ABSTRACT

Since the invention of synthetic polymers (e.g., plastic), polymeric materials have brought ease to a great extent in everyday life. Various applications of polymers encourage scientists to study the configurational properties and dynamics of polymers under different physical conditions. The polymer is a long chain molecule with repetitive units called a 'monomer.' The functionality of the monomers (number of reactive ends) classify the structure of the polymer. Polymers from living organisms are known as biopolymers, such as DNA (Deoxyribonucleic Acid), RNA (Ribonucleic Acid), Protein, etc. The cells have a very crowded environment because they are composed of different biomolecules that may occupy a large fraction of the total volume. This leads to the phenomenon called volume exclusion which is caused by the steric repulsion among different molecules. The confinement that arises due to this may influence the stability, dynamics, and function of biomolecules. In the context of polymer physics, confinement reduces a large number of configurations of biopolymers. Hence, there is a reduction in entropy which influences the free energy of the biopolymers. There is another contribution to the free energy arising due to attractive interaction among non-bonded nearest monomers. The polymeric system usually equilibrates at a constant temperature to minimize its free energy. However, change in temperature or solvent quality may lead biopolymer to change its states from coil or swollen to globule or collapsed state. The emphasis of this present thesis is to study the loss in configurational entropy and gain in free energy on different biological processes.

Chapter 1 deals with a brief literature survey on the biopolymers under confinement environments. This includes varying pore shapes in living organisms such as Mycobacterium Smegtatis Porin A (MSPA), Nuclear

Pore Complex (NPC), Viral capsid, etc. We highlight some significant issues associated with the confinement of biopolymers. The second part of this chapter consists of modeling polymers and biopolymers and techniques (Exact Enumeration and Monte Carlo simulation) required to calculate the physical observables in the framework of statistical mechanics.

In Chapter 2, we study the migration of the polymer chain across an entropic trap in quasi-equilibrium condition and explore the effect of solvent gradient present in the entropic trap which acts both parallel and perpendicular to the direction of migration. The Fokker-Planck formalism utilizes the free energy landscape of polymer chain across the channel in presence of entropic trap to calculate the migration time. It is revealed that the migration is fast when the solvent gradient acts along the migration axis (say, *x-axis*) inside the channel in compare to the channel having entropic trap. We also study for the first time that the entropic trap makes the migration faster at certain value of solvent gradient. We also study the effect of transverse solvent gradient (along *y-axis*) inside the trap and investigate the structural changes of the polymer during migration though the channel. We observe the non-monotonic dependence of migration time on the solvent gradient.

Chapter 3 deals with force induced unzipping of a dsDNA (double stranded DNA) by applying force on a single strand (while other strand is free) in presence of an attractive surface. Manipulation of force on pulled strand, surface attraction energy and temperature reveal various phases of dsDNA. We report that at low surface attraction dsDNA desorbs as zipped form and melts in bulk at higher temperature. While at high surface attraction dsDNA unzips from the surface itself below melting temperature. Noteworthy finding includes that at moderate surface attraction the desorbed but zipped dsDNA melts with increasing temperature and the free strand gets adsorbed to the surface.

The separation of two strands of dsDNA may be induced either by changing the temperature (DNA melting) or the pH value of the solvent (DNA denaturation). In chapter 4, we study the DNA melting and translo-

cation of a biopolymer (*cis*-side to *trans*-side) across a cone-shaped channel. The shape of MSPA protein pore looks like a cone-shaped channel. Motivated by this, we model the system on a square lattice in such a way that its 3/4 volume corresponds to the *trans*-side, and the remaining 1/4 volume is of *cis*-side. We study the melting profile of dsDNA across the pore, which differentiates two different kinds of solvents. If solvent across the pore remains the same, the dsDNA prefers to stay in the trans side for all temperatures due to the large configurational entropy of the dsDNA available on the trans side. When the *cis*-side contains poor solvent, we observe that the DNA prefers to stay on the trans side with relatively poor solvent.

Chapter 5 deals with the equilibrium properties of a dsDNA confined in a strip. One side of the strip contains a relatively poor solvent compare to another side. This induces a solvent interaction gradient which may be thought of as a temperature gradient. This allows us to model DNA thermophoresis, where DNA migrates from the hot side and gets accumulated near the cold side. We employed a simple lattice model of polymer to show that dsDNA transfers to the cold side in a zipped form at a particular solvent interaction gradient. We have also studied the effect of sequence (AT-rich, GC-rich, AT-GC diblock DNA) under varying solvent interaction gradients. We observed that GC-rich DNA migrated faster to the colder side in comparison to the AT-rich sequence.

In chapter 6, we summarize the overall results of the thesis and comment on the future perspective of our studies.