

Chapter 1

Introduction: Polymers, Membranes and Motors

1.1 A Brief History of Polymer Science

During the course of evolution of human civilization, humans have used different kinds of materials for diverse purposes. Humans have used naturally occurring polymers without realizing their “polymeric” nature; one such polymeric substance is natural rubber that comes from the rubber plant.

In the middle of the nineteenth century, chemists started synthesizing polymeric substances but a proper understanding of the molecular structure was lacking. In 1920, Staudinger [1, 2] proposed that polymers are molecules consisting of repetitive elementary units called “monomers” that are held by covalent bonds. Thereafter, our understanding of the chemical and the physical properties of polymers has developed and this has led to synthesis and applications of a large variety of polymeric substances. While there was a rapid development of the methods of polymer synthesis, most of our understanding of the physics of polymers also developed during this period (1930 - 1960). Kuhn, Flory, Huggins, Stockmayer and others developed the theories describing macromolecular sizes, self-avoidance and excluded volume effects, thermodynamics of mixing, polymer solutions etc. Rouse and Zimm developed the theories of the dynamics of single molecules[3].

Subsequently (1960 - 80) S.F. Edwards, de Gennes, des Cloizeaux and others developed the modern principles of polymer physics - the model of the polymer chain and its confining

tube, the theory of semidilute solutions and the reptation theory. Today, polymer physics is a vast body of knowledge with challenging open problems both at the theoretical and the experimental ends.

1.2 Synthetic and Natural Polymers

Different polymeric substances that find use in everyday life (eg. polyethylene, polypropylene, PVC, polystyrene) are being synthesized in the laboratory and synthetic polymers today form the basis of a burgeoning industry. The first completely synthetic polymer was *bakelite*[1] which was synthesized in 1909 by Leo Baekeland and finds extensive use in making casings of electrical appliances, kitchenware, toys and many other items where its electrical and thermally insulating properties are being used. Often, natural polymers are suitably modified for commercial use, one of the most popular examples being vulcanized rubber prepared from natural rubber. Paper is manufactured from cellulose which is a naturally occurring polymer. Many polymers occur in nature - polysaccharides (sugar polymers) and polypeptides like silk [4]. Another important class of natural polymers are biopolymers - DNA, RNA, Actin etc.[5]; these polymers are vital to different structures and processes related to life. For example, Actin, which is a semiflexible polymer, is a component of the cytoskeleton that gives rigidity to the cell. DNA, which carries the genetic code, also is a semiflexible polymer. A typical human DNA strand is about a metre long; the packaging of such a long molecule within the micron-sized nucleus of a cell is a mystery that raises questions about the elastic properties of DNA. Recently single molecule experiments have been performed to study such properties. We shall describe such experiments in the next chapter.

1.3 Theoretical Models: an overview

Several theoretical models have been proposed to capture different features of the polymers that have been observed experimentally. There have been efforts to explore the implications of these theoretical models and to conduct experiments to test them. A computer simulation, which is like a controlled experiment, is another valuable tool to fathom the merits and de-

merits of the theoretical models. Below we summarize the essential features of the proposed theoretical models [2, 6] -

(a) Freely Jointed Chain (FJC): The FJC consists of units each of which is a vector \vec{r}_i of length l ; each of these units can point in any directions in space and two consecutive units are uncorrelated. A conformation of the **FJC** is represented by a set of $(N + 1)$ position vectors $\{\vec{R}_i\}$ of the joints or equivalently by the set of N bond vectors $\{\vec{r}_i\}$ where $\vec{r}_j = \vec{R}_j - \vec{R}_{j-1}$. The end-to-end vector $\vec{R} = \sum_{i=1}^N \vec{r}_i$ and $\langle \vec{r}_i \cdot \vec{r}_j \rangle = 0$ if $i \neq j$. The total length of the polymer is $L = Nl$. Let us now find out how R , the magnitude of \vec{R} , and L are related; for a perfectly rigid rod we would have $R \sim L$. For the FJC we have

$$\langle R^2 \rangle = \sum_{i=1}^N \langle \vec{r}_i \cdot \vec{r}_i \rangle + \sum_{i \neq j} \langle \vec{r}_i \cdot \vec{r}_j \rangle = Nl^2 = Ll \quad (1.1)$$

We note two things about the above relation -

- i.** $\langle R^2 \rangle \sim N$ and
- ii.** If $l = L$, we recover the result for the rigid limit ie. $\langle R^2 \rangle \sim L^2$.

Normally in a solution, the polymer would assume a coiled configuration and stretching it requires work to be done on the polymer; we want to find out the force required to fix one end of the polymer at a distance R when the other end is fixed at the origin. We need to find the free energy F as a function of R , N and T . The required force is

$$f = \frac{\partial F}{\partial R} \quad (1.2)$$

The free energy is $F = -K_B T \log Z$ where $Z = \sum \exp -\beta H$ is the partition function; the sum is over all configurations that have end-to-end distance R . In case of the FJC, all configurations have the same energy which can be set to be equal to zero and then the partition function turns out to be $Z = \sum 1 = \Omega(R, N)$ where $\Omega(R, N)$ is the number of configurations with the end-to-end distance equal to R . If C_N is the total number of allowed configurations, then the probability that a chain with N units ends at \vec{R} is $P(R, N) = \frac{\Omega(R, N)}{C_N}$. The details of the evaluation of $\Omega(R, N)$ can be found in references[2, 3, 6]; we state the final result and discuss

it. For small extensions ($R/L \ll 1$), one gets[6]-

$$F = \frac{3K_B T R^2}{2Nl^2} - K_B T \log C_N \quad (1.3)$$

The force \vec{f} required to hold the free end at \vec{R} is

$$f = (3K_B T/Nl^2) \cdot R \quad (1.4)$$

If f and R denote the moduli of \vec{f} and \vec{R} respectively, then we have

$$f = (3K_B T/l) \cdot e \quad (1.5)$$

where e is the relative extension. If the extension is small, we have a Hookean relation with a spring-constant $k = 3K_B T/l$. It requires a force to stretch the chain though all the configurations of the chain have the same energy. This force is purely *entropic* in nature.

Till now we have discussed the situation where we are in the *constant extension* ensemble; however, the situation can change if we go to the *constant force* ensemble. Consider a 3-D freely jointed chain; a force f is applied along some arbitrary direction which we choose to call the z-axis. The partition function in this case is

$$Z = \sum_{all\ states} \exp[fR_z/K_B T] \quad (1.6)$$

This can be written as

$$Z = \int \exp\left[\frac{f}{K_B T} \cdot \sum_{i=1}^N l \cos \theta_i\right] \prod_{i=1}^N \sin \theta_i d\theta_i d\phi_i \quad (1.7)$$

The integration can easily be carried out[2] and we get

$$Z = [4\pi \sinh[fl/K_B T]/(fl/K_B T)]^N \quad (1.8)$$

In this case we have

$$\langle R \rangle / L = \coth[fl/K_B T] - 1/(fl/K_B T) \quad (1.9)$$

Note the limiting cases-

- i. $\langle R \rangle / L = fl/3K_B T$ for small f
- ii. $\langle R \rangle / L = 1 - K_B T/fl$ for large f

Note that the small force result is the same as obtained earlier.

Besides the force-extension relation, another expression of interest is the distribution of the end-to-end vector. Let $\Phi(\vec{R}, N)$ be the probability distribution that the end-to-end vector of a freely jointed chain is \vec{R} . Now, for the **FJC**, the distribution function for a conformation can be written as

$$\Psi(\{\vec{r}_i\}) = \prod_{i=1}^N \psi(\vec{r}_i) \quad (1.10)$$

where the random distribution of the vector \vec{r}_i of length l is given by

$$\psi(\vec{r}_i) = (1/4\pi l^2) \delta(|\vec{r}_i| - l) \quad (1.11)$$

So, we have

$$\Phi(\vec{R}, N) = \left(\prod_{i=1}^N \int d\vec{r}_i \right) \delta(\vec{R} - \sum_{i=1}^N \vec{r}_i) \Psi(\{\vec{r}_i\}) \quad (1.12)$$

Expressing the delta function as an integral, we get

$$\Phi(\vec{R}, N) = (1/2\pi)^3 \int d\vec{k} \left(\prod_{i=1}^N \int d\vec{r}_i \right) \Psi(\{\vec{r}_i\}) \exp(i\vec{k} \cdot (\vec{R} - \sum_{i=1}^N \vec{r}_i)) \quad (1.13)$$

Using the form of $\Psi(\{\vec{r}_i\})$, we get for the **FJC**

$$\Phi(\vec{R}, N) = (1/2\pi)^3 \int d\vec{k} \exp i\vec{k} \cdot \vec{R} \left[\int d\vec{r} \psi(\vec{r}) \exp(-i\vec{k} \cdot \vec{r}) \right]^N \quad (1.14)$$

The integral can be easily evaluated [3] and the result is

$$\Phi(\vec{R}, N) = (1/2\pi)^3 \int d\vec{k} \exp i\vec{k} \cdot \vec{R} \left[\frac{\sin kl}{kl} \right]^N \quad (1.15)$$

In the limit of large N , the last term in the integrand can be approximated by $\exp(-Nk^2 l^2/6)$ and finally we get

$$\Phi(\vec{R}, N) = (3/2\pi N l^2)^{3/2} \exp(-3R^2/2Nl^2) \quad (1.16)$$

Note that there is one thing that is unrealistic about the above distribution function- there is a small but still finite probability for conformations in which $|\vec{R}|$ exceeds Nl , the total length of the chain.

In the above discussions, the effect of self-avoidance has been ignored; Flory showed that if self-avoidance[2, 6] is taken into account, then in d -dimensions we have the following relation-

$$R \sim N^{3/(d+2)} \quad (1.17)$$

If $d = 3$, we have $R = N^{3/5}$ as opposed to an ideal chain for which $R = N^{1/2}$. Including self avoidance effects leads to a “swelling” of the polymer as expected.

(b) The Gaussian Chain:

In case of the Gaussian chain, the distribution of the bond length is Gaussian -

$$\psi(\vec{r}_i) = (3/2\pi l^2)^{3/2} \exp(-3r^2/2l^2) \quad (1.18)$$

The conformational distribution is given by

$$\Psi(\{\vec{r}_i\}) = \prod_{i=1}^N (3/2\pi l^2)^{3/2} \exp(-3r_i^2/2l^2) \quad (1.19)$$

which can be expressed as follows:

$$\Psi(\{\vec{r}_i\}) = (3/2\pi l^2)^{3N/2} \exp[-\sum_{i=1}^N 3(\vec{R}_i - \vec{R}_{i-1})^2/2l^2] \quad (1.20)$$

The Gaussian chain is often represented as a chain with $(N + 1)$ beads connected by a harmonic spring whose potential energy is $U_0(\{\vec{R}_i\}) = (3/2l^2)K_b T \sum_{i=1}^N (\vec{R}_i - \vec{R}_{i-1})^2$ [3].

(c) The Worm Like Chain:

In the WLC model, the polymer is modelled as a framed space curve of fixed total length L with an energy cost for bending and twisting. A configuration C of the polymer is described by a space curve $\vec{x}(s)$, with s the arc-length parameter ($0 \leq s \leq L$) ranging from 0 to L , the contour length of the polymer. The tangent vector $\hat{t} = d\vec{x}/ds$ to the curve is a unit vector $\hat{t} \cdot \hat{t} = 1$ and the curvature of the polymer is given by $\kappa = |d\hat{t}/ds|$. We shall study the exact solution to the WLC model in the next chapter; here we end with an interesting observation

regarding the mean square distance $\langle R^2 \rangle$ of a polymer in the WLC model. It can be shown that the [2, 6, 7]

$$\langle R^2 \rangle = 2L_p L - 2L_p^2 (1 - \exp(-L/L_p)) \quad (1.21)$$

where L_p is the persistence length of the polymer. For $L \gg L_p$, we get $\langle R^2 \rangle = lL = Nl^2$ where N is the number of monomers which is the flexible limit and for $L \ll L_p$, $\langle R^2 \rangle = L^2$ which is the rigid limit. We end with this preliminary description of the WLC model as we shall encounter more details of the model several times in the following sections.

1.4 Single Molecule Experiments

Micromanipulation techniques are now so sophisticated that experimenters can stretch and twist single DNA molecules to probe their elastic properties under a torsional constraint. In a typical experiment [8], one end of a single molecule of double stranded DNA is attached to a glass plate and the other to a magnetic bead. The glass plate is kept fixed and the bead is pulled by magnetic field gradients and rotated by magnetic fields. By such techniques the molecule is stretched and twisted by hundreds of turns and the extension of the molecule is measured as a function of the number of turns applied to the bead for a fixed force [8]. Another experiment measures the torque-twist relation at fixed force [9] using a slightly different experimental technique. The length of the DNA molecule is typically about $20 \mu m$, its thickness $2 nm$ and the bead is about $4.5 \mu m$ in diameter. In practice, this size of bead is adequate to prevent the molecule from untwisting by looping around the bead [10]. A typical experimental plot is shown in Ref. [8]. These curves are easy to understand qualitatively: as one twists the molecule, its extension progressively decreases as one can guess by playing with a cord or ribbon. Further twisting leads to buckling and the formation of twisted braids or “plectonemes” which are familiar on telephone cords. Electron micrographs [11] of DNA show branched polymeric structures which indicate the formation of plectonemes.

1.5 The Pure Bend WLC Model

In the last chapter we had briefly mentioned the basic features of the WLC model; this is the most popular model till now. However, it has one drawback in modelling real polymers - it neglects self-avoidance. Marko and Siggia had theoretically studied the flexible limit of very long polymers (long compared to the persistence length; $L \gg L_p$)[12]. An exact solution of the Worm-Like Chain (WLC) model for semi-flexible polymers valid over *the entire range of polymer lengths* had been developed by Joseph Samuel and Supurna Sinha in Ref.[13]. We shall discuss their treatment in some detail because a numerical scheme developed in this reference will be used later in studying stiff polymers analytically(chapter 2). The solution presented here is exact in the sense that the elastic properties can be determined to any desired accuracy.

Recall the features of the WLC model with pure bend - A configuration C of the polymer is described by a space curve $\vec{x}(s)$, with s the arc-length parameter ($0 \leq s \leq L$) ranging from 0 to L , the contour length of the polymer. The tangent vector $\hat{t} = d\vec{x}/ds$ to the curve is a unit vector $\hat{t} \cdot \hat{t} = 1$ (the inextensibility constraint) and the curvature of the polymer is given by $\kappa = |d\hat{t}/ds|$. Let one end of the polymer be tethered to the origin ($\vec{x}(0) = 0$) and the other end $\vec{x}(L) = \vec{r}$ be tagged. As the polymer configuration changes with thermal agitation, the location \vec{r} of its tagged end fluctuates. Let $Q(\vec{r})$ be the probability distribution for the location \vec{r} of the tagged end. If the tagged end is pulled from \vec{r} to $\vec{r} + d\vec{r}$, $Q(\vec{r})$ changes and consequently, the free energy. This implies that a force is needed to stretch the polymer. Thus $Q(\vec{r})$ is directly related to the force-extension relation of the polymer. To compute $Q(\vec{r})$ we need to sum over all polymer configurations C which end at \vec{r} , with a Boltzmann weight: $Z = \sum_C \exp(-\mathcal{E}[C]/k_B T)$, where the energy \mathcal{E} associated with a configuration C is $\mathcal{E}(C) = \frac{1}{2}A \int_0^L ds \kappa^2$ and A is the *bending modulus*. This is a standard counting problem in statistical mechanics and can be naturally addressed in the language of path integration[14]. However, the difficulties posed by the inextensibility constraint make the problem hard. The key to circumventing this difficulty is to consider [12, 15] Brownian motion in the space

of *tangent vectors* (\hat{t}) rather than (as is customary for flexible polymers) position vectors \vec{x} . The tangent vectors form a unit sphere and the problem reduces to studying Brownian motion on the unit sphere, which can be handled by standard operator techniques familiar from quantum mechanics.

Let us suppose to begin with that the initial ($\hat{t}_A = \frac{d\vec{x}}{ds}|_{s=0}$) and final ($\hat{t}_B = \frac{d\vec{x}}{ds}|_{s=L}$) tangent vectors are held fixed. $Q(\vec{r})$ has the path integral representation

$$\mathcal{N} \int \mathcal{D}[\hat{t}(s)] e^{-1/k_B T [A/2 \int_0^L (d\hat{t}/ds)^2 ds]} \delta^3(\vec{r} - \int_0^L \hat{t} ds) \quad (1.22)$$

where \mathcal{N} is a normalization constant. Instead of $Q(\vec{r})$ consider the quantity $P(z) = \int d\vec{r} Q(\vec{r}) \delta(r_3 - z)$, which is $Q(\vec{r})$ integrated over a plane of constant z . Note that $P(z)$ and $Q(\vec{r})$ vanish when the modulus of their arguments exceeds L . The generating function of $P(z)$ is defined as $\tilde{P}(f) = \int_{-L}^L dz e^{fz/L_p} P(z)$, where $L_p = A/k_B T$. Performing the elementary integrations involving δ - functions one finds that $\tilde{P}(f)$ can be expressed as $Z(f)/Z(0)$, where $Z(f)$ has the path integral representation

$$Z(f) = \mathcal{N} \int \mathcal{D}[\hat{t}(s)] e^{-L_p/2 [\int_0^L (d\hat{t}/ds)^2 ds]} e^{[f/L_p \int_0^L \hat{t}_z ds]} \quad (1.23)$$

Making the change of variable $\tau = s/L_p$, one arrives at the expression

$$Z(f) = \mathcal{N} \int \mathcal{D}[\hat{t}(\tau)] e^{-\int_0^\beta d\tau [1/2 (d\hat{t}/d\tau)^2 - f \hat{t}_z]} \quad (1.24)$$

where $\beta = L/L_p$. The equation can be interpreted as the path integral representation for the kernel of a *quantum* particle on the surface of a sphere at inverse temperature β . Thus one can express $Z(f)$ as the quantum amplitude to go from an initial tangent vector \hat{t}_A to a final tangent vector \hat{t}_B in imaginary time β in the presence of an external potential $-f \cos \theta$:

$$Z(f) = \sum_n e^{-[\beta E_n]} \psi_n^*(\hat{t}_A) \psi_n(\hat{t}_B). \quad (1.25)$$

Here $\{\psi_n(\hat{t})\}$, is a complete set of normalized eigenstates of the Hamiltonian $\hat{H} = -\frac{\nabla^2}{2} - f \cos \theta$ and E_n are the corresponding eigenvalues.

For free boundary conditions $Z(f)$ can be written as a “vacuum persistence amplitude”:

$$Z(f) = \langle 0 | \exp -\beta H_f | 0 \rangle \quad (1.26)$$

where $H_f = -\frac{1}{2}\nabla^2 - f \cos \theta$ is the Hamiltonian of the rigid rotor [12] in a potential and $|0\rangle$ is the ground state of the free Hamiltonian $H_0 = -\frac{1}{2}\nabla^2$. By choosing a basis in which H_0 is diagonal one finds that H is a symmetric tridiagonal matrix with diagonal elements $H_{ll} = l(l+1)/2$ and superdiagonal elements $H_{l,l+1} = f(l+1) \sqrt{1/((2l+1)(2l+3))}$. Upto this point the treatment is completely analytical. To evaluate the partition function, numerical methods are required. H_f is really an infinite matrix, but it is truncated it to $N \times N$ size, numerically evaluated (using Mathematica[16]) and the cutoff N is adjusted until the answer stabilizes to desired accuracy. From this all the properties of the model can be deduced, to an accuracy limited only by computational power. A property of direct experimental interest is the force-extension relation. In the constant f ensemble, the scaled mean extension $\bar{\zeta}(f)$ (defined by $\bar{\zeta} = -\partial G(f)/\partial f$) has been plotted in Fig.(1.1). Since the system under investigation has finite size, it is expected that the extension ζ will fluctuate about its mean value $\bar{\zeta}$. The theoretically expected root mean square value of these fluctuations $\Delta\zeta = \sqrt{1/\beta\partial\bar{\zeta}/\partial f}$ of ζ is shown in Fig. (1.1). These fluctuations clearly vanish in the limit of infinitely long polymers [12]. Ref. [13] presents a numerical solution to the WLC, which, given the power of modern personal computers is as useful as an exact analytic form. Using the techniques outlined in this paper one could work out the predictions of the WLC model to any desired accuracy, for example, experimental accuracy. The authors have presented force-extension curves for *all* lengths which can be tested against experiments. In this paper free boundary conditions for the tangent vectors have been used. Other boundary conditions can also be handled as explained in [17]. The boundary conditions depend on the particular experimental setup. Choice of theoretical weights consistent with experimental boundary conditions is particularly crucial in the context of short polymers as we shall see in chapter 2. The authors of ref.[13] have presented other results also like the distribution of the scaled extension but we shall be mainly concerned with the force-extension relation.

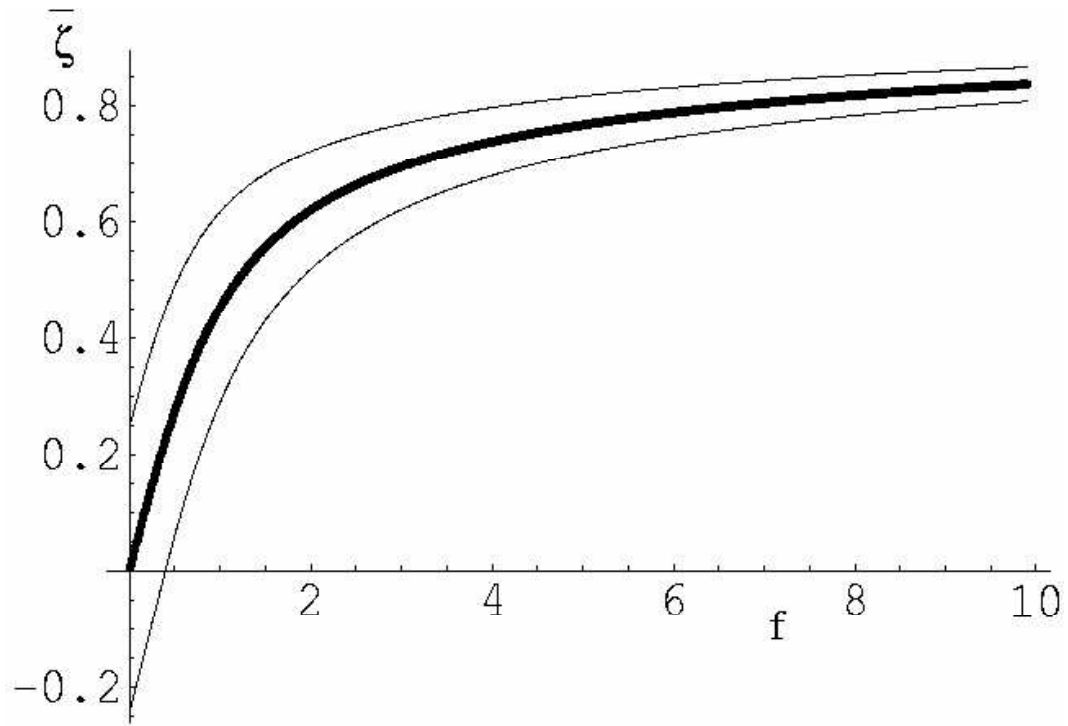


Figure 1.1: The mean extension as a function of the force (thick line) for $\beta = 10$; also shown on either side are the root mean square fluctuations (thin lines) of the extension about its mean value

1.6 The WLC Model With Twist

The above treatment can be extended to include the twist degrees of freedom as well. Such an extension is required to theoretically model *twist storing polymers* and interpret the results of experiments in which the elastic properties of such polymers are studied with torsional constraints. a theoretical model of twist storing polymers has been developed [18, 19]; the authors have derived the *hat curves* - plots of the extension of a twist storing polymer against the applied torque (to which we shall return in greater detail later in this chapter).

The polymer is modelled as an elastic rod which explores different configurations because of thermal fluctuations. Each configuration is associated with a twisting and bending energy and is statistically weighted accordingly. In the presence of torsional constraints, the twist and bending of the polymer backbone get coupled; the origin of this coupling lies in

Fuller's theorem[20, 21]:

$$Lk = Tw + Wr$$

Twist (Tw) is the winding of one edge of the polymer about the polymer backbone and involves local crossings when a projection of the polymer configuration on a plane is considered. Writhe involves the crossing of one part of the polymer with another and involves non-local crossings in the projected view [22].

One of the most important examples of twist storing polymers is DNA. DNA has a double helix structure; the monomers of DNA are joined by many covalent bonds that inhibit release of torsional stress by unwinding. In Ref.([19]) Moroz and Nelson have added chiral corrections to their calculations in view of the intrinsic helical nature of DNA. We shall ignore such corrections and describe the DNA strand under experimental investigation as a fluctuating elastic rod of uniform cross-section. Self-avoidance effects have also been neglected. Another aspect of DNA elasticity that has not been addressed is the sequence dependence.

The Elastic Energy of the Rod-Like Chain: A conformation of a continuous elastic thin rod can be described by a moving frame $\{\hat{e}_i(s)\} = \{\hat{u}(s), \hat{n}(s), \hat{t}(s)\}$ where s is the arc-length along the backbone curve of the rod, \hat{t} is the tangent vector to the backbone, \hat{u} is perpendicular to the tangent vector and $\hat{n} = \hat{t} \times \hat{u}$. The evolution of the frame along the rod is obtained by applying a rotation $\mathcal{R}(s)$ to a reference frame $\{\hat{e}_i^o\}$ attached to a rectilinear unstressed molecule. The rotation $\mathcal{R}(s)$ is expressed in terms of the Euler angles $\theta(s)$, $\phi(s)$ and $\psi(s)$. The moving frame is obtained from the reference frame as $\hat{e}_i(s) = \mathcal{R}(s) \cdot \hat{e}_i^o$. The evolution of the frame along the polymer is given by

$$d\hat{e}_i(s)/ds = \mathbf{\Omega}(s) \times \hat{e}_i(s) \quad (1.27)$$

The components of $\mathbf{\Omega}(s)$ are obtained as $\Omega_i = \mathbf{\Omega}(s) \cdot \hat{e}_i(s)$; $\hat{e}_1 = \hat{u}$, $\hat{e}_2 = \hat{n}$ and $\hat{e}_3 = \hat{t}$. In terms of the Euler angles, the components of $\mathbf{\Omega}$ can be shown to satisfy [18, 19]

$$\Omega_3 = \dot{\phi} \cos \theta + \dot{\psi} \quad (1.28)$$

$$\Omega_1^2 + \Omega_2^2 = (\dot{\phi} \sin \theta)^2 + (\dot{\theta})^2 \quad (1.29)$$

The stretched RLC energy can be written as

$$E_{RLC}/k_B T = \int_0^L ds (\mathcal{E}_b + \mathcal{E}_t + \mathcal{E}_s) \quad (1.30)$$

The bend, twist and stretch energy densities are given by

$$\mathcal{E}_b = (A/2)(\Omega_1^2 + \Omega_2^2) = (A/2)(d\hat{t}/ds)^2 = (A/2)((\dot{\phi} \sin \theta)^2 + (\dot{\theta})^2) \quad (1.31)$$

$$\mathcal{E}_t = (C/2)\Omega_3^2 = (C/2)(\dot{\phi} \cos \theta + \dot{\psi})^2 \quad (1.32)$$

$$\mathcal{E}_s = -F \cos \theta / k_B T \quad (1.33)$$

where the dot denotes derivative with respect to s . The symbols A and C denote the bending and the twist rigidities respectively and the bending and twist energies appear like the kinetic energies of a symmetric top, A and C being moments of inertia. However, for reasons that we discuss later, the problem at hand has a “twist” that makes things complicated! Eq. (1.33) gives the potential energy associated with the uniform stretching force applied along the free end of the molecule in a direction that we choose to call the z-axis. The rod is also subject to a torsional constraint which can be imposed either as a constant torque τ or as a constant link Lk ; in the limit of very long polymers, both ensembles give the same result [23]. We note that Lk denotes the excess link, that of an unstressed straight polymer being zero.

The connection with the quantum theory of a symmetric top- For given values of the Euler angles at $s = 0$ and at $s = L$ the partition function of the RLC model can be expressed as the following path integral:

$$Z(\theta_1, \phi_1, \psi_1 | \theta_0, \phi_0, \psi_0) = \int \mathcal{D}(\theta, \phi, \psi) \exp(-E_{RLC}/k_B T) \quad (1.34)$$

If we perform an analytic extension towards the imaginary s-axis, the elastic energy E_{RLC} becomes $-i \int_{t_0}^{t_1} dt \mathcal{L}(t)$, where we set $k_B T = 1$ and $s = -it$. The Lagrangian is that of a symmetric top in a static electric field f : $\mathcal{L} = \frac{1}{2} \sum_1^3 I_i \Omega_i^2 + f \cos \theta$ where $f = F/k_B T$; here the

moments of inertia $I_1 = I_2 = A$ and $I_3 = C$. The analytically continued partition function is then identified with the Feynman amplitude -

$$\langle \theta_1, \phi_1, \psi_1, t_1 | \theta_0, \phi_0, \psi_0, t_0 \rangle = \int \mathcal{D}(\theta, \phi, \psi) \exp(i \int_{t_0}^{t_1} dt \mathcal{L}(t)) \quad (1.35)$$

The right hand side of the last equation can be written as

$$\langle \theta_1, \phi_1, \psi_1, t_1 | \exp(-i(t_1 - t_0)\hat{\mathcal{H}}_{top} | \theta_0, \phi_0, \psi_0, t_0 \rangle$$

where $\hat{\mathcal{H}}_{top}$ denotes the Hamiltonian for a symmetric top expressed as a second order differential operator acting on the wave function with the Euler angles as its arguments. Now letting $i(t_1 - t_0) \rightarrow s_1 - s_0$, we get the partition function as a Quantum Mechanics matrix element; we set $\hbar = c = 1$ for convenience.

We introduce a complete set of eigenfunctions of the Hamiltonian to express the partition function as -

$$Z(\theta_1, \phi_1, \psi_1 | \theta_0, \phi_0, \psi_0) = \sum_n \exp(-L/AE_n) \Psi_n(\theta_1, \phi_1, \psi_1) \Psi_n^*(\theta_0, \phi_0, \psi_0) \quad (1.36)$$

The difference between the RLC model problem and the Quantum Mechanical problem of a symmetric top becomes clear when we consider the function space on which the differential operator for the Hamiltonian acts - *in the symmetric top problem, the functions of relevance are the ones that are periodic functions of the Euler angles ϕ and ψ with a period of 2π but in the RLC problem, the functions cannot be periodic functions of the Euler angles ϕ and ψ because the two states of the polymer described by ϕ and ψ and $(\phi + 2\pi)$ and $(\psi + 2\pi)$ differ by unit link and cannot be the same!* A simple suggestive case has been discussed in Ref([18]).

The torsional constraint- The torsional constraint can be expressed either as a constant torque [19] or as a constant supercoiling angle [18]; in the limit of extremely long polymers, both the ensembles are expected to give the same results. To impose the constraint however, we would like to express the imposed/resulting link (depending on the ensemble) as a local integral. Mezard and Bouchiat assume that the Euler angles are smooth functions of s and

express the total supercoiling angle as

$$\chi = \int_0^L ds(\psi + \phi) \quad (1.37)$$

Using Fuller's theorem, the total link can be expressed as a sum of twist and writhe. The twist can be expressed as a simple local integral [21] -

$$T_w = \frac{1}{2\pi} \int_0^L \Omega_3 ds \quad (1.38)$$

The writhe, however, turns out to be a more complicated object and is given by a double integral [20, 21]; however, there is a simpler result due to Fuller which allows the writhe of a space curve to be expressed, with respect to that of a reference curve, as a local formula. In this sense it is not really writhe but a change of writhe. Considering the case where the reference curve is the \hat{e}_3^0 axis, the "local" writhe formula allows the writhe to be expressed in terms of the Euler angles as [18]

$$\chi_w = \int_0^L \phi(1 - \cos \theta) ds \quad (1.39)$$

As we shall see later, this result holds if the conformations counted in the partition function can be reached by smooth deformations of the straight reference curve without self-intersections and such that the tangent vectors to the reference curve and the curve describing a particular polymer conformation never point in opposite directions. This formulation involves some surprising subtleties that we shall address in chapter 3. Mezard and Bouchiat have expressed the above as $\int d\phi A_\phi = \oint \vec{A}_m(\vec{r}) \cdot d\vec{r}$ where $\vec{A}_m(\vec{r})$ is the vector potential of a magnetic monopole of charge unity. The magnetic vector potential has been expressed as a local integral [18].

Expressing the delta function for the fixed supercoiling angle constraint in a Fourier representation with B as the variable conjugate to χ , it is seen that in the generating function space, the Fourier transformed partition function can be expressed as a product of the Fourier transformed writhe partition function and the Fourier transformed Twist partition function, the latter being simply a Gaussian term. The writhe partition function Fourier transform turns

out to be a path integral over θ and ϕ with effective energy $E_{WLC}/K_B T + iB\chi_w$. By doing an analytic continuation along the same lines as described earlier, one finally obtains the Fourier transformed writhe partition function as the action integral of a unit charge moving on the unit sphere under the joint action of an electric field f and a magnetic monopole of charge B .

We shall be studying the statistical physics of stiff polymers in the next chapter and shall be considering a limiting case of the above treatment. To set the stage for chapter 3, we mention that from the writhe partition function, Mezard and Bouchiat calculate the writhe fluctuations and encounter a divergence. They approach this problem by introducing a new intermediate-length cutoff into the problem. They show that such a cutoff provides a repulsive potential to prevent the “particle” from visiting the south pole or equivalently, the tangent vector to swing south at which the “local writhe” formula due to Fuller would break down. However the physical origin of this cutoff is not very well understood.

Mezard and Bouchiat have also presented an analytical treatment for the WLRC model subject to torsional constraints [18]. They have addressed the problem in the constant torque ensemble and have obtained the average extension and average link as a function of the applied forces and torques. They have carried out a perturbative analysis about the straight unstressed configuration. There is a long history of the use of path integrals in the study of polymers [3, 14]. Such methods have been used in the study of elasticity of semiflexible polymers [13, 24]. This connection between path integrals in quantum mechanics and statistical mechanics of polymers enables us to import ideas back and forth between these two distinct domains.

1.7 Membranes and Motors

Membranes: Membranes are a natural extension of polymers (which are one-dimensional objects) to two dimensions [25]. Because of the richness of two-dimensional geometry in comparison to that of one dimension, the study of random surfaces is far more complex than that of polymers. Examples of membranes in nature are not far to seek; one of the most im-

portant (and abundant) one being the cell membrane. Its importance in the biological world can hardly be overestimated - in fact it is usually the first topic to be discussed in any book on the study of cells. Flexible membranes are an important member of the enormous class of soft condensed matter systems, those which respond easily to external forces. Their physical properties are to a considerable extent dominated by the entropy of thermal fluctuations. One of the most widely studied examples is the membrane of a red blood cell. The cell membrane of a red blood cell is important for many vital life processes and a study of the elasticity properties of the RBC membrane offers new insights into their functioning and opens new vistas for applications of these insights. The cytoskeleton is a heterogeneous network of dynamic filamentous proteins like actin and Spectrin and it provides structural stability to the cells. Filamentary actin is a semiflexible polymer; an understanding of the elasticity of the network of such a semiflexible polymer offers new insights into the functioning of the cytoskeleton.

Motors: The study of molecular motors is vitally important for an understanding of the cellular processes[26, 27]. These are naturally occurring complex molecules called *motor proteins* which function like machines inside a cell; they perform important tasks like intracellular transport, participating in complex processes like cell division and cell locomotion. Collectively, such complex molecules perform important roles like facilitating bacterial swimming, producing forces by muscle contractions etc. The general principle of operation of the motor proteins is the conversion of chemical energy into mechanical energy through stochastic processes; the key feature is the coupling between the chemical and the mechanical degrees of freedom. Recent progress in optical techniques and other experimental techniques have made it possible to measure forces in the range of pico-Newtons and offer new insights into the functioning of the molecular machines. Besides biologists, physicists also have had a role to play in such studies. Some of the questions of interest to a physicist are the physical principles underlying the transformation of the chemical energy into mechanical energy, the coupling between the chemical and the mechanical cycles and the efficiency of the motors. The track along which the motors move within the cell are biopolymers formed of asymmetric units (monomers) and therefore are periodic and polar, properties that have an important

bearing on the motion of motors.

Bibliography

- [1] <http://en.wikipedia.org/wiki/Polymer>
- [2] M Rubinstein and R H Colby, *Polymer Physics*, Oxford University Press, New York 2003
- [3] M Doi and S F Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford 1986
- [4] Lon J Mathias, **Natural Polymers**, <http://www.pslc.ws/mactest/natupoly.htm>
- [5] Supurna Sinha, “Study Circle”, **1**, (2003); arxiv:physics/0308003 v1 1 Aug 2003
- [6] Abhishek Dhar, Personal Homepage, Lecture Notes: “On Random Walks and Polymers”, <http://www.rri.res.in/dabhi/>
- [7] Randall D. Kamien, *Rev. Mod. Phys.*, **74** 953-971 (2002)
- [8] Strick, T.R., Allemand, J.-F., Bensimon, D., Bensimon, A., Croquette, V., *Science* **271**, 1835 (1996).
- [9] Z. Bryant et al., *Nature* **424**, 338 (2003).
- [10] V. Rossetto and A. C. Maggs, *Phys. Rev. Lett.* **88**, 089801-1 (2002). A. C. Maggs and V. Rossetto, *Phys. Rev. Lett.* **87**, 253901 (2001); V. Rossetto and A. C. Maggs, *J. Chem. Phys.* **118**, 8864 (2003)
- [11] H. B. Gray, W. B. Upholt, J. Vinograd, *J. Mol. Biol.* **62**, 1 (1971).
- [12] J. Marko and E. D. Siggia, *Macromolecules* **28**, 8759 (1995).

- [13] J. Samuel and S. Sinha, *Physical Review E*, **66** 050801(R) (2002)
- [14] L. S. Schulman, *Techniques and Applications of Path Integration*, (Wiley Interscience, 1981).
- [15] S. Sinha and J. Samuel, *Phys. Rev.* **B 50**, 13871 (1994).
- [16] Stephen Wolfram, *The Mathematica Book*, Third Edition (Wolfram Media/ Cambridge University Press, 1996).
- [17] M.M.G. Krishna, J. Samuel and S. Sinha, *J. Phys. A* **33**, 5965 (2000).
- [18] C. Bouchiat and M. Mezard, *Phys. Rev. Lett.* **80**, 1556 (1998)
- [19] Moroz J D and Nelson P, *Proc. Natl. Acad. Sci. USA* **94**, 14418 (1997).
- [20] G. Călugăreanu, *Czechoslovak Mathematical Journal* **11**, 588 (1961); See also J. H. White *Am. J. Math* **91**, 693 (1969).
- [21] F.B. Fuller, *Proc. Nat. Acad. Sci. USA* **68**, 815 (1971); *Proc. Nat. Acad. Sci. USA* **75**, 3557 (1978).
- [22] M. R. Dennis and J. H. Hannay, *Proceedings of the Royal Society A*, **461**, 2062, 3245 (2005); arXiv:math-ph/0503012 (2005).
- [23] S. Sinha and J. Samuel, *Physical Review E*, **71** 021104 (2005)
- [24] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics and Financial Markets*, (World scientific, Singapore, 2006, 4. ed.)
- [25] M. J. Bowick and A. Travesset, *Phys. Rept.* **344**, 255 (2001)
- [26] Erwin Frey, *CHEMPHYSICHEM* **3**, 270-275 (2002)
- [27] F. Jülicher, A. Adjari and J. Prost, *Rev. Mod. Phys.* **69**, 1269 (1997)