001$ . The Fig. 2.9(b) and Fig. 2.10(b) increases more significantly when compared to the plot in Fig. 2.3(b) and

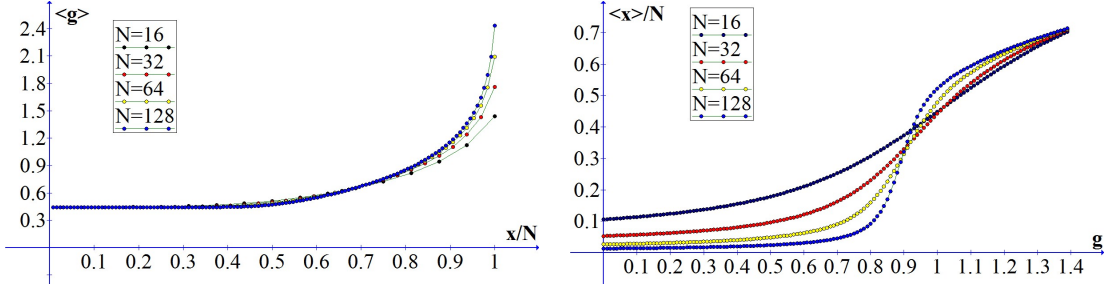


Figure 2.11: (a)  $\langle g \rangle$  Vs  $x/N$  and (b)  $\langle x \rangle / N$  Vs  $g$  isotherms at  $T = 1.0$  for various length of polymers for a hard wall following a Motzkin path

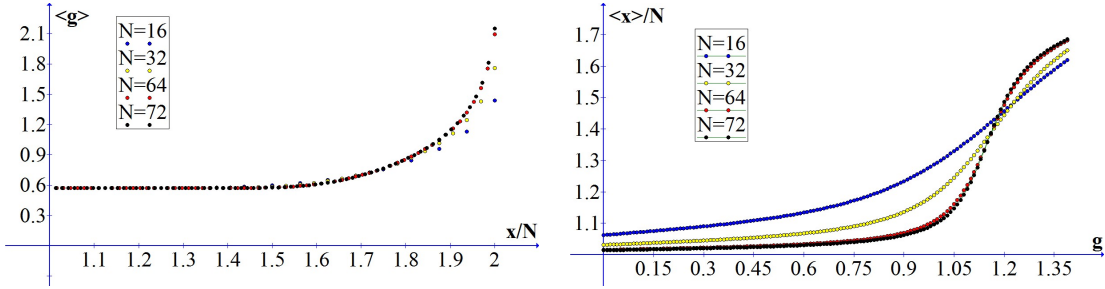


Figure 2.12: (a)  $\langle g \rangle$  Vs  $x/N$  and (b)  $\langle x \rangle / N$  Vs  $g$  isotherms at  $T = 1.0$  for various length of polymers for a soft wall following a Motzkin path

Fig 2.4(b); but the nature of the curve remains same. For small temperatures. the average separation is proportional to  $N$ , once the applied force  $g$  is above the critical force; however for large value of temperature  $T$ , it is due to finite size effects.

The resemblance in the nature of the curve continues in the  $x/N$  Vs  $\langle g \rangle$  and  $\langle x \rangle / N$  Vs  $g$  isotherms at  $T = 1.0$  for various length of polymers, for both soft wall and hard wall. The scaled separation between the polymer and the wall,  $x/N$ , versus the corresponding average force, for both soft wall and hard wall are shown in Fig. 2.11(a) and Fig. 2.12(a) respectively; whereas the  $\langle x \rangle / N$  Vs  $g$  isotherms for the polymer of various length at  $T = 1.0$ , for a hard wall is shown in Fig. 2.11(b); for a soft wall in Fig. 2.12(b) The absorption-desorption transition takes place in the phase diagram Fig. 2.11(b) and Fig. 2.12(b), if the pulling force exceeds a critical value, with  $\langle x \rangle / N$  proportional to the length of polymer  $N$ .

## 2.3 Conclusion

In this chapter we studied the unzipping and adsorption-desorption transition of an adsorbed polymer in  $D = 1 + 1$  dimensions for both Motzkin and Dyck path. We have obtained the exact phase diagrams for both hard and soft walls with uniform affinities on either sides of the wall. We studied the unzipping transition of an adsorbed polymer by pulling one end of the polymer by a force keeping the other end anchored. Some of the important results we have found are:

- An adsorbed polymer unzips from the wall, if the pulling force exceeds a critical value which is dependent on the temperature.
- The unzipping and the adsorption-desorption transition for both Dyck and Motzkin path shows striking resemblance. Therefore, many features of the latter can be understood(qualitatively) by studying the transition of the Dyck path and vice versa.
- The resemblance clearly indicates that the number of configuration in the recursion relation has no role to play in the qualitative nature of isotherms.
- The exact formulation through the language of generating function resembles with the isotherms drawn through exact transfer matrix technique for both Dyck and Motzkin path.

# Appendix A

In Chap.3, we set up recursion relation for the partition function which can be used to study the unzipping transition of an adsorbed polymer for a Dyck path. We stated the recursion relation for the pure case can be solved exactly using the generating function technique. In this appendix we give the details of its calculations.

## A.1 Phase Boundary

As stated in sec 3.3, we consider the general case by assuming a uniform potential at each lattice points on either side of the wall. The recursion relation in the presence of potential is:

**Soft Wall**

$$Z_{N+1}(x) = \begin{cases} [Z_N(x+1) + Z_N(x-1)] & \text{for } x < 0 \\ [Z_N(x+1) + Z_N(x-1)] & \text{for } x > 0 \\ [Z_N(+1) + Z_N(-1)]e^{\beta\epsilon} & \text{for } x = 0 \end{cases} \quad (\text{A.1})$$

**Hard Wall**

$$Z_{N+1}(x) = \begin{cases} [Z_N(x+1) + Z_N(x-1)] & \text{for } x > 0 \\ [Z_N(+1) + Z_N(-1)]e^{\beta\epsilon} & \text{for } x = 0 \end{cases} \quad (\text{A.2})$$

with the initial condition  $Z_0(x) = e^{\beta\epsilon}\delta_{x,0}$ . The partition function for the above recursion relation is:

$$G(z, x) = \sum_N z^N Z_N(x) \quad (\text{A.3})$$

which can be taken in the form of (ansatz)

$$G(z, x) = \begin{cases} \lambda^x A & \text{for } x > 0 \\ \lambda^{-x} A & \text{for } x < 0 \end{cases} \quad (\text{A.4})$$

with  $\lambda$  and  $A$  to be determined. The convergence test tells us that the singularity closest to origin (on the positive real axis) in the complex  $z$ - plane determines the partition function for  $N \rightarrow \infty$  [19]. For finite  $N$ , using contour integration around the singularities yield the recursion relation  $Z_N$ .

Using the ansatz equation, we get  
for soft wall

$$\begin{aligned} \frac{\lambda^x}{z} &= [\lambda^{x+1} + \lambda^{x-1}] & \text{for } x > 0 \\ \frac{\lambda^{-x}}{z} &= [\lambda^{-x-1} + \lambda^{-x+1}] & \text{for } x < 0 \\ \frac{A}{z} &= [2\lambda A + \frac{1}{z}]e^{\beta\epsilon} & \text{for } x = 0 \end{aligned} \quad (\text{A.5})$$

and for hard wall

$$\begin{aligned} \frac{\lambda^x}{z} &= [\lambda^{x+1} + \lambda^{x-1}] & \text{for } x > 0 \\ \frac{A}{z} &= [\lambda A + \frac{1}{z}]e^{\beta\epsilon} & \text{for } x = 0 \end{aligned} \quad (\text{A.6})$$

from which one obtains

**Soft Wall**

$$\lambda = \frac{1 - \sqrt{1 - 4z^2}}{2z} \quad (\text{A.7})$$

$$A = \frac{e^{\beta\epsilon}}{1 - 2\lambda z e^{\beta\epsilon}} \quad (\text{A.8})$$

**Hard Wall**

$$\lambda = \frac{1 - \sqrt{1 - 4z^2}}{2z} \quad (\text{A.9})$$

$$A = \frac{e^{\beta\epsilon}}{1 - \lambda z e^{\beta\epsilon}} \quad (\text{A.10})$$

The singularities coming from  $\lambda$  is

$$z_1 = \frac{1}{2} \quad (\text{A.11})$$



A has the singularity

$$z_2(\beta\epsilon) = \begin{cases} \frac{1}{2}\sqrt{1 - (1 - \exp(-\beta\epsilon))^2} & \text{for soft-wall} \\ \frac{1}{2}\sqrt{1 - (1 - 2\exp(-\beta\epsilon))^2} & \text{for hard-wall} \end{cases} \quad (\text{A.12})$$

### Fixed Distance Ensemble

In the fixed distance ensemble, the relevant quantity  $Z_N(x)$  for  $N \rightarrow 0$  can be determined using the contour integration [3]

$$Z_N(x) = \frac{1}{2\pi i} \oint \frac{\lambda^x(z)A(z)}{z^{N+1}} dz \quad (\text{A.13})$$

where the integration is over a contour around origin. This can be distorted to contours around  $z_2$  and  $z_1$ , with the leading contribution coming from the contour around  $z_2$ . For the large length  $N$  we get

$$Z_N(x) \sim \frac{\lambda^x(z_2)}{z_2^{N+1}}, \quad (x > 0) \quad (\text{A.14})$$

with the free energy

$$\beta F(x) = N \log z_2 - x \log \lambda(z_2) \quad (\text{A.15})$$

The force required to maintain the distance  $x$  is given by  $g = 2\frac{\partial F}{\partial x}$ . A factor of 2 is needed as per our definition of unit length as the diagonal of a unit square. The phase boundary is then given by

$$g_c(T) = -2T \log \lambda(z_2) \quad (\text{A.16})$$

or,

$$g_c(T) = \begin{cases} T \log [2e^{\beta\epsilon} - 1] & \text{for soft-wall,} \\ T \log [e^{\beta\epsilon} - 1] & \text{for hard-wall.} \end{cases} \quad (\text{A.17})$$

### Fixed Force Ensemble

In the fixed force ensemble, apart from the above mentioned singularities, an addition force dependent singularity,

$$z_3 = \frac{e^{\beta g}}{e^{2\beta g} + 1} = \frac{1}{2 \cosh(\beta g)} \quad (\text{A.18})$$

comes from the generating function

$$\mathcal{G}(z, g) = \sum_{N=0}^{\infty} z^N \sum_x Z_N(x) e^{\beta g x} \quad (\text{A.19})$$

The phase boundary in the fixed force ensemble comes from equating the leading singularity above  $z_2$  with  $z_3$  ( $z_2 = z_3$ ). It is

$$g_c(T) = \begin{cases} 2T \cosh^{-1}[(\sqrt{1 - (1 - \frac{1}{e^{\beta \epsilon}})^2})^{-1}] & \text{for soft-wall,} \\ 2T \cosh^{-1}[(\sqrt{1 - (1 - \frac{2}{e^{\beta \epsilon}})^2})^{-1}] & \text{for hard-wall.} \end{cases} \quad (\text{A.20})$$

# Appendix B

In this appendix, we'll give the details of calculations for a exact solution for unzipping transition of an adsorbed polymer for a Motzkin path. The attempt is similar as above - through the language of generating function.

## B.1 Phase Boundary

As stated in the above appendix, the assumption are same, a uniform potential at each lattice points on either side of the wall. The recursion relation in the presence of potential is:

**Soft Wall**

$$Z_{N+1}(x) = \begin{cases} [Z_N(x+1) + Z_N(x) + Z_N(x-1)] & \text{for } x < 0 \\ [Z_N(x+1) + Z_N(x) + Z_N(x-1)] & \text{for } x > 0 \\ [Z_N(+1) + Z_N(0) + Z_N(-1)]e^{\beta\epsilon} & \text{for } x = 0 \end{cases} \quad (\text{B.1})$$

**Hard Wall**

$$Z_{N+1}(x) = \begin{cases} [Z_N(x+1) + Z_N(x) + Z_N(x-1)] & \text{for } x > 0 \\ [Z_N(+1) + Z_N(0) + Z_N(-1)]e^{\beta\epsilon} & \text{for } x = 0 \end{cases} \quad (\text{B.2})$$

with the initial condition  $Z_0(x) = e^{\beta\epsilon}\delta_{x,0}$ . The partition function for the above recursion relation then can be given as:

$$G(z, x) = \sum_N z^N Z_N(x) \quad (\text{B.3})$$

which can be taken in the form of (ansatz)

$$G(z, x) = \begin{cases} \lambda^x A & \text{for } x > 0 \\ \lambda^{-x} A & \text{for } x < 0 \\ A & \text{for } x = 0 \end{cases} \quad (\text{B.4})$$

with  $\lambda$  and  $A$  to be determined. We know the singularity closest to origin (on the positive real axis) in the complex  $z$ - plane determines the partition function for  $N \rightarrow \infty$ .

Using the ansatz equation, we get

for soft wall

$$\begin{aligned} \frac{\lambda^{-x}}{z} &= [\lambda^{-x-1} + \lambda^{-x} + \lambda^{-x+1}] & \text{for } x < 0 \\ \frac{\lambda^x}{z} &= [\lambda^{x+1} + \lambda^x + \lambda^{x-1}] & \text{for } x > 0 \\ \frac{A}{z} &= [(2\lambda + 1)A + \frac{1}{z}]e^{\beta\epsilon} & \text{for } x = 0 \end{aligned} \quad (\text{B.5})$$

for hard wall

$$\begin{aligned} \frac{\lambda^x}{z} &= [\lambda^{x+1} + \lambda^x + \lambda^{x-1}] & \text{for } x > 0 \\ \frac{A}{z} &= [(\lambda + 1)A + \frac{1}{z}]e^{\beta\epsilon} & \text{for } x = 0 \end{aligned} \quad (\text{B.6})$$

from which one obtains

**Soft Wall**

$$\lambda(z) = \frac{(1-z) - \sqrt{(1+z)(1-3z)}}{2z} \quad (\text{B.7})$$

$$A(z) = \frac{e^{\beta\epsilon}}{1 - (2\lambda + 1)ze^{\beta\epsilon}} \quad (\text{B.8})$$

**Hard Wall**

$$\lambda(z) = \frac{(1-z) - \sqrt{(1+z)(1-3z)}}{2z} \quad (\text{B.9})$$

$$A(z) = \frac{e^{\beta\epsilon}}{1 - (\lambda + 1)ze^{\beta\epsilon}} \quad (\text{B.10})$$

The singularities coming from  $\lambda$  is

$$z_1 = \frac{1}{3} \quad (\text{B.11})$$

A has the singularity

$$z_2(\beta\epsilon) = \begin{cases} \frac{1}{3} \left[ e^{-2\beta\epsilon} \sqrt{e^{2\beta\epsilon}(-3 + e^{\beta\epsilon}(6 + e^{\beta\epsilon}) - 1)} - 1 \right] & \text{for soft-wall} \\ \frac{1}{2e^{\beta\epsilon}} \left[ \sqrt{(e^{\beta\epsilon} - 1)(e^{\beta\epsilon} + 3)} - (e^{\beta\epsilon} - 1) \right] & \text{for hard-wall} \end{cases} \quad (\text{B.12})$$

### Fixed Distance Ensemble

In the fixed distance ensemble, using contour integration, one can calculate the relevant  $Z_N(x)$  for  $N \rightarrow 0$

$$Z_N(x) = \frac{1}{2\pi i} \oint \frac{\lambda^x(z)A(z)}{z^{N+1}} dz \quad (\text{B.13})$$

where the integration is over a contour around origin. However, the integration could be influenced by the contribution made by the leading singularity which is coming out from  $z_x$ . Therefore, as above

The phase boundary is then given by

$$g_c(T) = -2T \log \lambda(z_2) \quad (\text{B.14})$$

with  $\lambda$  given by Eq. B.7 and  $z_2$  given by Eq. B.12

### Fixed Force Ensemble

In the fixed force ensemble, the addition force dependent singularity, arises from the generating function

$$\mathcal{G}(z, g) = \sum_{N=0}^{\infty} z^N \sum_x Z_N(x) e^{\beta g x} \quad (\text{B.15})$$

is:

$$z_3 = \frac{e^{\beta g}}{e^{2\beta g} + e^{\beta g} + 1} = \frac{1}{2 \cosh(\beta g) + 1} \quad (\text{B.16})$$

The phase boundary in the fixed force ensemble comes from equating the leading singularity above  $z_2$  with  $z_3$  ( $z_3 = z_3$ ). It is

$$g_c(T) = T \cosh^{-1} \left[ \frac{1}{2} \left( \frac{1}{z_2(\beta\epsilon)} - 1 \right) \right], \quad (\text{B.17})$$

where  $z_2(\beta\epsilon)$  for both the softwall and the hardwall cases are given by the above equation Eq. B.12.

# Appendix C

In this appendix we show the numerical procedure to calculate the generating function of the Dyck Path studied above.

## Dyck Path

Let  $D_t(x)$  denote the partition function for a Dyck path in a fixed distance ensemble. At a given inverse temperature  $\beta$  ( $\beta = \frac{1}{k_B T}$ ), where  $k_B$  is the Boltzmann constant, which we choose as  $k_B=1$ , the partition function follows the recursion:

$$D_{t+1}(x) = \sum_{j=\pm 1} D_t(x)[1 + (e^{\beta\epsilon} - 1)\delta_{x,0}] \quad (\text{C.1})$$

In order to obtain the partition function for a polymer of length  $N$ , we have to iterate the above expression with an initial condition  $D_0(0) = 1.0$

One may note that in the expression of the partition function, there is a term  $e^{\beta\epsilon}$  which grows exponentially, which allows the partition function to grow exponentially as well. At low temperature, the partition can easily flow over the upper limit ( $10^{\pm 300}$ ) [19] of the floating point representation. Hereby, the partition function of only short chain polymer can be exactly solved at a low temperature.

In the following codes, we have calculated the quantity of interest in a fixed distance and fixed force ensemble for both soft and hard wall. In this case, the quantity of interest is the average distance from the wall and the average force required.

# Code A

-----  
This program calculates the quantities of interest in a fixed force and fixed distance ensemble for a soft wall as discussed in Chap. 3  
-----

```
#include <math.h>
#include <stdio.h>
#include <stdlib.h>

#define N 2
#define T 1.0
#define EPS -1.0

int main ( )
{
    double beta, Z[N+1][2*N+3] , g ,xavg, xavg2, P[2*N+1] , Ztot;
    int x, t;
    beta = 1./T;
    for (t = 0; t <=N; t++){
    for (x = 0; x <=2*N+2; x++)
    Z[t][x] = 0.0;
    }
```

-----  
Recursion relation for a Soft Wall  
-----

```
Z[0][N+1] = 1.0;
for (t=1; t <= N; t++) {
for (x = -t; x <= t; x += 2)
    Z[t][x+N+1] = Z[t-1][x+N] + Z[t-1][x+N+2] ;
```

```
Z[t][N+1] *= exp(-beta * EPS);
}
```

```
-----
Isotherm in Fixed distance ensemble
-----
```

```
printf("# Isotherm Fixed distance ensemble\n");
for (x=1; x<=2*N-1; x+=2) {
printf("%d\t%lf\n", x, - 0.5* T* (log(Z[N][x+2]) - log(Z[N][x])));
}
```

```
-----
Fixed force ensemble
-----
```

```
printf("\n\n");
printf("# Isotherm Fixed force ensemble\n");

for (g = 0.0; g <= 1.4; g+= 0.01) {

Ztot = 0.0;
for (x=1; x<=2*N+1; x+=2)
Ztot += Z[N][x] * exp( beta * g * x);

for (x=1; x<=2*N+1; x+=2)
P[x] = Z[N][x] * exp( beta * g *x) / Ztot;

xavg=0.0; xavg2 = 0.0;
for (x=1; x<=2*N+1; x+=2){
xavg += x * P[x];
xavg2 += x * x * P[x];
}
printf ("%lf\t%lf\t%lf\n",g, xavg, xavg2);
}
```



```
return 0;
}
```

## Code B

-----  
This program calculates the quantities of interest in a fixed force and fixed distance ensemble for a Hard Wall as discussed in Chap. 3  
-----

```
#include <math.h>
#include <stdio.h>
#include <stdlib.h>

#define N 2
#define T 2.0
#define EPS -1.0

int main ( )
{
    double beta, Z[N+1][N+3], P[N+1], Ztot;
    double g, xavg, xavg2;
    int x, t;
    beta = 1./T;
    for (t = 0; t <= N; t++){
        for (x = 0; x <= N+2; x++)
            Z[t][x] = 0.0;
    }
}
```

---

Recursion relation for a Hard Wall

---

```
Z[0][1] = 1.0;
for (t=1; t <= N; t++) {
    for (x=1; x<=t+1; x++)
        Z[t][x] = Z[t-1][x-1] + Z[t-1][x+1] ;
```

```
Z[t][1] *= exp(-beta*EPS);
}
```

---

Fixed Distance ensemble

---

```
printf("# Isotherm Fixed distance ensemble\n");
```

```
if(N%2==0){
    for (x=1; x<=N-1; x+=2)
        printf("%d\t%lf\n", x, - 0.5* T* (log(Z[N][x+2]) - log(Z[N][x])));
}
else{
    for (x=2; x<=N-1; x+=2)
        printf("%d\t%lf\n", x, - 0.5* T* (log(Z[N][x+2]) - log(Z[N][x])));
}
```

---

Fixed force ensemble

---

```
printf("\n\n");
printf("# Isotherm Fixed force ensemble\n");
```

```
for (g = 0.0; g <= 1.4; g+= 0.01) {
```

```

Ztot = 0.0;
if(N%2==0)
{
    for (x=1; x<=N+1; x+=2)
        Ztot += Z[N][x] * exp( beta * g * x);
    }
    else
    {
        for (x=2; x<=N+1; x+=2)
            Ztot += Z[N][x] * exp( beta * g * x);
    }

    if(N%2==0)
    {
        for (x=1; x<=N+1; x+=2)
            P[x] = Z[N][x] * exp (beta * g *x) / Ztot;
    }
    else
    {
        for (x=2; x<=N+1; x+=2)
            P[x] = Z[N][x] * exp (beta * g *x) / Ztot;
    }

xavg=0.0; xavg2 = 0.0;
if(N%2==0)
{
    for (x=1; x<=N+1; x+=2){
xavg += x * P[x];
xavg2 += x * x * P[x];
    }
}
else
{
    for (x=2; x<=N+1; x+=2){

```

```
        xavg += x * P[x];
        xavg2 += x * x * P[x];
    }
}
printf ("%lf\t%lf\t%lf\n",g, xavg, xavg2);
}
return 0;
}
```

# Appendix D

In this appendix we show the numerical procedure to calculate the generating function of the Motzkin Path.

## Motzkin Path

Let  $M_t(x)$  denote the partition function for a Motzkin path in a fixed distance ensemble. However, unlike Dyck path, Motzkin path has iteration coming from  $\sum_{j=0,\pm 1} M_t(x)$ . As a consequence, at a given inverse temperature  $\beta$ , the partition function follows the recursion:

$$M_{t+1}(x) = \sum_{j=0,\pm 1} M_t(x)[1 + (e^{\beta\epsilon} - 1)\delta_{x,0}] \quad (\text{D.1})$$

In order to obtain the partition function for a polymer of length  $N$ , we have to iterate the above expression with an initial condition as given  $M_0(0) = 1.0$

The codes for Motzkin path follow the same procedure as for Dyck. However, the fundamental difference is in the number of configuration which accounts for  $3^N$  configurations in Motzkin path. The quantities of interest calculated are same as above.

# Code A

-----  
This program calculates the quantities of interest for a Hard Wall  
as discussed in Chap. 3  
-----

```
#include <math.h>
#include <stdio.h>
#include <stdlib.h>

#define N 128
#define T 2.0
#define EPSY -1.0

int main ( )
{
    double beta, M[N+1][N+3], P[N+1], Mtot;
    double g, xavg, xavg2;
    int x, t;
    beta = 1./T;

    for (t = 0; t <= N; t++){
        for (x = 0; x <= N+2; x++)
            M[t][x] = 0.0;
    }
```

-----  
Recursion relation  
-----

```
M[0][1] = 1.0;
```

```

for (t=1; t <= N; t++) {
for (x=0; x<=t; x++)
    M[t][x+1] = M[t-1][x] + M[t-1][x+2] + M[t-1][x+1];

M[t][1] *= exp(-beta*EPSY);
}

-----

Fixed distance Ensemble

-----

printf("# Isotherm Fixed distance ensemble\n");
for (x=1; x<=N; x++) {
    printf("%d\t%lf\n", x, - 0.5* T* (log(M[N][x+1])-log(M[N][x])));
}

-----

Fixed force Ensemble

-----

printf("\n\n");
printf("# Isotherm Fixed force ensemble\n");

for (g = 0.0; g <= 1.4; g+= 0.01) {

Mtot = 0.0;
for (x=1; x<=N+1; x++)
Mtot += M[N][x] * exp( beta * g * x);

for (x=1; x<=N+1; x++)
P[x] = M[N][x] * exp( beta * g *x) / Mtot;

xavg=0.0; xavg2 = 0.0;
for (x=1; x<=N+1; x++){

```

```

xavg += x * P[x];
xavg2 += x * x * P[x];
}
printf ("%lf\t%lf\t%lf\n",g, xavg, xavg2);
}
return 0;
}

```

## Code B

-----

This program calculates the quantities of interest for a Soft Wall  
as discussed in Chap. 3

-----

```

#include <math.h>
#include <stdio.h>
#include <stdlib.h>

#define N 3
#define T 1.0
#define EPSY -1.0

int main ( )
{
    double beta, M[N+1][2*N+3] , g ,xavg, xavg2, P[2*N+2] , Mtot;
    int x, t;
    beta = 1./T;
    for (t = 0; t <=N; t++){
    for (x = 0; x <=2*N+2; x++)
    M[t][x] = 0.0;
    }
}

```



---

Recursion relation

---

```
M[0][N+1] = 1.0;
for (t=1; t <= N; t++) {
    for (x = -t; x <= t; x ++ )
M[t][x+N+1] = M[t-1][x+N] + M[t-1][x+N+2] + M[t-1][x+N+1];
    M[t][N+1] *= exp(-beta * EPSY);
}
```

---

Fixed Distance Ensemble

---

```
printf("# Isotherm Fixed distance ensemble\n");
for (x=1; x<=2*N; x++) {
    printf("%d\t%lf\n", x, - 0.5* T*(log(M[N][x+1])-log(M[N][x])));
}
```

---

Fixed force Ensemble

---

```
printf("\n\n");
printf("# Isotherm Fixed force ensemble\n");

for (g = 0.0; g <= 1.4; g+= 0.01) {

Mtot = 0.0;
for (x=1; x<=2*N+1; x++)
Mtot += M[N][x] * exp( beta * g * x);

for (x=1; x<=2*N+1; x++)
```

```
P[x] = M[N][x] * exp (beta * g *x) / Mtot;

xavg=0.0; xavg2 = 0.0;
for (x=1; x<=2*N+1; x++){
xavg += x * P[x];
xavg2 += x * x * P[x];
}
printf ("%lf\t%lf\t%lf\n",g, xavg, xavg2);
}
return 0;
}
```

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