การดึงพอลิเมอร์ที่มีพันธะยืดหยุ่นชนิดกึ่งโค้งงอได้

นางสาว อรพิน เนียมพลอย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาฟิสิกส์ ภาควิชาฟิสิกส์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2547

ISBN 974-17-6214-3

STRETCHING OF SEMIFLEXIBLE POLYMER WITH ELASTIC BONDS

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Physics
Department of Physics
Faculty of Science
Chulalongkorn University
Academic year 2004
ISBN 974-17-6214-3

Thesis Title Stretching of Semiflexible Polymer with Elastic Bonds

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Field of Study Physics

Thesis Advisor Professor Virulh Sa-yakanit

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctor's Degree

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อรพิน เนียมพลอย : การดึงพอลิเมอร์ที่มีพันธะยืดหยุ่นชนิดกึ่งโค้งงอได้. (STRETCHING OF SEMIFLEXIBLE POLYMER WITH ELASTIC BONDS) อ. ที่ปรึกษา : ศ.ดร. วิรุฬห์ สายคณิต. 67หน้า. ISBN 974-17-6214-3.

โครงสร้างลูกโซ่ฮาร์โมนิคชนิดกึ่งโค้งงอได้ ที่มีพันธะซึ่งยืดขยายออกได้ถูกนำมาใช้ และถูกประยุกต์ใช้กับการดึงพอลิเมอร์ชนิดกึ่งโค้งงอได้ โครงสร้างลูกโซ่ฮาร์โมนิคชนิดกึ่งโค้งงอได้ที่นำมาศึกษานี้ได้รับผลมาจาก bending rigidity, การยืดขยายของพันธะ, โครงสร้างลูกโซ่แบบแยกส่วน และการจำกัดความยาวของพอลิเมอร์ชนิดกึ่งโค้งงอ เราได้ความสัมพันธ์ของแรงกับการยืดขยาย ในกรณีการดึงด้วยแรงอย่างแรงและอย่างอ่อน ในโครงสร้างลูกโซ่ฮาร์โมนิคชนิดกึ่งโค้งงอ โดยใช้วิธีการอินทิเกรทตามเส้นทาง ซึ่งประกอบด้วยผลของ พันธะที่ยืดขยาย, โครงสร้างลูกโซ่แบบแยกส่วน และความยาวที่จำกัดของเส้นพอลิเมอร์ นอกจากนี้วิธี Variationalและ Numerical transfer matrix ถูกใช้ในการหาความสัมพันธ์ของแรงกับการยืดขยาย

ภาควิชา...............ฟิสิกส์........................ ลายมือชื่อนิสิต..
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ปีการศึกษา ...... 2547......

4273853323 : MAJOR PHYSICS

KEY WORD: SEMIFLEXIBLE POLYMER/EXTENSION/STRECHING/PATH INTEGRAL/INEXTENSIBLE.

ORAPIN NIAMPLOY : STRETCHING OF SEMIFLEXIBLE POLYMER WITH ELASTIC BONDS. THESIS ADVISOR: PROFESSOR VIRULH SA-YAKANIT, 67 pp. ISBN 974-17-6214-3.

A semiflexible harmonic chain model with extensible bonds is introduced and applied to the stretching of semiflexible polymer. The semiflexible harmonic chain model allowed to study effect from bending rigidity, bond extension, discrete chain structure, and finite length of a semiflexible polymer. We derived the force-extension relations for strong and weak stretching in semiflexible harmonic chain model by using the path integration method which include the effects of extensible bonds, discrete chain structure and finite polymer length. The Variational and numerical transfer matrix method are used to find the force-extension relation.

Department............Physics...........................Student's signature...Orapin Niamploy....

Field of study...........Physics...........................Advisor's signature...Virulh Sa-yakanit...

Academic year ....2004..........

Contents

List of Figures

Acknowledgements

I wish to express my gratitude to Professor Dr. Virulh Sa-yakanit, my supervisor, who has generously provided the advice and the assistances. Also thanks Dr. Jan Kierfeld and Profressor Reinhard Lipowsky for their kindness and carefulness when I was in Golm, Germany.

Special thank must also go to my thesis committees: Assistant Profressor Pisistha Ratanavararak, Associate Profressor Anantasin Techagumpuch, Professor Orapin Rangsiman and Dr. Somchai Kiatgamolchai for their valuable suggestions and comments.

I wish to thank my friends and all colleagues; Mr. Porncharoen Palotaidamkerng, Dr. Varakorn Pipatchollatee, Dr. Santipong Boribarn, Mr. Sutee Boonchui and Mr. Uthai Pinmung.

Final support from Chulalongkorn university to me. Physics Department, Chulalongkorn university is acknowledged for allowing me absence for my study.

I wish to express my gratitude to my parents for their love and everything that they have done for me. Finally, special thank go to my husband, Major Thawatchai Wannadelok for his love, always encourages and provides me a lot of helps.

Chapter 1
Introduction

1.1 Polymer

The word "polymer" comes from Greek words, "poly" meaning many and "mer" meaning unit. Thus, the basis formula of each of polymer consists of a long chain of the monomeric units which bind together by chemical bonds; for example, Deoxyribonucleic acid(DNA) is composed of the nucleotides (sugar, base and phosphate group) with an accurately repeating pattern of nucleotides along the chain (Sugar-phosphate chain or S-P backbone) (see Fig 1.1). A protein is also a biopolymer which is composed of about 50 to thousand aminoacids (monomers) linked together by peptide bonds. The structure of protein in three dimensions is very important. That is the prediction of protein structure is not only of a pure theoretical interest in biophysics but also of great importance in drug design and the design of artificial protein based on genetic engineering.

In nature, polymer may be composed of hundreds or thousands of basic units. Some of them may have more than one simple unit, that is, it is repeated in an diatomic polymer (ABABABAB....), triatomic polymer (ABCABCABC.....) and so on. The size of polymer chain is introduced by the degree of polymerization (the number of basic unit that it is obtained). Most natural polymer are found in biopolymers; for example, a cell may contain hundreds of different many nucleic acids and proteins. We can find polymer everywhere: in our bodies (biopolymers) i.e., DNA, actin filament, microtubule and so on, in organic molecules and

Figure 1.1: Sketch of double helix. The sugar-phosphate backbone is shown by ribbons. The bases are shown by short transverse rods(Yakushevich (1998)).

plastics; for example, polyvinyl chloride (PVC), nylon, teflon, etc. Polymers have three important molecular structural types, i.e. the linear polymer, the branched polymer and the network polymer (see Fig 1.2).

1.2 The Model

In this thesis, we shall study the statistical properties of the polymers in the thermal equilibrium state. The simplest model of the flexible polymer is the freely jointed chain or random walk model (see Fig.1.3). It consists of N monomers separated by bond of fixed length b_0 and these bonds are free to rotate; i.e., the direction of end-to-end distance of each bond should be independent of the orientation of nearest neighbor bonds (see more details in Doi and Edwards (1986) and Bueche (1962)).

Since many polymeric molecules have internal stiffness, they are the semi-

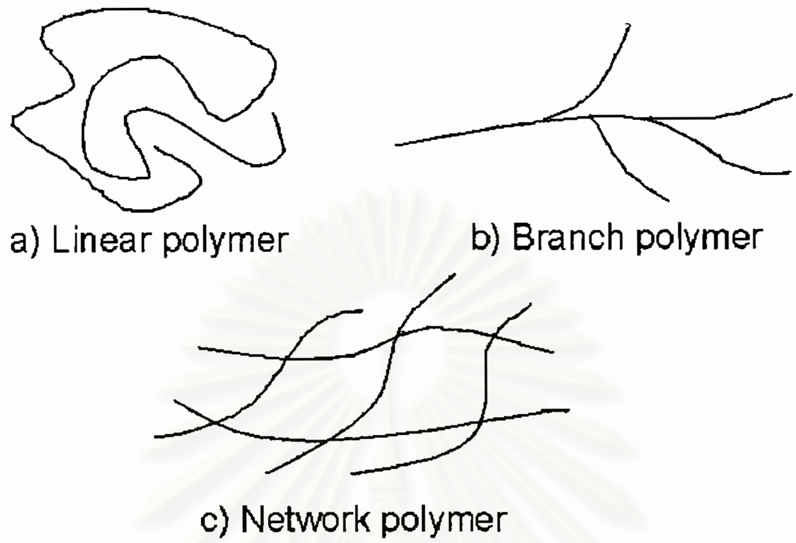

Figure 1.2: Three kinds of polymers; Linear, Branched and Network polymers

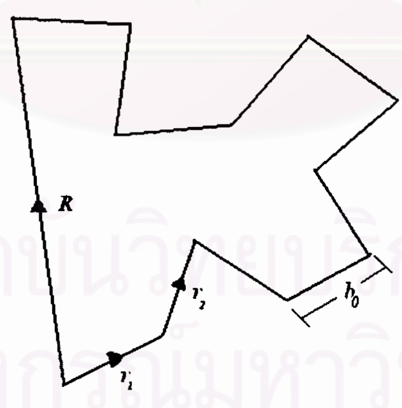

Figure 1.3: Freely jointed chain model.

flexible polymer. Then we cannot model them as freely jointed chains. The famous model that is successful in describing an inextensible polymer is the Kratky-Porod or the worm-like chain (WLC) model. In the past decades several scientists have tried to understand the elastic properties of the WLC because they are important in many basic life processes. Many stretching experiments on the single polymer chain want to find the relation between the external force and the extension of the chain, see more details in Bustamante et al. (1995), Smith et al. (1996), Odijk (1993) and Rief et al. (1998). The force-extension relation of an inextensible worm-like chain has been successful correspondingly with them. One method for handling the polymer problem is proposed by Marko and Siggia (1995). The main assumption of their work is that the polymer chain is very stiff so that the energy associated with the conformational fluctuations may be modelled by using merely linear elasticity of a thin, uniform rod, i.e., using the WLC and the self-interactions or the excluded volume effects will be ignored. In real polymers, long-range interactions such as steric effects, Van der Waals attraction and solvent molecules effect must be taken into account. Fortunately for the long-length interaction due to cancellation of different interactions the detail of the interaction can be omitted. Therefore the equilibrium features of stretched semiflexible polymer chain are determined by the interplay of the energies within the framework of canonical Boltzmann statistical mechanics $exp\left[-E/k_BT\right]$ (the probability for the system to have the energy E). Marko and Siggia (1995) used the variational and the numerical methods to solve the extension. They showed that for large force limit, the extension is proportional to $1/(f)^{1/2}$ and for small force limit, the extension is proportional to f where f is the applied force. In this thesis, we focus on the properties of the semiflexible polymer chains with extensible bonds (an extensible polymer) when an external force applied to one end of the chain and the excluded volume effects is ignored. We find that in the small force limit, the force-extension relation is proportional to f (linear behaviour).

The outline of this thesis is as follows: in chapter 2, we present necessary basic property of the chain. In chapters 3 and 4, we present the path integration and the variational method to solve the problem. The conclusion and discussion are given in the last chapter.

Chapter 2
The Basic Properties of Polymer Chains

2.1 Some Foundation of Statistical Mechanics

In this section, the thermal equilibrium state at the temperature T will be discussed; for more details see some standard text books: Feynman and Hibbs, 1995; Kleinert, 1995 and so on. In statistical mechanics, the probability of the system to have the energy E obviously correlates to the Maxwell-Boltzmann factor e^{-E/k_BT}, which depends on the temperature of the system, where k_B is the Boltzmann constant ($1.38054 \times 10^{-23}\text{JK}^{-1}$).

So to speak, the probability of finding the system in the particular state i of energy E can be written in form

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \tag{2.1}$$

where $\beta = \frac{1}{k_BT}$ and $\sum_i e^{-\beta E_i}$ is the sum extends over all states that the system can be. Let $\sum_i e^{-\beta E_i}$ be denoted by the letter Z (it comes from the German word "Zustandsumme"), the partition function. The probability distribution in Eq. (2.1) is known as the "canonical distribution."

The representative statistical ensemble of the system can be distributed over their states with the canonical distribution. For instance, the mean energy of the system is given by

$$\overline{E} = \frac{\sum_i e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} \tag{2.2}$$

where the summations are over all state of the system and we can write the mean energy in terms of the partition function, as

$$\begin{aligned}\overline{E} &= \frac{-\sum_i \frac{\partial e^{-\beta E_i}}{\partial \beta}}{\sum_i e^{-\beta E_i}} \\ &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial \ln Z}{\partial \beta}. \qquad (2.3)\end{aligned}$$

Consider the case in the quasi-static process. Let f_i be the external parameters of the system and then the energy of the system in state i is

$$E_i = E_i(f_1.......f_N). \qquad (2.4)$$

Hence, the energy will be changed when the values of the external parameters are changed. If they are changed by small values, $f_j \rightarrow f_j + df_j$, then the energy will change in quantity

$$d\overline{E_i} = \sum_j^N \frac{\partial \overline{E_i}}{\partial f_j} df_j. \qquad (2.5)$$

The work when the system is in the state i can be written as

$$dw_i = -d\overline{E_i} = \sum_j^N \overline{\xi_j} df_j \qquad (2.6)$$

where $\overline{\xi_j} \equiv -\frac{\partial \overline{E_i}}{\partial f_j}$ is the mean generalized force conjugate to the external parameter f_j in the state i.

In our system, we consider only a single external parameter f. Then the energy of the system in state i is changed by

$$\triangle E_i = \frac{\partial E_i}{\partial f} df \qquad (2.7)$$

then the work will be

$$\begin{aligned} dw &= \bar{\xi} df \\ &= -\overline{\frac{\partial E_i}{\partial f}} df \\ &= \frac{\sum_i e^{-\beta E_i}(-\frac{\partial E_i}{\partial f} df)}{\sum_i e^{-\beta E_i}}. \end{aligned} \tag{2.8}$$

Once again we can write the last equation in terms of the partition function Z, that is

$$\begin{aligned} dw &= \frac{\frac{1}{\beta}\frac{\partial \sum_i e^{-\beta E_i}}{\partial f} df}{Z} \\ &= \frac{1}{\beta Z}\frac{\partial Z}{\partial f} df \\ &= \frac{1}{\beta}\frac{\partial \ln Z}{\partial f} df. \end{aligned} \tag{2.9}$$

Thus, the work can be written in form of the product of a displacement multiplied by the force,

$$\overline{L} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial f} \tag{2.10}$$

In addition, the physical quantity of the system in thermal equilibrium at the temperature T can be derived from the partition function. Assume that, we are interested in the state of the system which is in a configuration space with a coordinate x and we want to know the probability of the system at the point x. Also, we know that the wave function of the system at state i is $\phi_i(x)$. We can write the average over all possible states or the probability of the system at the point x as

$$P(x) = \frac{1}{Z}\sum_i \phi_i^*(x)\phi_i(x)e^{-\beta E_i}. \tag{2.11}$$

In general, the average value or the expectation value of some function of x is given by

$$\begin{aligned}\langle f(x)\rangle &= \sum_i f(x)P(x)\\ &= \frac{1}{Z}\sum_i \int \phi_i^*(x)f(x)\phi_i(x)e^{-\beta E_i}dx. \end{aligned} \tag{2.12}$$

We can define a new function, the density matrix,

$$\rho(x',x) \equiv \sum_i \phi_i^*(x')\phi_i(x)e^{-\beta E_i}. \tag{2.13}$$

From the definition of the density matrix, we can rewrite the probability in Eq. (2.11) as

$$P(x) = \frac{1}{Z}\rho(x,x) \tag{2.14}$$

then the expection value $\langle f(x)\rangle$ will be

$$\begin{aligned}\langle f(x)\rangle &= \frac{1}{Z}\int f(x)\rho(x,x)dx\\ &= \frac{1}{Z}Tr(f\rho). \end{aligned} \tag{2.15}$$

The density matrix is an important quantity because we can find the thermodynamics quantity from it. By the way, the important physical quantity, the Helmholtz free energy F can written in term of $\ln Z$. We recall that the definition of the partition function is the function of β and coordinate q.

$$Z = Z(\beta,q). \tag{2.16}$$

For $\ln Z$, if there are some small changes in β and q, then

$$\begin{aligned} d\ln Z &= \frac{\partial \ln Z}{\partial \beta}d\beta + \frac{\partial \ln Z}{\partial q}dq\\ &= -\overline{E}d\beta + \beta dw. \end{aligned} \tag{2.17}$$

It's better that we write the first term in r.h.s. of Eq. (2.17) in terms of the change of $\overline{E}$, thus

$$d\ln Z = -d(\overline{E}\beta) + \beta d\overline{E} + \beta dw$$

$$\begin{aligned} d(\ln Z + \overline{E}\beta) &= \beta(dw + d\overline{E}) \\ &= \beta dQ, \end{aligned} \tag{2.18}$$

where Q is the heat. From the second law of thermodynamics, the increase in entropy of the system times temperature is equal to an infinitesimal amount of heat

$$TdS = dQ \tag{2.19}$$

Inserting this relation into Eq. (2.18),

$$\begin{aligned} d(\ln Z + \overline{E}\beta) &= \beta T dS = \frac{dS}{k_B} \\ k_B(\ln Z + \overline{E}\beta) &= S \\ k_B \ln Z + \frac{\overline{E}}{T} &= S \\ TS &= k_B T \ln Z + \overline{E} \end{aligned}$$

or

$$F \equiv \overline{E} - TS = -k_B T \ln Z. \tag{2.20}$$

That is, the Helmholtz free energy F can be expressed in terms of $\ln Z$.

2.2 The Relation between the Propagator and the Density Matrix

In quantum mechanics, the probability amplitude of having particle at the initial point x at time t and later at a final point x' at time t' is the probability amplitude

$K(x^{'},x)$, the propagator. It is the sum over all the amplitudes of each path that the particle can go from point x to point $x^{'}$. For the case of the particle starting at the begin point x, going to point $x^{''}$ and then going to the end point $x^{'}$, the amplitude of this event is the product of the amplitude of going from x to $x^{''}$ and the amplitude of going from $x^{''}$ to $x^{'}$or $K(x^{'},x) = \int_{x^{''}} K(x^{'},x^{''}) \cdot K(x^{''},x)dx^{''}$. Consider the system which is described by the amplitude wave function $\Psi(x,t)$, Let the initial and the final state of the system be $\Psi(x,t)$ and $\Psi(x^{'},t^{'})$ respectively. We can write the relation of the initial and the final states as

$$\Psi(x^{'},t^{'}) = \int K(x^{'},t^{'};x,t)\Psi(x,t)dx. \tag{2.21}$$

From the Schrödinger equation,

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = H^{'}\Psi(x,t) \tag{2.22}$$

where the Hamiltonian $H^{'} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,t)$. Let consider in the particular case, the time-independent Schrödinger equation (the potential does not depend on time) and then we can write the solution in form

$$\Psi(x,t) = f(t)\phi(x). \tag{2.23}$$

Inserting the solution into the Schrödinger equation, we will obtain two equations. The first equation is

$$i\hbar\frac{\partial f(t)}{\partial t} = Ef(t) \tag{2.24}$$

or we can write in another form as $f(t) = C\exp[-\frac{iEt}{\hbar}]$. The second one is

$$H\phi(x) = E\phi(x) \tag{2.25}$$

where the time-independent hamiltonian $H = -\frac{\hbar^2}{2m}\nabla^2 + V(x)$.

As we know, the general solution of the the time-dependent Schrödinger equation can be written in terms of the energy eigenfunctions as

$$\Psi(x,t) = \sum_n C_n^{'}(t)\phi_n(x). \tag{2.26}$$

$C_n^{'}(t)$ are the expansion coefficients that depend on time and we can find them by multiplying with the quantity $\phi_m^*(x)$ and integrating Eq. (2.26) over all x. Then we will get

$$\begin{aligned}\int \phi_m^*(x)\Psi(x,t)dx &= \sum_n C_n^{'}(t)\int \phi_m^*(x)\phi_n(x)dx \\ &= \sum_n C_n^{'}(t)\delta_{mn} \\ &= C_m^{'}(t). \end{aligned} \tag{2.27}$$

In the case of the time-independent Schrödinger equation, we can find the expansion coefficients $C_n(t)$ from the general solution of time-dependent Schrödinger equation, that is

$$\begin{aligned} i\hbar\frac{\partial\Psi(x,t)}{\partial t} &= H\Psi(x,t) \\ i\hbar\frac{\partial\sum_n C_n^{'}(t)\phi_n(x)}{\partial t} &= H\sum_n C_n^{'}(t)\phi_n(x) \\ &= \sum_n C_n^{'}(t)H\phi_n(x) \end{aligned}$$

From the eigenvalue equation of time-independent Schrödinger equation $H\phi_n(x) = E_n\phi_n(x)$. We will obtain

$$i\hbar\frac{\partial}{\partial t}\sum_n C_n^{'}(t)\phi_n(x) = \sum_n C_n^{'}(t)E_n\phi_n(x) \tag{2.28}$$

after that, multiply by $\phi_m^*(x)$ and integrate over all x

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\sum_n C_n^{'}(t)\int \phi_m^*(x)\phi_n(x)dx &= \sum_n C_n^{'}(t)E_n\int \phi_m^*(x)\phi_n(x)dx \\ i\hbar\frac{d}{dt}C_m^{'}(t) &= C_m^{'}(t)E_m. \end{aligned}$$

We will get

$$C_m'(t) = C_m(t_0)\exp[-iE_m(t-t_0)/\hbar]. \tag{2.29}$$

Putting this equation into Eq. (2.26), we obtain the general solution of the time-independent Schrödinger equation

$$\Psi(x,t) = \sum_m C_m(t_0)\exp[-iE_m(t-t_0)/\hbar]\phi_m(x) \tag{2.30}$$

we can find the expansion coefficients from

$$C_m(t_0) = \int \phi_m^*(x')\Psi(x',t_0)dx'. \tag{2.31}$$

Then Eq. (2.30) can be written in the form of

$$\begin{aligned}\Psi(x,t) &= \sum_m \int \phi_m^*(x')\Psi(x',t_0)dx' \exp[-iE_m(t-t_0)/\hbar]\phi_m(x) \\ &= \int \sum_m \phi_m^*(x')\phi_m(x)\exp[-iE_m(t-t_0)/\hbar]\Psi(x',t_0)dx' \end{aligned} \tag{2.32}$$

Comparing this equation with Eq. (2.21), we will get the propagator

$$K(x',t';x,t) = K(x',x,t'-t) = \sum_m \phi_m^*(x)\phi_m(x')\exp[-iE_m(t'-t)/\hbar] \tag{2.33}$$

In the previous section, we know that the system in thermal equilibrium at temperature T is described by the canonical density matrix. Let it be denoted by $\rho(x',x,\beta)$, i.e.,

$$\rho(x',x,\beta) = \sum_i \phi_i^*(x')\phi_i(x)e^{-\beta E_i}. \tag{2.34}$$

So we can see that, if we replace the time interval $t'-t$ in Eq. (2.33) by $-i\hbar\beta$, we will get the density matrix. Thus the relation between the density matrix and the propagator is

$$\rho(x',x,\beta) = K(x',x,-i\hbar\beta). \tag{2.35}$$

We can write the propagator in the path integral form

$$K(x',x,t'-t) = K(x',x,\tau) = \int_{x(0)}^{x(\tau)} \exp[\frac{i}{\hbar}S]D[x(t)] \tag{2.36}$$

where the action S is given by

$$S = \int_0^{\tau} L(\dot{x},x,t)dt \tag{2.37}$$

and L is the Lagrangian of the system, $L = T - V$. Then we can write the density matrix in form of path integral by replacing τ by $-i\hbar\beta$.

$$\begin{aligned} K(x',x,-i\hbar\beta) &= \int_{x(0)}^{x(-i\hbar\beta)} D[x(t)]\exp[\frac{i}{\hbar}\int_0^{-i\hbar\beta} L(\dot{x},x,t)dt] \\ &= -\int_{x(0)}^{x(\hbar\beta)} D[x(it)]\exp[\frac{-1}{\hbar}\int_0^{\hbar\beta} L'(\dot{x}',x,it)d(it)] \end{aligned} \tag{2.38}$$

where $L'(\dot{x}',x,it) = -\frac{m}{2}(\dot{x}')^2 - V(x,it)$, $\dot{x}' = \frac{dx}{d(it)} = \frac{1}{i}\frac{dx}{dt}$ and let it denoted by t', we will get

$$K(x',x,-i\hbar\beta) = \int_{x(0)}^{x(\hbar\beta)} D[x(t')]\exp[\frac{-1}{\hbar}\int_0^{\hbar\beta} L'd(t')] \tag{2.39}$$

where $L' = T + V$.

Finally, we obtain the density matrix

$$\rho(x',x,\beta) = \int_{x(0)}^{x(\hbar\beta)} D[x(t')]\exp[\frac{-S'}{\hbar}] \tag{2.40}$$

where the action S' is given by

$$S' = \int_0^{\tau} L'(\dot{x}',x,t')dt' \tag{2.41}$$

2.3 The Persistance Length of WLC

A semiflexible polymer is a polymer which bending costs energy and it has the bending rigidity κ. We parameterize the polymer by arc length s such that $|\mathrm{t}(s)| = |\partial_s \mathbf{r}(s)| = 1$. The tangent vector of the polymer $\mathrm{t}(s)$ is equal to $\partial_s \mathbf{r}(s)$; $\mathbf{r}(s)$ is a position vector on the chain. We can explicitly resolve the constraint $|\mathrm{t}(s)| = 1$ (for an inextensible polymer, there is no fluctuations in the length of the tangent vector) by introducing a tangent angle $\phi(s)$ (the simplest model is in two-dimensional plane)

$$\mathrm{t}(s) = \begin{pmatrix} \cos\phi(s) \\ \sin\phi(s) \end{pmatrix} = \cos\phi(s)\widehat{i} + \sin\phi(s)\widehat{j}. \tag{2.42}$$

Now we can calculate the tangent-tangent correlations from

$$\begin{aligned} \langle \mathrm{t}(s_1)\cdot \mathrm{t}(s_2)\rangle &= \langle \cos\phi(s_1)\cos\phi(s_2) + \sin\phi(s_1)\sin\phi(s_2)\rangle \\ &= \langle \cos(\phi(s_1)-\phi(s_2))\rangle = \exp(-\frac{1}{2}\left\langle (\phi(s_1)-\phi(s_2))^2\right\rangle) \\ &= \exp(-\frac{1}{2}\frac{k_BT}{\kappa}|s_1-s_2|) = \exp(-\frac{|s_1-s_2|}{L_p}). \end{aligned} \tag{2.43}$$

See more details in appendix A. We can introduce the persistance length $L_p = \frac{2\kappa}{k_BT}$. The persistance length is the correlation length for the tangent-tangent correlation. This means that the tangent direction become uncorrelated over distance bigger than L_p. Therefore L_p can also be intepreted as the length beyond which the polymer starts to crumple and behaves effectively like a fully flexible chain or, we can say, it is a quantity which measures the flexibility of polymers. In general we can write the tangent-tangent correlation functions of WLC, that is, $\langle \mathbf{t}(s_1)\cdot\mathbf{t}(s_2)\rangle \sim \exp(-\frac{(d-1)|s_1-s_2|}{L_p})$. Polymers in nature have very different persistance length, for instance, $L_p \approx 50$ nm for DNA (Bustamante., 1994), $L_p \approx 17$ μm for actin (Ott et al.,1993 and Janmey et al.) and $L_p \approx 5.2$ mm for microtubules.

On the other hand, the mean squared end-to-end distance of the polymer can be used to describe the conformations of the chain, that is

$$\begin{aligned} \left\langle (\mathbf{r}(L) - \mathbf{r}(0))^2 \right\rangle &= \int_0^L ds_1 \int_0^L ds_2 \left\langle \mathbf{t}(s_1) \cdot \mathbf{t}(s_2) \right\rangle \\ &= 2\int_0^L ds_1 \int_0^{s_1} ds_2 \exp(-\frac{|s_1 - s_2|}{L_p}) \\ &= 2L_p^2 \left[\frac{L}{L_p} - 1 + \exp(-\frac{L}{L_p}) \right]. \end{aligned} \tag{2.44}$$

One can consider now in two limiting cases:

$$\left\langle \mathbf{R}^2 \right\rangle = \left\langle (\mathbf{r}(L) - \mathbf{r}(0))^2 \right\rangle \approx \begin{cases} 2L_pL & ; \quad L \gg L_p \\ L^2 & ; \quad L \ll L_p \end{cases} . \tag{2.45}$$

For $L \gg L_p$, the semiflexible polymer behaves like a fully flexible chain with $\langle(\mathbf{r}(L) - \mathbf{r}(0))^2\rangle \propto L$. For a fully flexible chain consisting of N bonds of length b_0 ; $L = Nb_0$ then we find(see Doi and Edwards, 1995)

$$\left\langle (\mathbf{r}(L) - \mathbf{r}(0))^2 \right\rangle = Nb_0^2 = Lb_0 \tag{2.46}$$

and the semiflexible polymer chain is similar to a flexible chain with an effective bond length $b_{eff} = 2L_p$ which is also called Kuhn length.

That is the basic relationship for the size of ideal polymers which are described by a random walk. We observe that Eq. (2.46) is the example of a scaling law. The size of the random walk can be classed in the "scaling equation"(Sayakanit et al. (2000)), i.e.,

$$R = b_0 N^{\nu} \text{ where } \nu = \frac{1}{2}. \tag{2.47}$$

We can define the radius of gyration by considering the configuration of the polymer because the polymer in nature do not take on a straight line structure, rigid rod, since all the joints have some flexible. The radius of gyration R_g is the average distance of the mass in a polymer molecule from the center of mass and we can write it as the length of the end-to-end vector R; i.e.,

$$\mathbf{R} \equiv \mathbf{R}_n - \mathbf{R}_0 = \sum_{n=1}^{N} \mathbf{r}_n. \tag{2.48}$$

In the case of flexible polymers, monomers are jointed together by perfectly flexible joints so that the direction in which a link point is completely uncorrelated with the direction of the link to which it is directly jointed on either end. The radius of gyration of the flexible polymer is

$$R_g \equiv [\langle \mathbf{R}^2 \rangle]^{\frac{1}{2}} = b_0\sqrt{N}. \tag{2.49}$$

So the flexible polymer has a radius of gyration very large compared to the unit size b_0 but very small compared to its contour length.

Chapter 3
The Path Integral Approach

We study the stretching of an extensible semiflexible polymer by the force applied to one end of the polymer. In order to account for the extensibility of semiflexible polymers we introduced the *semiflexible harmonic chain*(SHC) model which incorporates the elastics bonds with non-zero equilibrium bond length as microscopic degree of freedom into a discrete version of the worm-like chain model.

3.1 The Semiflexible Harmonic Chain Model

To describe an extensible semiflexible polymer, we will introduce a discrete chain of $N+1$ monomers separated by bonds of length $b(n)$,the integer bond number $n = 1, ..., N$. Its direction can be described by the unit tangent vector $\mathbf{t}(n)$ with the local constraint $|\mathbf{t}(n)| = 1$. Each bond has an equilibrium length of b_0. $L = Nb_0$ is the contour length of the polymer (see Fig. 3.1). The position vector $\mathbf{r}\,(i) = \mathbf{r}(0) + \sum_{n=1}^{i} b_0\mathbf{t}(n)$ where i is the integer monomer number; $i = 0, ..., N$ and $\mathbf{r}(0)$ is the position of the monomer at the fix end.

The energy of a stretched SHC in discrete model can be expressed in three terms. The first term is from the incline of nearest bonds costs the bending

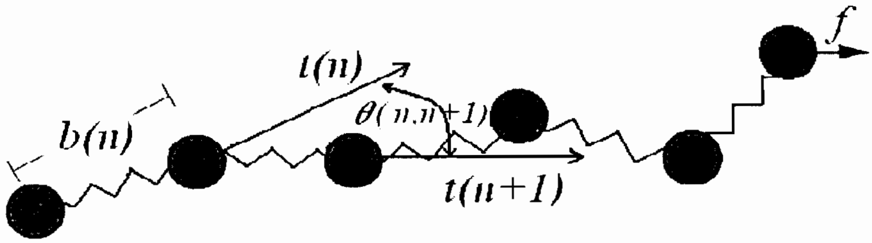

Figure 3.1: The semiflexible harmonic chain model. $\mathbf{t}(n)$ are bond directions with $|\mathbf{t}(n)| = 1, b(n)$ are the bond lengths and $\mathbf{f}$ is the external force applied to the one end of the polymer. The other end is fixed.

energy ,

$$\begin{aligned} E_b &= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0} (\ \mathbf{t}(n+1) - \mathbf{t}(n))^2 \\ &= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0} \left(\ \mathbf{t}^2(n+1) - 2\mathbf{t}(n+1)\cdot\mathbf{t}(n) + \mathbf{t}^2(n)\right) \\ &= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0} (\ 2 - 2\cos\boldsymbol{\theta}(n,n+1)) \\ &= \sum_{n=1}^{N-1} \frac{\kappa}{b_0} (\ 1 - \cos\boldsymbol{\theta}(n,n+1)) , \end{aligned} \tag{3.1}$$

where $\boldsymbol{\theta}(n, n+1)$ is the angle between the unit tangent vector $\mathbf{t}(n+1)$ and $\mathbf{t}(n)$, κ is the bending rigidity (the parameter characterizing the bending energy of a semiflexible polymer). In fact, the bending energy in the SHC model does not depend on the bond extension or compression but depends on only the angle $\boldsymbol{\theta}(n, n+1)$ between the nearest bonds.

The second term is denoted by the elastic displacement $b(n)$ and characterized by the bond stretch stiffness $k(n)$, which depends on the bond index n (in general form). Each bond acts as an elastic spring whose stretching costs an energy

$$
\begin{aligned}
E_s &= \sum_{n=1}^{N} \frac{k(n)}{2} \left(b(n) - b_0 \right)^2 \\
&= \sum_{n=1}^{N} \frac{k(n) b_0^2}{2} \frac{\left(b(n) - b_0 \right)^2}{b_0^2} \\
&= \sum_{n=1}^{N} \frac{k(n)\ b_0^2}{2} \epsilon^2(n),
\end{aligned} \tag{3.2}
$$

where the relative bond extension $\epsilon(n) \equiv (b(n) - b_0)/b_0$.

The last term is the work done by the external tensile force $\mathbf{f}$ applied to one end with the other end fixed (Odijk (1995)), that is,

$$
\begin{aligned}
E_f &= -\mathbf{f} \cdot (\mathbf{r}(N) - \mathbf{r}(0)) \\
&= -\mathbf{f} \cdot \sum_{n=1}^{N} b(n) \mathbf{t}(n) \\
&= -\sum_{n=1}^{N} b(n) \mathbf{f} \cdot \mathbf{t}(n) \\
&= -\sum_{n=1}^{N} b_0 (1 + \epsilon(n)) \mathbf{f} \cdot \mathbf{t}(n).
\end{aligned} \tag{3.3}
$$

The sum of the bending, the stretching and the work done by the external force gives the Hamiltonian of the extensible semiflexible polymer chain, which includes a discrete chain configuration of finite length with extensible bonds and bending energy:

$$
\begin{aligned}
H[\mathbf{t}(n), \epsilon(n)] &= E_b + E_s + E_f \\
&= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0} \left(\mathbf{t}(n+1) - \mathbf{t}(n) \right)^2 \\
&\quad + \sum_{n=1}^{N} \frac{k(n)\ b_0^2}{2} \epsilon^2(n) - \sum_{n=1}^{N} b_0 (1 + \epsilon(n)) \mathbf{f} \cdot \mathbf{t}(n).
\end{aligned} \tag{3.4}
$$

In the experiments, the position vector at the ends $\mathbf{r}(0)$ and $\mathbf{r}(N)$ are always fixed. Then we can consider two kinds of the boundary conditions of clamped ends; the fixed tangent vector $\mathbf{t}(1)$ and $\mathbf{t}(N)$ as in Kroy and Frey (1996) or the free ends where $\mathbf{t}(1)$ and $\mathbf{t}(N)$ can fluctuate.

From the definition of the partition function, we can write it in terms of the Hamiltonian which is parameterized by two degrees of freedom, bond extensions $\epsilon(n)$ and bond directions $\mathbf{t}(n)$.The partition function of the discrete extension SHC does not only sum over all tangent configuration $\mathbf{t}(n)$ (subject to the local constraint $|\mathbf{t}(n)| = 1$) but also all possible bond length $b(n)$ or relative bond extension $\epsilon(n)$. For the fixed ends tangent vectors, we can write the bound partition function as

$$Z(\mathbf{t}(1), \mathbf{t}(N)) = \prod_{n=2}^{N-1} \int d\mathbf{t}(n)\delta(|t(n)| - 1)\prod_{n=1}^{N} \int d\epsilon(n)e^{-H[\mathbf{t}(n),\epsilon(n)]/k_BT}. \tag{3.5}$$

For the free ends, we integrate Eq. (3.5) over the initial tangent $\mathbf{t}(1)$ and the final tangent $\mathbf{t}(N)$ vectors then we obtain the partition function

$$\begin{aligned} Z &= \prod_{n=1,N} \int d\mathbf{t}(n)\delta(|\mathbf{t}(n)| - 1)Z(\mathbf{t}(1), \mathbf{t}(N)) \\ &= \prod_{n=1}^{N} \int d\mathbf{t}(n)\delta(|\mathbf{t}(n)| - 1)\prod_{n=1}^{N} \int d\epsilon(n)e^{-H[\mathbf{t}(n),\epsilon(n)]/k_BT}. \end{aligned} \tag{3.6}$$

We will focus on the free ends boundary condition where all bond directions fluctuate and Eq. (3.6) is the partition function of the system. In Eq. (3.6), we can integrate over relation bond extension because it is Gaussian. We define a new function as

$$\begin{aligned}\tilde{Z} &= \prod_{n=1}^{N}\int d\epsilon(n)e^{-H[\mathbf{t}(n),\epsilon(n)]/k_BT}\\ &= \left(e^{-H_i[\mathbf{t}(n)]/k_BT}\right)\int d\epsilon(1)\int d\epsilon(2)...\int d\epsilon(n)\\ &\cdot e^{\left\{-\frac{k(1)\ b_0^2}{2}\epsilon^2(1)-\frac{k(2)\ b_0^2}{2}\epsilon^2(2)-...-\frac{k(N)\ b_0^2}{2}\epsilon^2(N)+b_0\epsilon(1)\mathbf{f}\cdot\mathbf{t}(1)+b_0\epsilon(2)\mathbf{f}\cdot\mathbf{t}(2)+...b_0\epsilon(N)\mathbf{f}\cdot\mathbf{t}(N)\right\}/k_BT}\end{aligned} \tag{3.7}$$

whereas the Hamiltonian of an inextensible discrete SHC is

$$H_i[\mathbf{t}(n)] = \sum_{n=1}^{N-1}\frac{\kappa}{2b_0}\left(\mathbf{t}(n+1)-\mathbf{t}(n)\right)^2 - \sum_{n=1}^{N} b_0\mathbf{f}\cdot\mathbf{t}(n) \tag{3.8}$$

which is obtained in the limit of large stretching modulus $k(n)$.

Performing all the Gaussian integrations in Eq. (3.7) by using

$$\int_{-\infty}^{\infty}\exp[ax^2+bx]dx = \sqrt{\frac{\pi}{-a}}\exp[-b^2/4a] \tag{3.9}$$

we will obtain

$$\begin{aligned}\tilde{Z} &= e^{-H_i[\mathbf{t}(n)]/k_BT}\prod_{n=1}^{N}\sqrt{\frac{2\pi}{k(n)\ b_0^2}}e^{\frac{(\mathbf{f}\cdot\mathbf{t}(n))^2}{2k(n)k_BT}}\\ &= e^{-H_i[\mathbf{t}(n)]/k_BT+\sum_{n=1}^{N}\frac{(\mathbf{f}\cdot\mathbf{t}(n))^2}{2k(n)k_BT}}\prod_{n=1}^{N}\sqrt{\frac{2\pi}{k(n)\ b_0^2}}.\end{aligned} \tag{3.10}$$

Then we will get the new partition function which depends on only the tangent configuration, the effective partition function

$$Z_{eff}(t(n)) = \prod_{n=1}^{N}\int d\mathbf{t}(n)\sqrt{\frac{2\pi}{k(n)\ b_0^2}}e^{-\left\{H_i[\mathbf{t}(n)]-\frac{(\mathbf{f}\cdot\mathbf{t}(n))^2}{2k(n)}\right\}/k_BT}.$$

That means, the Hamiltonian which only depends on the tangent configurations, the effective Hamiltonian can be written as

$$
\begin{aligned}
H_{eff}[\mathbf{t}(n)] &= H_i[\mathbf{t}(n)] - \sum_{n=1}^{N} \frac{(\mathbf{f}\cdot\mathbf{t}(n))^2}{2k(n)} \\
&= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0} (\ \mathbf{t}(n+1) - \mathbf{t}(n))^2 - \sum_{n=1}^{N} b_0 \mathbf{f}\cdot\mathbf{t}(n) \\
&\quad - \sum_{n=1}^{N} \frac{(\mathbf{f}\cdot\mathbf{t}(n))^2}{2k(n)}.
\end{aligned} \tag{3.11}
$$

The last term is the coupling of elastic bonds and the external force. In an extensible limit, $k(n)$ is large and this term vanishes.

If the bond length b_0 is small, we can consider the continuous model. We parameterize the arclength $s = nb_0$ for the unstretched configuration and write the contour length $\mathbf{r}(s)$ of the extensible chain as $\mathbf{r}(s) - \mathbf{r}(0) = \int_0^s d\tilde{s}(\frac{b(\tilde{s})}{b_0})\mathbf{t}(\tilde{s})$. The fixed end is at $s = 0$ and the another end is at $s = Nb_0 = L$. Then the Hamiltonian given by the bending energy can be written as

$$
H_b[\mathbf{t}(s)] = \int_0^L ds \frac{\kappa}{2} (\partial_s \mathbf{t})^2. \tag{3.12}
$$

The stretching energy of semiflexible polymer with stretching stiffness $k(s)$ is

$$
H_s[\epsilon(s)] = \int_0^L ds \frac{k(s)\ b_0}{2} \epsilon^2(s). \tag{3.13}
$$

The energy terms related to the external force in the continuous limitting case is

$$
H_f[\mathbf{t}(s), \epsilon(s)] = -\int_0^L ds(1+\epsilon(s))\mathbf{f}\cdot\mathbf{t}(s). \tag{3.14}
$$

The sum of the elastic energy of the bending and stretching semiflexible polymer and the work of the external force gives the Hamiltonian for the extensible SHC that parameterized in arclength of the unstretched polymer as

$$
H[\mathbf{t}(s), \epsilon(s)] = \int_0^L ds \left[\frac{\kappa}{2}(\partial_s \mathbf{t})^2 + \frac{k(s)\ b_0}{2} \epsilon^2(s) - (1+\epsilon(s))\mathbf{f}\cdot\mathbf{t}(s) \right]. \tag{3.15}
$$

If the stretching modulus $k(s)$ are very large (in the inextensible limit), the semiflexible polymer do not elongate then the relative bond extensions $\epsilon(s)$ can be omitted. The inextensible worm-like chain Hamiltonian becomes(see more details in Marko and Siggia (1995))

$$H_i\left\{\mathbf{t}(s)\right\} = \int_0^L ds \left[\frac{\kappa}{2}(\partial_s \mathbf{t})^2 - \mathbf{f}\cdot\mathbf{t}(s)\right]. \tag{3.16}$$

Again, we can write the partition function of the continuous SHC not only sum over all tangent configurations $\mathbf{t}(s)$ (subject to the local constraint $|\mathbf{t}(s)| = 1$) but also all possible bond lengths $b(s)$ or relative bond extensions $\epsilon(s)$,

$$Z = \int D[\mathbf{t}(s)]\delta(|\mathbf{t}(s)|-1)\int D[\epsilon(s)]\exp[-H[\mathbf{t}(s),\epsilon(s)]/k_BT], \tag{3.17}$$

where $\int D[\mathbf{t}(s)]$ and $\int D[\epsilon(s)]$ mean a "functional integral" over all configurations of the tangent vectors $\mathbf{t}(s)$ and the fluctuation in bond length $\epsilon(s)$, respectively. In other words, the partition function in Eq. (3.17) is written in form of the path integral. It is the sum over all possible paths. $\int D[\mathbf{t}(s)]$ and $\int D[\epsilon(s)]$ are the identifying notation that are $\int D[\mathbf{t}(s)] = \int_{-\infty}^{\infty}\frac{dt_1(s)}{A}\int_{-\infty}^{\infty}\frac{dt_2(s)}{A}...\int_{-\infty}^{\infty}\frac{dt_N(s)}{A}$ and $\int D[\epsilon(s)] = \int_{-\infty}^{\infty}\frac{d\epsilon_1(s)}{A}\int_{-\infty}^{\infty}\frac{d\epsilon_2(s)}{A}...\int_{-\infty}^{\infty}\frac{d\epsilon_N(s)}{A}$, where A is the normalizing factor.

To obtain the effective Hamiltonian we can eliminate the bond extensions $\epsilon(s)$ degree of freedoms in Eq. (3.17) because it is Gaussian path integration

$$\begin{aligned}
\tilde{Z} &= \int D[\epsilon(s)]\exp[-H[\mathbf{t}(s),\epsilon(s)]/k_BT] \\
&= \int D[\epsilon(s)]\exp\left[-\int_0^L ds\left[\frac{\kappa}{2}(\partial_s\mathbf{t})^2 + \frac{k(s)\ b_0}{2}\epsilon^2(s) - (1+\epsilon(s))\mathbf{f}\cdot\mathbf{t}(s)\right]/k_BT\right] \\
&= \exp\left[-\int_0^L ds\left[\frac{\kappa}{2}(\partial_s\mathbf{t})^2 - \mathbf{f}\cdot\mathbf{t}(s)\right]/k_BT\right] \\
&\quad \cdot\int D[\epsilon(s)]\exp\left[-\int_0^L ds\left[\frac{k(s)\ b_0}{2}\epsilon^2(s) - \epsilon(s)\mathbf{f}\cdot\mathbf{t}(s)\right]/k_BT\right] \\
&= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right] \\
&\quad \cdot\int D[\epsilon(s)]\exp\left[-\int_0^L ds\left[\frac{k(s)\ b_0}{2}\epsilon^2(s) - \epsilon(s)\mathbf{f}\cdot\mathbf{t}(s)\right]/k_BT\right].
\end{aligned} \tag{3.18}$$

Since we have to discretize the polymer into monomers, i.e., into molecules separated by bonds of fixed length l such that the total length L is the $L = Nl$. This means we discretize all integrals over the arclength s by using $\Delta s = l$. For the integral over an arbitrary function $x(s)$ this means:

$$\int_0^L dsx(s) \rightarrow \sum_{n=1}^{N} \Delta sx(n\Delta s) = \sum_{n=1}^{N} lx(nl). \tag{3.19}$$

In particular, we do this for the bond extensions $\epsilon(s)$ and introduce a discrete set of bond extensions $\epsilon_n = \epsilon(nl)$, tangent vectors $t_n = t(nl)$ and stretching modulus $k_n = k(nl)$. Then the functional integral in Eq. (3.18) can be computed as

$$\begin{aligned}
\tilde{Z} &= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right] \\
&\quad \cdot \int D[\epsilon(n\Delta s)] \exp\left[-\sum_{n=1}^{N} \Delta s \left[\frac{k(n\Delta s)\ b_0}{2}\epsilon^2(n\Delta s) - \epsilon(n\Delta s)\mathbf{f}\cdot\mathbf{t}(n\Delta s)\right]/k_BT\right] \\
&= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right] \\
&\quad \cdot \int D[\epsilon(nl)] \exp\left[-\sum_{n=1}^{N} l \left[\frac{k(nl)\ b_0}{2}\epsilon^2(nl) - \epsilon(nl)\mathbf{f}\cdot\mathbf{t}(nl)\right]/k_BT\right] \\
&= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right] \\
&\quad \cdot \int_{-\infty}^{\infty} \frac{d\epsilon_1}{A} \int_{-\infty}^{\infty} \frac{d\epsilon_2}{A} \ldots \int_{-\infty}^{\infty} \frac{d\epsilon_n}{A} \exp\left[-\sum_{n=1}^{N} l \left[\frac{k_n\ b_0}{2}\epsilon_n^2 - \epsilon_n\mathbf{f}\cdot\mathbf{t}_n\right]/k_BT\right],
\end{aligned} \tag{3.20}$$

where the normalizing factor $A = \sqrt{\frac{2\pi k_BT}{lk_n\ b_0}}$. We choose a range of integration from $\epsilon(s) \in (-\infty, \infty)$ for each bond and perform all the Gaussian integrations in Eq. (3.20) by using

$$\int_{-\infty}^{\infty} \exp[ax^2 + bx]dx = \sqrt{\frac{\pi}{-a}} \exp[-b^2/4a]. \tag{3.21}$$

The result should be

$$\begin{aligned}\tilde{Z} &= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right]\prod_{n=1}^{N}\left(\int_{-\infty}^{\infty}\frac{d\epsilon_n}{A}\exp\left[\frac{-l}{k_BT}\left[\frac{k_n\ b_0}{2}\epsilon_n^2-\epsilon_n\mathbf{f}\cdot\mathbf{t}_n\right]\right]\right)\\ &= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right]\prod_{n=1}^{N}\left(\exp\left[\frac{\left(\frac{l}{k_BT}\right)^2(\mathbf{f}\cdot\mathbf{t}_n)^2}{-4\frac{l}{k_BT}\frac{k_n\ b_0}{2}}\right]\right)\\ &= \exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right]\prod_{n=1}^{N}\left(\exp\left[\frac{-l(\mathbf{f}\cdot\mathbf{t}_n)^2}{2k_n\ b_0k_BT}\right]\right). \qquad (3.22)\end{aligned}$$

Inserting Eq. (3.22) into Eq. (3.17), the partition function will be

$$\begin{aligned}Z &= \int D[\mathbf{t}(s)]\tilde{Z}\\ &= \int D[\mathbf{t}(s)]\exp\left[-H_i\left\{\mathbf{t}(s)\right\}/k_BT\right]\prod_{n=1}^{N}\left(\exp\left[\frac{-l(\mathbf{f}\cdot\mathbf{t}_n)^2}{2k_n\ b_0k_BT}\right]\right). \qquad (3.23)\end{aligned}$$

Note $\prod_{i=1}^{N}e^{x_i}=e^{\sum_{i=1}^{N}x_i}$. We will obtain

$$\begin{aligned}Z_{eff} &= \int D[\mathbf{t}(s)]\exp\left\{-\int_0^L ds\left[\frac{\kappa}{2}(\partial_s\mathbf{t}(s))^2-\mathbf{f}\cdot\mathbf{t}(s)\right]/k_BT\right\}\exp\left\{\sum_{i=1}^{N}\frac{-l(\mathbf{f}\cdot\mathbf{t}_n)^2}{2k_n\ b_0k_BT}\right\}\\ Z_{eff} &= \int D[\mathbf{t}(s)]\exp\left\{-\int_0^L ds\left[\frac{\kappa}{2}(\partial_s\mathbf{t}(s))^2-\mathbf{f}\cdot\mathbf{t}(s)-\frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0}\right]/k_BT\right\}. \qquad (3.24)\end{aligned}$$

Therefore the effective continuous Hamiltonian becomes

$$H_{eff}\left\{\mathbf{t}(s)\right\} = \int_0^L ds\left[\frac{\kappa}{2}(\partial_s\mathbf{t})^2-\mathbf{f}\cdot\mathbf{t}(s)-\frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0}\right]. \qquad (3.25)$$

which is analogous with the effective discrete Hamiltonian in Eq. (3.11) and has also been derived in Netz (2001).

3.2 Large Force Limit

For the strong stretching, $\frac{fL_p}{2T} \gg 1$, the extension will approach the total length and the tangent vector will oscillate only slightly around the force direction. We choose the x-direction as same as the force direction and the tangent vector $\mathbf{t}$ split into components, $\mathbf{t} \equiv (\mathbf{t}_x, \mathbf{t}_\perp)$ and $\mathbf{t}_\perp \equiv (\mathbf{t}_y, \mathbf{t}_z)$. From the constraint $|\mathbf{t}| = 1$, the tangent vector fluctuations $\mathbf{t}_x$ can be write in terms of $t_\perp^2$, that is $\mathbf{t}_x = 1 - \frac{t_\perp^2}{2} + \vartheta(t_\perp^4)$ or $\mathbf{t}_x = (1 - t_\perp^2)^{\frac{1}{2}}$(Maier B., Seifert U. and Radler J.Ö. (2002)) and for the large force limit $< t_\perp^2 > \ll 1$. Then we will obtain the effective Hamiltonian Eq. (3.11) in $\mathbf{t}_\perp$ as

$$
\begin{aligned}
H_{eff}\{\mathbf{t}_\perp(n)\} &= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0}(\ \mathbf{t}_\perp(n+1) - \mathbf{t}_\perp(n))^2 - \sum_{n=1}^{N} b_0 f t_x(n) - \sum_{n=1}^{N} \frac{(f t_x(n))^2}{2k(n)} \\
&= \sum_{n=1}^{N-1} \frac{\kappa}{2b_0}(\ \mathbf{t}_\perp(n+1) - \mathbf{t}_\perp(n))^2 - \sum_{n=1}^{N} b_0 f (1 - t_\perp^2(n))^{\frac{1}{2}} \\
&\quad - \sum_{n=1}^{N} \frac{(f(1 - t_\perp^2(n))^{\frac{1}{2}})^2}{2k(n)} \\
&= -b_0 N f - \sum_{n=1}^{N} \frac{f^2}{2k(n)} + \sum_{n=1}^{N-1} \frac{\kappa}{2b_0}(\ \mathbf{t}_\perp(n+1) - \mathbf{t}_\perp(n))^2 \\
&\quad + \sum_{n=1}^{N} \frac{b_0 f_{eff}}{2} t_\perp^2(n), \qquad (3.26)
\end{aligned}
$$

where the effective increasing force due to the coupling of the external force and the elastic bond is

$$f_{eff} = f\left(1 + \frac{f}{b_0 k(n)}\right). \qquad (3.27)$$

The first term -$b_0 N f$ or $-Lf$ described the potential of the fully stretched chain, the second term is the overall elastic energy of the bonds and f_{eff} in the last term denotes the effective force arising from the coupling of the elastic bonds with the external force.

In the homogeneous bond case $k(n) = k$, we can integrate the partition function by performing the path integral over the degree of freedom $\mathbf{t}_\perp(n)$ (Feynman and Hibbs (1995); Sa-yakanit, Kunsombat and Niamploy (2000)); that is

$$Z(f) = \prod_{n=1}^{N} \int d[\mathbf{t}_\perp(n)] \exp\{-H_{eff}\{\mathbf{t}_\perp(n)\}/k_BT\}. \qquad (3.28)$$

We can write the partition function in terms of the classical path $\mathbf{t}_\perp^0(n)$ and their fluctuations $\delta\mathbf{t}_\perp(n)$ as

$$\begin{aligned} Z(f) &= \exp\left\{\frac{Lf}{k_BT} + \frac{Lf^2}{2k_BTkb_0}\right\} \prod_{n=1,N} \int d[\mathbf{t}_\perp^0(n)] \exp\left\{-\tilde{H}_{eff}\{\mathbf{t}_\perp^0(n)\}/k_BT\right\} \\ &\prod_{n=2}^{N-1} \int d[\delta\mathbf{t}_\perp(n)] \exp\left\{-\tilde{H}_{eff}\{\delta\mathbf{t}_\perp(n)\}/k_BT\right\}, \end{aligned} \qquad (3.29)$$

where

$$\tilde{H}_{eff}\{\mathbf{t}_\perp(n)\} = H_{eff}\{\mathbf{t}_\perp(n)\} + \frac{Lf}{k_BT} + \frac{Lf^2}{2k_BTkb_0}, \qquad (3.30)$$

and the boundary conditions are $\mathbf{t}_\perp^0(1) = \mathbf{t}_\perp(1)$, $\mathbf{t}_\perp^0(N) = \mathbf{t}_\perp(N)$ and $\delta\mathbf{t}_\perp(n) = \mathbf{t}_\perp(n) - \mathbf{t}_\perp^0(n)$.

Fourier transforms will be needed to calculate things more complicated as the partition function Eq. (3.28), in particular to calculate correlation function like

$$\langle \mathbf{t}_\perp(n) \cdot \mathbf{t}_\perp(\acute{n}) \rangle := \frac{\int D[\mathbf{t}_\perp(s)] \mathbf{t}_\perp(n) \cdot \mathbf{t}_\perp(\acute{n}) \exp\{-H_{eff}\{\mathbf{t}_\perp(n)\}/k_BT\}}{\int D[\mathbf{t}_\perp(s)] \exp -H_{eff}\{\mathbf{t}_\perp(n)\}/k_BT}, \qquad (3.31)$$

for the effective Hamiltonian Eq. (3.26). For the discrete set of $\mathbf{t}_\perp(n)$ with N degrees of freedom, we also have N degrees of freedom in Fourier space and the magnitude $|q| < \frac{\pi}{b_0}$. The allowed wave vector will be

$$q = \frac{2\pi}{L} m \qquad \text{with} \quad m = -N/2, ..., N/2 \qquad (3.32)$$

Using the Fourier transform $\tilde{\mathbf{t}}_\perp(q)$ of the discrete version $\mathbf{t}_\perp(n)$ is defined as

$$\begin{aligned}\mathbf{t}_\perp(n) &= \frac{1}{L}\sum_{m=-N/2}^{m=N/2}\tilde{\mathbf{t}}_\perp(\frac{2\pi m}{L})\exp\{i\frac{2\pi m}{L}nb_0\} \\ &= \frac{1}{L}\sum_{q,|q|<\frac{\pi}{b_0}}\tilde{\mathbf{t}}_\perp(q)\exp\{iqnb_0\} \\ \tilde{\mathbf{t}}_\perp(q) &= \sum_m b_0\mathbf{t}_\perp(n)\exp\{-iqmb_0\}. \end{aligned} \tag{3.33}$$

Some important relations are

$$\begin{aligned}\frac{1}{L}\sum_q \exp\{iqs\} &= \delta(s) \\ \frac{1}{L}\sum_{q,|q|<\frac{\pi}{b_0}}\exp\{iqnb_0\} &= \frac{1}{b_0}\delta_{n,0} \\ \int_0^L ds\exp\{-iqs\} &= L\delta_{q,0} \\ \sum_n b_0\exp\{-iqnb_0\} &= L\delta_{q,0}. \end{aligned} \tag{3.34}$$

The Fluctuation Partition Function

After Fourier transforming (see more details in appendix B) of the last term of Eq.(3.29) , the fluctuation term, we get the partition function for the Hamiltonian

$$\begin{aligned}\tilde{H}_{flu-eff}\left\{\delta\tilde{\mathbf{t}}_\perp(q)\right\} &= \frac{\kappa}{b_0^2 L}\sum_{q,|q|<\frac{\pi}{b_0},q>0}\left((1-\cos qb_0)+\frac{b_0^2 f_{eff}}{2\kappa}\right) \\ &\quad \left(\left(\mathrm{Re}\,\delta\tilde{\mathbf{t}}_\perp(q)\right)^2+\left(\mathrm{Im}\,\delta\tilde{\mathbf{t}}_\perp(q)\right)^2\right), \end{aligned} \tag{3.35}$$

which is the Fourier transform of the discrete Hamiltonian

$$H_{flu-eff}\left\{\delta\mathbf{t}_\perp(n)\right\} = \sum_{n=1}^{N-1}\frac{\kappa}{2b_0}\left(\,\boldsymbol{\delta}\mathbf{t}_\perp(n+1)-\delta\mathbf{t}_\perp(n)\right)^2+\sum_{n=1}^{N}\frac{b_0 f_{eff}}{2}\delta t_\perp^2(n) \tag{3.36}$$

as

$$
\begin{aligned}
Z_{flu} &= \int D\delta\tilde{\mathbf{t}}_{\perp}(q)\exp\{-\tilde{H}_{flu-eff}\left[\delta\tilde{\mathbf{t}}_{\perp}(q)/k_BT\right]\} \\
&= \left(\prod_{q,|q|\prec\frac{\pi}{b_0},q>0}^{N}\int d\,\mathrm{Re}\,\delta\tilde{\mathbf{t}}_{\perp}(q)d\,\mathrm{Im}\,\delta\tilde{\mathbf{t}}_{\perp}(q)\right) \\
&\quad \exp\left\{-\frac{\kappa}{b_0^2Lk_BT}\sum_q\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right)\left(\left(\mathrm{Re}\,\delta\tilde{\mathbf{t}}_{\perp}(q)\right)^2+\left(\mathrm{Im}\,\delta\tilde{\mathbf{t}}_{\perp}(q)\right)^2\right)\right\} \\
&= \prod_{q,|q|\prec\frac{\pi}{b_0},q>0}^{N}\left(\int d\delta\tilde{\mathbf{t}}_{\perp}(q)\exp\left\{-\frac{\kappa}{b_0^2Lk_BT}\sum_q\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right)\tilde{\mathbf{t}}_{\perp}^2\right\}\right)^2.
\end{aligned} \tag{3.37}
$$

Here we use the fact that, the exponential factor is completely (this is the advantage of the Fourier transform) and for the limit $L \longrightarrow \infty$, note that $\frac{1}{L}\sum_q = \sum_q \frac{\Delta q}{2\pi} \rightarrow \int \frac{dq}{2\pi}$ with $\Delta q \rightarrow 0$.

$$
\begin{aligned}
Z_{flu}(f) &= \prod_{q,|q|\prec\frac{\pi}{b_0},q>0}^{N}\left(\sqrt{\frac{\pi b_0^2Lk_BT}{\kappa\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right)}}\right)^2 \\
&= \exp\left\{\sum_{q,|q|\prec\frac{\pi}{b_0},q>0}\ln\left(\frac{\pi b_0^2Lk_BT}{\kappa\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right)}\right)\right\} \\
&= \exp\left\{L\int_0^{\pi/b_0}\frac{dq}{2\pi}\ln\left(\frac{\pi b_0^2Lk_BT}{\kappa\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right)}\right)\right\}.
\end{aligned} \tag{3.38}
$$

Then we obtain the force-fluctuation partition function $Z_{flu}(f)$ in Eq.(3.38). In the same way, we can find the fluctuation partition function $Z_{flu}(0)$, that it is

$$
Z_{flu}(0) = \exp\left\{L\int_0^{\pi/b_0}\frac{dq}{2\pi}\ln\left(\frac{\pi b_0^2Lk_BT}{\kappa\left((1-\cos qb_0)\right)}\right)\right\}. \tag{3.39}
$$

In chapter 2, the free energy F can be expressed in terms of $\ln Z$:

$$F = -k_B T \ln Z. \tag{3.40}$$

Then we can find the free energy from the fluctuating free ends which is

$$\begin{aligned} F_{flu} &= F(f) - F(0) = k_B T \ln Z(0) - k_B T \ln Z(f) \\ &= k_B T \ln \frac{Z(0)}{Z(f)} \\ &= k_B T \ln \frac{\exp\left\{L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{\pi b_0^2 L k_B T}{\kappa((1-\cos qb_0))}\right)\right\}}{\exp\left\{L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{\pi b_0^2 L k_B T}{\kappa\left((1-\cos qb_0)+\frac{b_0^2 f_{eff}}{2\kappa}\right)}\right)\right\}} \\ &= k_B T L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{(1-\cos qb_0)+\frac{b_0^2 f_{eff}}{2\kappa}}{(1-\cos qb_0)}\right) \\ &= \frac{k_B T L}{b_0} \operatorname{arcsin} h\left[\frac{b_0}{2}\left(\frac{f_{eff}}{\kappa}\right)^{\frac{1}{2}}\right]. \end{aligned} \tag{3.41}$$

The Classical Path Partition Function

For the clamped end, the classical path partition function $\mathbf{t}_\perp^0(x)$ with $x = nb_0$. For b_0 small, the tangent vector satisfies the equation

$$\partial_x^2 \mathbf{t}_\perp^0(x) - \frac{1}{\varpi^2}\mathbf{t}_\perp^0(x) = 0, \text{ where } \varpi^2 = \frac{\kappa}{f_{eff}}. \tag{3.42}$$

The solution is approximately

$$\mathbf{t}_\perp^0(x) \approx \mathbf{t}_\perp^0(1)\exp\{-x/\varpi\} + \mathbf{t}_\perp^0(N)\exp\{-(L-x)/\varpi\} \tag{3.43}$$

Inserting this solution into Eq.(3.30), we will get the effective Hamiltonian

$$\tilde{H}_{eff}\left\{\mathbf{t}_\perp^0(n)\right\} \approx \frac{\sqrt{\kappa f_{eff}}}{2}\left(\left(\mathbf{t}_\perp^0(1)\right)^2 + \left(\mathbf{t}_\perp^0(N)\right)^2\right). \tag{3.44}$$

In chapter 2, the free energy F can be expressed in terms of $\ln Z$:

$$F = -k_B T \ln Z. \tag{3.40}$$

Then we can find the free energy from the fluctuating free ends which is

$$\begin{aligned} F_{flu} &= F(f) - F(0) = k_B T \ln Z(0) - k_B T \ln Z(f) \\ &= k_B T \ln \frac{Z(0)}{Z(f)} \\ &= k_B T \ln \frac{\exp\left\{L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{\pi b_0^2 L k_B T}{\kappa((1-\cos qb_0))}\right)\right\}}{\exp\left\{L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{\pi b_0^2 L k_B T}{\kappa\left((1-\cos qb_0)+\frac{b_0^2 f_{eff}}{2\kappa}\right)}\right)\right\}} \\ &= k_B T L \int_0^{\pi/b_0} \frac{dq}{2\pi} \ln\left(\frac{(1-\cos qb_0)+\frac{b_0^2 f_{eff}}{2\kappa}}{(1-\cos qb_0)}\right) \\ &= \frac{k_B T L}{b_0} \operatorname{arcsin} h\left[\frac{b_0}{2}\left(\frac{f_{eff}}{\kappa}\right)^{\frac{1}{2}}\right]. \end{aligned} \tag{3.41}$$

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For the clamped end, the classical path partition function $\mathbf{t}_\perp^0(x)$ with $x = nb_0$. For b_0 small, the tangent vector satisfies the equation

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The solution is approximately

$$\mathbf{t}_\perp^0(x) \approx \mathbf{t}_\perp^0(1)\exp\{-x/\varpi\} + \mathbf{t}_\perp^0(N)\exp\{-(L-x)/\varpi\} \tag{3.43}$$

Inserting this solution into Eq.(3.30), we will get the effective Hamiltonian

$$\tilde{H}_{eff}\left\{\mathbf{t}_\perp^0(n)\right\} \approx \frac{\sqrt{\kappa f_{eff}}}{2}\left(\left(\mathbf{t}_\perp^0(1)\right)^2 + \left(\mathbf{t}_\perp^0(N)\right)^2\right). \tag{3.44}$$

Again, to obtain the free energy from $Z = \prod_{n=1,N} \int d\mathbf{t}_{\perp}^{0}(n) \exp\left\{-\tilde{H}_{eff}\left\{\mathbf{t}_{\perp}^{0}(n)\right\}/k_B T\right\}$ and $F_{cl} = F(f) - F(0) = k_B T \ln \frac{Z(0)}{Z(f)}$. Finally we will get,

$$F_{cl} = k_B T L \ln \left[\frac{b_0^2 f_{eff}}{\kappa}\right] \tag{3.45}$$

Therefore the Free Energy of the system for the large stretching forec will be

$$\begin{aligned} \frac{1}{L}[F(f) - F(0)] &= -f - \frac{f^2}{2kb_0} + F_{flu} + F_{cl} \\ &= -f - \frac{f^2}{2kb_0} + \frac{k_B T}{b_0} \arcsin h \left[\frac{b_0}{2}\left(\frac{f_{eff}}{\kappa}\right)^{\frac{1}{2}}\right] + k_B T \ln \left[\frac{b_0^2 f_{eff}}{\kappa}\right]. \end{aligned} \tag{3.46}$$

From the thermodynamic relation Eq.(2.10), we will obtain the force-extension relation in the large forec limit as

$$\begin{aligned} \frac{L_f}{L} &= -\frac{\partial_f F}{L} \\ &= 1 + \frac{f}{kb_0} - \frac{k_B T}{2\sqrt{\kappa f}}\left(1 + \frac{3}{2}\frac{f}{kb_0}\right)\left(1 + \frac{b_0^2}{4}\frac{f_{eff}}{\kappa}\right)^{\frac{-1}{2}} - \frac{k_B T}{f_{eff}}\left(1 + \frac{2f}{kb_0}\right). \end{aligned} \tag{3.47}$$

We will discuss it more in the detail in the last chapter.

3.3 Small Force Limit

For the small stretching, $\frac{fL_p}{2T} \ll 1$, we consider the continuous model and the homogeneous bonds $k(s)$ is constant $= k$, the free energy can be calculated from the effective continuous Hamiltonian in Eq.(3.25) and it satisfies the relation

$$\exp\left\{[F(f) - F(0)]/k_B T\right\} = \left\langle \exp\left\{H_f/k_B T\right\}\right\rangle_{f=0}, \tag{3.48}$$

where $H_f = -\int_0^L ds \left[\mathbf{f}\cdot\mathbf{t}(s) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0}\right]$. We expand the energy in the force up to the second order by using the cumulant expansion

$$\langle \exp\{H_f/k_BT\}\rangle_{f=0} = \exp\left\{\langle H_f/k_BT\rangle_{f=0} - \frac{1}{2}\left[\left\langle H_f^2/k_BT\right\rangle_{f=0} - \langle H_f/k_BT\rangle_{f=0}^2\right]\right\} \tag{3.49}$$

and then (see Eq.(2.44) also) we will get,

$$\begin{aligned} F &= F(f) - F(0) \\ &= -\int_0^L ds \frac{1}{2kb_0}\left\langle(\mathbf{f}\cdot\mathbf{t}(s))^2\right\rangle_{f=0} - \frac{1}{2k_BT}\int_0^L ds \int_0^L ds' \langle(\mathbf{f}\cdot\mathbf{t}(s))(\mathbf{f}\cdot\mathbf{t}(s'))\rangle_{f=0} \\ &= -\frac{f^2L}{6kb_0} - \frac{f^2\widetilde{L}_p}{3k_BT}\pounds(\widetilde{L}_p/L), \end{aligned} \tag{3.50}$$

where $\widetilde{L}_p = L_p/2$ and a function

$$\begin{aligned} \pounds(x) &= (1 - x + xe^{-1/x}) \\ &= \begin{cases} 1-x & \text{for } x \ll 1 \\ 1/2x & \text{for } x \gg 1 \end{cases} \end{aligned}$$

The average $\langle ...\rangle_{f=0}$ is taken in the absence of force by using

$$\langle \mathbf{t}_i(s)\mathbf{t}_j(s')\rangle_{f=0} = \frac{1}{3}\exp\left\{-\left|s - s'\right|/\widetilde{L}_p\right\}\delta_{ij}. \tag{3.51}$$

From the thermodynamic relation in Eq.(2.10) we will obtain the force-extension relation in the small force limit as

$$\begin{aligned} \frac{\overline{L}}{L} &= \frac{f}{3kb_0} + \frac{2}{3}\frac{f\widetilde{L}_p}{k_BT}\pounds(\widetilde{L}_p/L) \\ &= \frac{f}{3kb_0} + \begin{cases} \frac{2}{3}\frac{f\kappa}{(k_BT)^2} & \text{for } L \gg L_p \\ \frac{1}{3}\frac{fL}{k_BT} & \text{for } L \ll L_p \end{cases}. \end{aligned} \tag{3.52}$$

We will discuss in more details in the last chapter.

Chapter 4
The Variational Approach

4.1 The Variational and Transfer matrix Calculation

In this chapter, we will discuss the study of the semiflexible polymer with extensible bonds under tension based on the condition that the self-interactions or the excluded volume effects are negligible. By using the variational methods, we consider the bound partition function $Z(\mathbf{t}, \mathbf{t}_0, L)$ of the extensible SHC and use the boundary conditions of fixing the first and last unit tangent vectors of polymer ends: $\mathbf{t}(0) = \mathbf{t}_0$ and $\mathbf{t}(L) = \mathbf{t}$. Then we can write

$$Z(\mathbf{t}, \mathbf{t}_0, L) = \int_{(\mathbf{t}_0;0)}^{(\mathbf{t};L)} D[\mathbf{t}(s)]\delta(|\mathbf{t}| - 1) \exp\{-H_{eff}\{\mathbf{t}(s)\}/k_B T\} \tag{4.1}$$

where the effective Hamiltonian $H_{eff} = \int_0^L ds \left[\frac{\kappa}{2}(\partial_s \mathbf{t}(s))^2 - \mathbf{f} \cdot \mathbf{t}(s) - \frac{(\mathbf{f} \cdot \mathbf{t}(s))^2}{2k(s)\ b_0}\right]$.

Consider the special case where the initial length differs only by an interval Δs from the final length. The partition function Z is proportional to the exponential of energy for the interval 0 to L. For a short interval $\Delta s = s - s'$, the energy is approximately Δs times the Hamiltonian for this interval.

The probability distribution ψ for the tangent vector at s is

$$\psi(\mathbf{t}, s) = \int_{-\infty}^{\infty} d\mathbf{t}_0 Z(\mathbf{t}, \mathbf{t}_0, L)\psi(\mathbf{t}_0, s') \tag{4.2}$$

Using the approximation, we have

$$\begin{aligned}\psi(\mathbf{t}, s'+\Delta s) &= \int_{-\infty}^{\infty} \frac{1}{A'} \exp\left[-\frac{\Delta s}{k_B T} H(\frac{\mathbf{t}-\mathbf{t}_0}{\Delta s}, \frac{\mathbf{t}+\mathbf{t}_0}{2}, \frac{s+s'}{2})\right] \psi(\mathbf{t}_0, s') d\mathbf{t}_0 \\ &= \int_{-\infty}^{\infty} \frac{1}{A'} \exp\left[-\frac{\Delta s}{k_B T}\frac{\kappa}{2}(\partial_s \mathbf{t}(s))^2\right] \\ &\quad \cdot \exp\left[\frac{\Delta s}{k_B T}(\mathbf{f}\cdot\mathbf{t}(s-\Delta s) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0})\right]\psi(\mathbf{t}_0, s')d\mathbf{t}_0 \qquad (4.3)\end{aligned}$$

where A' is a normalizing factor, $\partial_s \mathbf{t}(s) = \frac{\mathbf{t}(s'+\Delta s)-\mathbf{t}(s')}{\Delta s} = \frac{\Delta \mathbf{t}}{\Delta s}$ and $\Delta\mathbf{t}$ is small, we will obtain

$$\begin{aligned}\psi(\mathbf{t}, s'+\Delta s) &= \int_{-\infty}^{\infty} \frac{1}{A'} \exp\left[-\frac{\kappa}{2k_B T}\frac{(\Delta \mathbf{t})^2}{\Delta s}\right] \exp\left[\frac{\Delta s}{k_B T}(\mathbf{f}\cdot\mathbf{t}(s) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0})\right] \\ &\quad \cdot\psi(\mathbf{t}-\Delta\mathbf{t}, s')d\Delta\mathbf{t} \qquad (4.4)\end{aligned}$$

After that, we expand the probability distribution $\psi(\mathbf{t}, s'+\Delta s)$ in a power series and need only keep terms of order Δs.

$$\begin{aligned}\psi(\mathbf{t}, s') + \Delta s \partial_s \psi(\mathbf{t}, s') &= \int_{-\infty}^{\infty} \frac{1}{A'} \exp[-\frac{\kappa}{2k_B T}\frac{(\Delta \mathbf{t})^2}{\Delta s}] \\ &\quad \left(1 + \frac{\Delta s}{k_B T}(\mathbf{f}\cdot\mathbf{t}(s) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2k(s)\ b_0})\right)\psi(\mathbf{t}-\Delta\mathbf{t}, s')d\Delta\mathbf{t}, \\ &\qquad (4.5)\end{aligned}$$

and then we expand $\psi(\mathbf{t}-\Delta\mathbf{t}, s')$ in a series

$$\psi(\mathbf{t}-\Delta\mathbf{t}, s') = \psi(\mathbf{t}, s') - \Delta t \partial_t \psi(\mathbf{t}, s') + \frac{(\Delta\mathbf{t})^2}{2}\partial_t^2 \psi(\mathbf{t}, s') \qquad (4.6)$$

Putting it in the previous equation, we calculated the r.h.s. and rewrite it. Finally we will get the probability distribution ψ which satisfies a linear Schrödinger-like equation:

$$\begin{aligned}-E\psi_E(\mathbf{t}) &= \left[\frac{(k_B T)^2}{2\kappa}\mathbf{L}^2 + (\mathbf{f}\cdot\mathbf{t}) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2kb_0}\right]\psi_E(\mathbf{t}) \\ &\equiv -\widehat{H}\psi_E(\mathbf{t}) \qquad (4.7)\end{aligned}$$

where the angular momentum operator $L \equiv \mathbf{t} \times \nabla_{\mathbf{t}}$ (Doi (1983); Fixman and Kovac (1973) and Yamakawa(1976)), $\widehat{H}$ is the Hamiltonian operator that corresponding to the quantum problem. We want to find the ground state energy E_0 of the linear Schrödinger-like equation in Eq.(4.7). We introduce the trial probability distribution function.

$$\psi_a(\mathbf{t}) \propto exp[\frac{a}{2}(\mathbf{f} \cdot \mathbf{t})] \tag{4.8}$$

where a is the variational parameter. The variational result of the ground state energy can be found by minimizing the expectation value of the Hamiltonian operator $\widehat{H}$ with respect to a,

$$E_0 = \min_a \left\{ \frac{\langle \psi_a | \widehat{H} \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \right\} \tag{4.9}$$

$$\begin{aligned}
\frac{\langle \psi_a | \widehat{H} \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} &= \frac{-\langle \psi_a | [\frac{(k_B T)^2}{2\kappa} \mathbf{L}^2 + (\mathbf{f} \cdot \mathbf{t}) + \frac{(\mathbf{f} \cdot \mathbf{t}(s))^2}{2kb_0}] \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&= \frac{-\langle \psi_a | \frac{(k_B T)^2}{2\kappa} (\mathbf{t} \times \nabla_{\mathbf{t}}) \cdot (\mathbf{t} \times \nabla_{\mathbf{t}}) \psi_a \rangle - \langle \psi_a | (\mathbf{f} \cdot \mathbf{t}) \psi_a \rangle - \langle \psi_a | \frac{(\mathbf{f} \cdot \mathbf{t}(s))^2}{2kb_0} \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&= \frac{-\langle \psi_a | \frac{(k_B T)^2}{2\kappa} \left(\frac{a^2}{4} f^2 - \frac{a^2}{4} (\mathbf{f} \cdot \mathbf{t})^2 - \frac{a}{2} (\mathbf{f} \cdot \mathbf{t}) \right) \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} - \frac{\langle \psi_a | (\mathbf{f} \cdot \mathbf{t}) \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&\quad - \frac{\langle \psi_a | \frac{(\mathbf{f} \cdot \mathbf{t})^2}{2kb_0} \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&= -\frac{a^2 f^2 (k_B T)^2}{8\kappa} + \left(\frac{a^2 (k_B T)^2}{8\kappa} - \frac{1}{2kb_0} \right) \frac{\langle \psi_a | (\mathbf{f} \cdot \mathbf{t})^2 \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&\quad + \left(\frac{a (k_B T)^2}{4\kappa} - 1 \right) \frac{\langle \psi_a | (\mathbf{f} \cdot \mathbf{t}) \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} \\
&= -\frac{a^2 f^2 (k_B T)^2}{8\kappa} + \left(\frac{a^2 (k_B T)^2}{8\kappa} - \frac{1}{2kb_0} \right) \frac{f^2 I''(af)}{I(af)} \\
&\quad + \left(\frac{a (k_B T)^2}{4\kappa} - 1 \right) \frac{f I'(af)}{I(af)}
\end{aligned} \tag{4.10}$$

where $I(af) \equiv \langle \psi_a | \psi_a \rangle$.

4.1.1 In Two Dimensions

We have $I(af) = \langle\psi_a|\psi_a\rangle = 2\pi I_0(af)$ where $I_0(af)$ is the Modified Bessel function (Abramowitz and Stegun (1965)). Then, the variational free energy is

$$\frac{\langle\psi_a|\widehat{H}\psi_a\rangle}{\langle\psi_a|\psi_a\rangle} = \frac{I_1(af)}{I_0(af)}\left[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\right] - \frac{f^2}{2kb_0} \tag{4.11}$$

To find the variational free energy by minimizing the energy with respect to the parameter a, set the new parameter $y = af$ then we can write the energy as:

$$E = \frac{I_1(y)}{I_0(y)}\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] - \frac{f^2}{2kb_0} \tag{4.12}$$

thus

$$\begin{aligned}
\frac{\partial E}{\partial y} &= \frac{\partial}{\partial y}\left[\frac{I_1(y)}{I_0(y)}\left(\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right) - \frac{f^2}{2kb_0}\right] \\
&= \left(\frac{[I_0(y) - \frac{I_1(y)}{y}]I_0(y) - I_1^2(y)}{I_0^2(y)}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] \\
&\quad + \left[\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{2y^2kb_0}\right]\left(\frac{I_1(y)}{I_0(y)}\right) \\
0 &= \left(1 - \frac{1}{y}\frac{I_1(y)}{I_0(y)} - \frac{I_1^2(y)}{I_0^2(y)}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] \\
&\quad + \left[\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{2y^2kb_0}\right]\left(\frac{I_1(y)}{I_0(y)}\right)
\end{aligned} \tag{4.13}$$

in case of weak stretching $y \ll 1$ then $\frac{I_1(y)}{I_0(y)} \approx \frac{y}{2} - \frac{y^3}{16} + \frac{y^5}{96} - \ldots$ that is the Eq.(4.10) will be

$$\begin{aligned}
0 &\approx \left(1 - \frac{1}{y}\frac{y}{2} - \frac{y^2}{4}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] + \left[\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{2y^2kb_0}\right]\left(\frac{y}{2}\right) \\
&\approx \frac{y(k_BT)^2}{16\kappa} - \frac{f}{2} + \frac{f^2}{4ykb_0} - \frac{y^3(k_BT)^2}{32\kappa} + \frac{fy^2}{4} - \frac{f^2y}{8kb_0} + \frac{y(k_BT)^2}{16\kappa} - \frac{f^2}{4ykb_0} \\
&\approx \frac{y(k_BT)^2}{8\kappa} - \frac{f}{2} - \frac{f^2y}{8kb_0} \\
\frac{f}{2} &\approx y\left(\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{8kb_0}\right) \\
y &\approx 4f\left(\frac{(k_BT)^2}{\kappa} - \frac{f^2}{kb_0}\right)^{-1}
\end{aligned}$$

At the minnimun af is

$$af \approx \frac{4f\kappa}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-1} \tag{4.14}$$

Insert Eq.(4.14) into Eq.(4.12) to obtain the variational free energy,

$$\begin{aligned} E_0(f) &= \frac{I_1(af)}{I_0(af)}\,[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\,] - \frac{f^2}{2kb_0} \\ &= \frac{af}{2}\,[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\,] - \frac{f^2}{2kb_0} \\ &= \frac{a^2f^2(k_BT)^2}{16\kappa} - \frac{af^2}{2} - \frac{f^2}{4kb_0} \\ &= \frac{\kappa f^2}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-2} - \frac{2\kappa f^2}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-1} \\ &\quad -\frac{f^2}{4kb_0}. \end{aligned} \tag{4.15}$$

From the force-extension relation

$$\frac{L_f}{L} = -\frac{\partial E_0(f)}{\partial f} \tag{4.16}$$

then we will get

$$\begin{aligned} \frac{L_f}{L} &= \frac{f}{2kb_0} + \frac{\partial\left(\frac{2\kappa f^2}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-1}\right)}{\partial f} - \frac{\partial\left(\frac{\kappa f^2}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-2}\right)}{\partial f} \\ &= \frac{f}{2kb_0} + \frac{4\kappa f}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-1} - \frac{4\kappa^2 f^3}{kb_0(k_BT)^4}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-2} \\ &\quad -\frac{2\kappa f}{(k_BT)^2}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-2} + \frac{8\kappa^2 f^3}{kb_0(k_BT)^4}\left(1-\frac{\kappa f^2}{kb_0(k_BT)^2}\right)^{-3} \end{aligned} \tag{4.17}$$

Using the asymtotic expansion $(1+x)^n \approx 1 + nx + \frac{n(n-1)}{2}x^2 + ...$

$$
\begin{aligned}
\frac{L_f}{L} &\approx \frac{f}{2kb_0} + \frac{4\kappa f}{(k_BT)^2}\left(1 + \frac{\kappa f^2}{kb_0(k_BT)^2}\right) - \frac{4\kappa^2 f^3}{kb_0(k_BT)^4}\left(1 + \frac{2\kappa f^2}{kb_0(k_BT)^2}\right) \\
&\quad - \frac{2\kappa f}{(k_BT)^2}\left(1 + \frac{2\kappa f^2}{kb_0(k_BT)^2}\right) - \frac{8\kappa^2 f^3}{kb_0(k_BT)^4}\left(1 + \frac{3\kappa f^2}{kb_0(k_BT)^2}\right) \\
&\approx \frac{f}{2kb_0} + \frac{4\kappa f}{(k_BT)^2} + \frac{4\kappa^2 f^3}{kb_0(k_BT)^4} - \frac{4\kappa^2 f^3}{kb_0(k_BT)^4} - \frac{2\kappa f}{(k_BT)^2} \\
&\quad - \frac{8\kappa^3 f^5}{(kb_0)^2(k_BT)^6} - \frac{4\kappa^2 f^3}{kb_0(k_BT)^4} + \frac{8\kappa^2 f^3}{kb_0(k_BT)^4} + \frac{24\kappa^3 f^5}{(kb_0)^2(k_BT)^6} \\
&\approx \frac{f}{2kb_0} + \frac{2\kappa f}{(k_BT)^2} + \frac{4\kappa^2 f^3}{kb_0(k_BT)^4} + \frac{16\kappa^3 f^5}{(kb_0)^2(k_BT)^6} \qquad (4.18)
\end{aligned}
$$

The force-extension for the weak stretching is

$$
\frac{L_f}{L} = \frac{f}{2kb_0} + \frac{2\kappa f}{(k_BT)^2} + \frac{4\kappa^2 f^3}{kb_0(k_BT)^4} + \frac{16\kappa^3 f^5}{(kb_0)^2(k_BT)^6} \qquad (4.19)
$$

In case of strong stretching $y \gg 1$,where $I_\nu(z) \sim \frac{e^z}{\sqrt{2\pi z}}\left\{1 - \frac{(\mu-1)}{8z} + \frac{(\mu-1)}{2!}\frac{(\mu-9)}{(8z)^2} - ...\right\}$ and $\mu = 4\nu^2$ then $I_1(y) \approx \frac{e^y}{\sqrt{2\pi y}}\left\{1 - \frac{3}{8y}\right\}$, $I_0(y) \approx \frac{e^y}{\sqrt{2\pi y}}\left\{1 + \frac{1}{8y}\right\}$ and $\frac{I_1(y)}{I_0(y)} =$

$\frac{\{1-\frac{3}{8y}\}}{\{1+\frac{1}{8y}\}} = \frac{8y-3}{8y+1}$. That is

$$\begin{aligned}
E &= \frac{I_1(y)}{I_0(y)}\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] - \frac{f^2}{2kb_0} \\
&= \left(\frac{8y-3}{8y+1}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] - \frac{f^2}{2kb_0} \\
\frac{\partial E}{\partial y} &= \frac{\partial}{\partial y}\left[\left(\frac{8y-3}{8y+1}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] - \frac{f^2}{2kb_0}\right] \\
0 &= \left(\frac{8(8y+1)-8(8y-3)}{(8y+1)^2}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] \\
&\quad + \left(\frac{8y-3}{8y+1}\right)\left[\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{2y^2kb_0}\right] \\
&= \left(\frac{4}{y}\right)\left[\frac{y(k_BT)^2}{8\kappa} - f + \frac{f^2}{2ykb_0}\right] + (8y-3)\left[\frac{(k_BT)^2}{8\kappa} - \frac{f^2}{2y^2kb_0}\right] \\
&= \frac{(k_BT)^2}{2\kappa} - \frac{4f}{y} + \frac{2f^2}{y^2kb_0} + \frac{y(k_BT)^2}{\kappa} - \frac{4f^2}{ykb_0} - \frac{3(k_BT)^2}{8\kappa} + \frac{3f^2}{2y^2kb_0} \\
&= \frac{(k_BT)^2}{\kappa}(\frac{1}{8} + y) - \frac{4f}{y}(1 + \frac{f}{kb_0}) \\
&= \frac{(k_BT)^2}{\kappa}(y) - \frac{4f}{y}(1 + \frac{f}{kb_0}) \\
\frac{y(k_BT)^2}{\kappa} &= \frac{4f}{y}(1 + \frac{f}{kb_0}) \\
y &= \frac{2\sqrt{f\kappa}}{k_BT}(1 + \frac{f}{kb_0})^{\frac{1}{2}} \qquad (4.20)
\end{aligned}$$

At the minimun af is

$$af \approx \frac{2\sqrt{f\kappa}}{k_BT}(1 + \frac{f}{kb_0})^{\frac{1}{2}} \qquad (4.21)$$

Insert Eq.(4.21) into Eq.(4.12) to obtain the variational free energy,

$$
\begin{aligned}
E_0(f) &= \frac{I_1(af)}{I_0(af)}\left[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\right] - \frac{f^2}{2kb_0} \\
&= \left(\frac{8af-3}{8af+1}\right)\left[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\right] - \frac{f^2}{2kb_0} \\
&= \left(1-\frac{3}{8af}\right)\left(1-\frac{1}{8af}\right)\left[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\right] - \frac{f^2}{2kb_0} \\
&= \left(1-\frac{1}{2af}\right)\left[\frac{af(k_BT)^2}{8\kappa} - f + \frac{f^2}{2afkb_0}\right] - \frac{f^2}{2kb_0} \\
&= \frac{af(k_BT)^2}{8\kappa} - f + \frac{f}{2af}\left(1+\frac{f}{kb_0}\right) - \frac{(k_BT)^2}{16\kappa} - \frac{f^2}{2kb_0} \\
E_0(f) &= -f - \frac{f^2}{2kb_0} - \frac{(k_BT)^2}{16\kappa} + \sqrt{\frac{f}{\kappa}}\frac{k_BT(1+\frac{f}{kb_0})^{\frac{1}{2}}}{2}
\end{aligned}
\tag{4.22}
$$

From the force-extension relation , then we will get

$$
\begin{aligned}
\frac{L_f}{L} &= 1 + \frac{f}{kb_0} - \frac{k_BT}{2\sqrt{\kappa}}\frac{\partial\left(\sqrt{f}(1+\frac{f}{kb_0})^{\frac{1}{2}}\right)}{\partial f} \\
&= 1 + \frac{f}{kb_0} - \frac{k_BT}{2\sqrt{\kappa}}\left[\frac{1}{2\sqrt{f}}(1+\frac{f}{kb_0})^{\frac{1}{2}} + \frac{\sqrt{f}}{2kb_0}(1+\frac{f}{kb_0})^{\frac{-1}{2}}\right] \\
&= 1 + \frac{f}{kb_0} - \frac{k_BT}{4\sqrt{f\kappa}}\left[(1+\frac{f}{kb_0})^{\frac{1}{2}} + \frac{f}{kb_0}(1+\frac{f}{kb_0})^{\frac{-1}{2}}\right]
\end{aligned}
\tag{4.23}
$$

This coresponds to the the result for $k \to \infty$ with an effective κ

$$
\begin{aligned}
\kappa_{eff} &= \frac{\kappa}{\left[(1+\frac{f}{kb_0})^{1/2} + \frac{f}{kb_0}(1+\frac{f}{kb_0})^{-1/2}\right]^2} \\
&= \kappa\left[1 - \frac{3f}{kb_0}\right] \\
&< \kappa.
\end{aligned}
\tag{4.24}
$$

We may also find the exact free energy E numerically by diagonalizing H in a representation by spherical harmonics $\psi(\phi) = \sum_m \psi_m e^{im\phi}$ which the angle

$\phi = \arccos(\mathbf{f}\cdot\mathbf{t})$. Finally, we get the matrix eigenvalue equation

$$\begin{aligned} E\psi_{m'} &= \sum_m \psi_m[(\frac{m^2(k_BT)^2}{2\kappa} - \frac{f^2}{4kb_0})\delta_{mm'} - \frac{f}{2}(\delta_{m,m'+1} + \delta_{m+1,m'}) \\ &\quad -\frac{f^2}{8kb_0}(\delta_{m,m'+2} + \delta_{m+2,m'})] \end{aligned} \quad (4.25)$$

4.1.2 In Three Dimensions

From the Eq.(4.10) and the Modified Bessel function in three dimension $I(af) = \langle\psi_a|\psi_a\rangle = \frac{4\pi}{af}\sinh(af)$, the variational free energy is

$$\begin{aligned} \frac{\langle\psi_a|\widehat{H}\psi_a\rangle}{\langle\psi_a|\psi_a\rangle} &= -\frac{a^2f^2(k_BT)^2}{8\kappa} + \left(\frac{a^2(k_BT)^2}{8\kappa} - \frac{1}{2kb_0}\right)\frac{f^2I''(af)}{I(af)} \\ &\quad + \left(\frac{a(k_BT)^2}{4\kappa} - 1\right)\frac{fI'(af)}{I(af)} \\ &= \left(\frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0} - f\right)\left(\coth(af) - \frac{1}{af}\right) - \frac{f^2}{2kb_0} \end{aligned} \quad (4.26)$$

To find the variational free energy by minimizing the energy with respect to the parameter a. Set the new parameter $y = af$ then we can write the energy as:

$$\frac{\langle\psi_a|\widehat{H}\psi_a\rangle}{\langle\psi_a|\psi_a\rangle} = \left(\frac{y(k_BT)^2}{4\kappa} + \frac{f^2}{ykb_0} - f\right)\left(\coth(y) - \frac{1}{y}\right) - \frac{f^2}{2kb_0} \quad (4.27)$$

Differentiate the above equation with respect to y

$$\begin{aligned} \frac{\partial E}{\partial y} &= \frac{\partial}{\partial y}\left[\left(\frac{y(k_BT)^2}{4\kappa} + \frac{f^2}{ykb_0} - f\right)\left(\coth(y) - \frac{1}{y}\right) - \frac{f^2}{2kb_0}\right] \\ 0 &= \left(\frac{(k_BT)^2}{4\kappa} - \frac{f^2}{y^2kb_0}\right)\left(\coth(y) - \frac{1}{y}\right) \\ &\quad + \left(\frac{y(k_BT)^2}{4\kappa} + \frac{f^2}{ykb_0} - f\right)\left(-\frac{1}{\sinh^2 y} + \frac{1}{y^2}\right) \end{aligned} \quad (4.28)$$

in case of weak stretching $y \ll 1$ then $\coth(y) \approx \frac{1}{y} + \frac{y}{3} - \frac{y^5}{45} + \ldots$ $\frac{1}{\sinh^2 y} \approx \frac{1}{y} - \frac{y}{6} + \frac{7y^5}{360} + \ldots$and we find that the minimum at $af \approx \left(\frac{2\kappa f}{(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-1}$

then the variational free energy is

$$
\begin{aligned}
E_0 &= \left(\frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0} - f\right)\left(\frac{1}{af} + \frac{af}{3} - \frac{1}{af}\right) - \frac{f^2}{2kb_0} \\
&= \left(\frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0} - f\right)\left(\frac{af}{3}\right) - \frac{f^2}{2kb_0} \\
&= \frac{(af)^2(k_BT)^2}{12\kappa} - \frac{f^2}{6kb_0} - \frac{af^2}{3} \\
&= -\frac{f^2}{6kb_0} - \frac{f}{3}\left(\frac{2\kappa f}{(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-1} \\
&= -\frac{f^2}{6kb_0} - \left(\frac{2\kappa f^2}{3(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-1} \qquad (4.29)
\end{aligned}
$$

From the force-extension relation

$$
\frac{L_f}{L} = -\frac{\partial E_0(f)}{\partial f} \qquad (4.30)
$$

then we will get

$$
\begin{aligned}
\frac{L_f}{L} &= \frac{f}{3kb_0} + \left(\frac{4\kappa f}{3(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-1} \\
&\quad - \left(\frac{2\kappa f^2}{3(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-2}\left(-\frac{8f\kappa}{15kb_0(k_BT)^2}\right) \\
&= \frac{f}{3kb_0} + \left(\frac{4\kappa f}{3(k_BT)^2}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-1} \\
&\quad + \left(\frac{16\kappa^2 f^3}{45kb_0(k_BT)^4}\right)\left(1 - \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right)^{-2} \qquad (4.31)
\end{aligned}
$$

Using the asymtotic expansion $(1+x)^n \approx 1 + nx + \frac{n(n-1)}{2}x^2 + \ldots$

$$
\begin{aligned}
\frac{L_f}{L} &= \frac{f}{3kb_0} + \left(\frac{4\kappa f}{3(k_BT)^2}\right)\left(1 + \frac{4f^2\kappa}{15kb_0(k_BT)^2}\right) \\
&\quad + \left(\frac{16\kappa^2 f^3}{45kb_0(k_BT)^4}\right)\left(1 + \frac{8f^2\kappa}{15kb_0(k_BT)^2}\right) \\
&= \frac{f}{3kb_0} + \frac{4\kappa f}{3(k_BT)^2} + \frac{16\kappa^2 f^3}{45kb_0(k_BT)^4} + \frac{16\kappa^2 f^3}{45kb_0(k_BT)^4} + \frac{128\kappa^3 f^5}{675(kb_0)^2(k_BT)6} \\
&= \frac{f}{3kb_0} + \frac{4\kappa f}{3(k_BT)^2} + \frac{8\kappa^2 f^3}{45kb_0(k_BT)^4}. \qquad (4.32)
\end{aligned}
$$

Then, the force-extension for the weak stretching is

$$\frac{L_f}{L} = \frac{f}{3kb_0} + \frac{4\kappa f}{3(k_BT)^2}\left(1 + \frac{2\kappa f^2}{15kb_0(k_BT)^2}\right) \tag{4.33}$$

In case of strong stretching $y \gg 1$,where $\coth(y) \approx \frac{1+e^{-2y}}{1-e^{-2y}} \approx 1$ and $\frac{1}{\sinh^2 y} \approx \frac{2}{e^y(1-e^{-2y})} \approx \frac{2}{e^y}$.and we find that the minimum at $af \approx 2\left(\frac{\kappa f}{(k_BT)^2}\right)^{1/2}\left(1+\frac{f}{kb_0}\right)^{1/2}$ then the variational free energy is

$$\begin{aligned}
E &= \left(\frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0} - f\right)\left(1 - \frac{1}{af}\right) - \frac{f^2}{2kb_0} \\
&= \frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0} - f - \frac{\kappa}{4(k_BT)^2} - \frac{f^2}{(af)^2kb_0} + \frac{f}{af} - \frac{f^2}{2kb_0} \\
&= -f - \frac{\kappa}{4(k_BT)^2} - \frac{f^2}{2kb_0} + \frac{af(k_BT)^2}{4\kappa} + \frac{f^2}{afkb_0}\left(1 - \frac{1}{af}\right) \\
&= -f - \frac{\kappa}{4(k_BT)^2} - \frac{f^2}{2kb_0} + \frac{(k_BT)^2}{\kappa}\left(\frac{\kappa f}{(k_BT)^2}\right)^{1/2}\left(1 + \frac{f}{kb_0}\right)^{1/2}
\end{aligned} \tag{4.34}$$

From the force-extension relation , then we will get

$$\begin{aligned}
\frac{L_f}{L} &= 1 + \frac{f}{kb_0} - \frac{k_BT}{\sqrt{\kappa}}\frac{\partial\left(\sqrt{f}(1+\frac{f}{kb_0})^{\frac{1}{2}}\right)}{\partial f} \\
&= 1 + \frac{f}{kb_0} - \frac{k_BT}{\sqrt{\kappa}}\left[\frac{1}{2\sqrt{f}}(1+\frac{f}{kb_0})^{\frac{1}{2}} + \frac{\sqrt{f}}{2kb_0}(1+\frac{f}{kb_0})^{\frac{-1}{2}}\right] \\
&= 1 + \frac{f}{kb_0} - \frac{k_BT}{2\sqrt{\kappa f}}\left[(1+\frac{f}{kb_0})^{\frac{1}{2}} + \frac{f}{kb_0}(1+\frac{f}{kb_0})^{\frac{-1}{2}}\right]
\end{aligned} \tag{4.35}$$

This coresponds to the the result for $k \to \infty$ with an effective κ

$$\begin{aligned}
\kappa_{eff} &= \frac{\kappa}{\left[(1+\frac{f}{kb_0})^{1/2} + \frac{f}{kb_0}(1+\frac{f}{kb_0})^{-1/2}\right]^2} \\
&= \kappa\left[1 - \frac{3f}{kb_0}\right] \\
&< \kappa.
\end{aligned} \tag{4.36}$$

We may also find the exact free energy E numerically by diagonalizing H in a representation by spherical harmonics $\psi(\hat{\mathbf{t}}) = \sum_l \psi_l Y_{l0}(\hat{\mathbf{t}})$ where ψ_l are the expansion coefficients and where we have anticipated that the ground state must have axial symmetry and thus no $m = 0$ components. Finally, we get the matrix eigenvalue equation (see more details in appendix C),

$$
\begin{aligned}
E\psi_l &= \sum_{l'} \psi_{l'} \{ [\frac{(k_B T)^2}{2\kappa} l(l+1) \\
&\quad - \frac{f^2}{2kb_0(2l+1)} (\frac{(l+1)^2}{(2l+3)} + \frac{l^2}{(2l-1)})] \delta_{l,l'} \\
&\quad - \frac{f}{((2l'+1)(2l+1))^{1/2}} [(l'+1)\delta_{l,l'+1} + l'\delta_{l,l'-1}] \\
&\quad - \frac{f^2}{2kb_0((2l'+1)(2l+1))^{1/2}} [\frac{(l'+1)(l'+2)}{2l'+3} \delta_{l,l'+2} + \frac{l'(l'-1)}{2l'-1} \delta_{l,l'-2}] \}
\end{aligned}
\tag{4.37}
$$

The lowest eigenvalue E_0 of which is the ground state energy.

The extension versus force curves for Eq. (4.35) and the numerical exact results are shown in Fig. 4.1, Fig 4.2 and Fig 4.3 by using the mathematica program (see more details in appendix D). For all of them, the force range is [10,100], $k_B T = \kappa = 1$(They do not real values, just only easy to show the graphs), k = 100,000 and 10,000, where $k_B T$ has the dimension of energy, κ has the dimension energy times length, k has the dimension energy devided by length squared and f has the dimension energy per length.

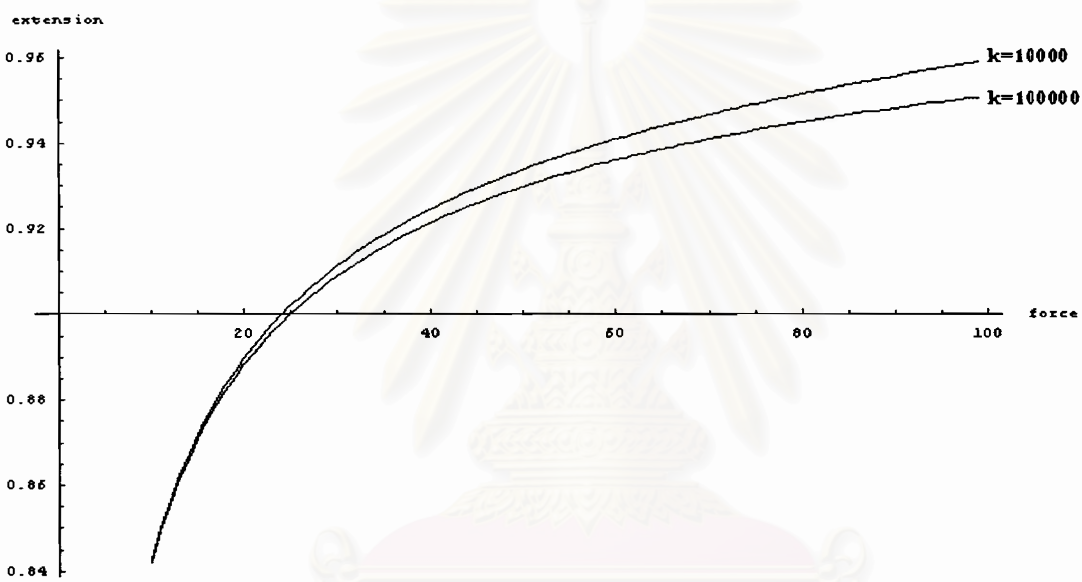

Figure 4.1: Characteristic shapes of the extension versus force in 3D is plotted from Eq. (4.35)

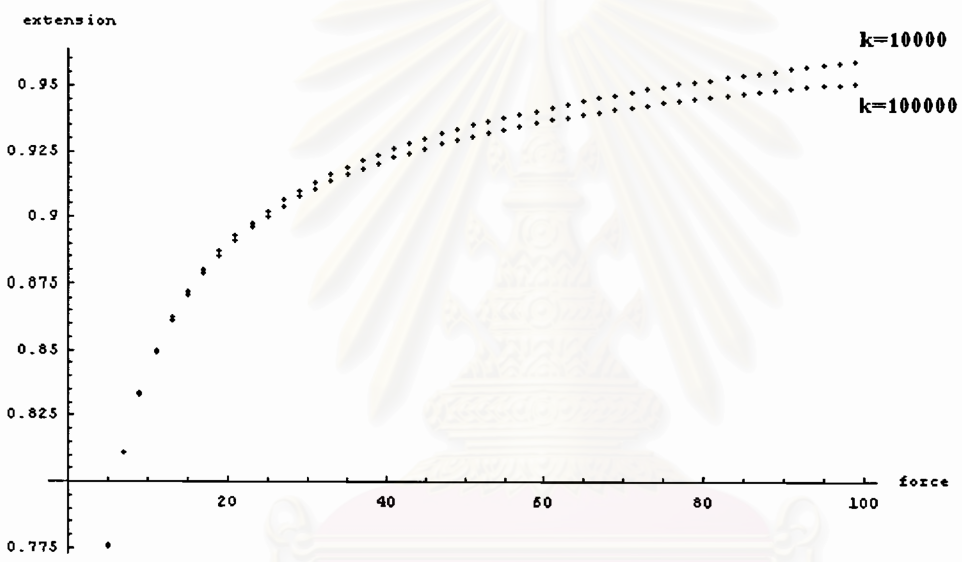

Figure 4.2: Characteristic shapes of the extension versus force in 3D is plotted from Eq. (4.37)

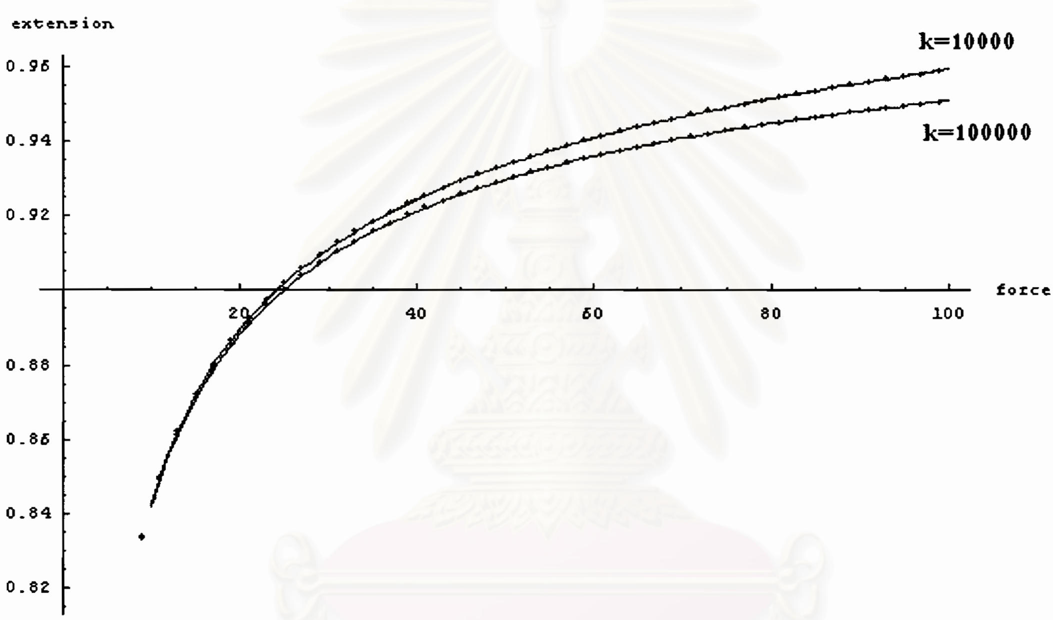

Figure 4.3: The comparison of Fig 4.1 and 4.2

Chapter 5
Discussions and Conclusions

We have studied the effects of the external force when it is applied to the semiflexible chain, the elastic bonds couple directly to the external force. We introduce an extensible harmonic chain model and consider the problem in two cases, strong and weak stretching and solved the problems by using the path integral method and we also solved them by using the variational and numerical method to obtain the partition function. After that, we find the force-extension relation from the thermodynamic relation. In this section we summarize the results, the force-extension relations.

For the strong stretching, $\frac{fL_p}{2T} \gg 1$, we find that the interaction between bond extension and external force can be described by an effective inextensible SHC model with increased stretching force.

$$f_{eff} = f\left(1 + \frac{f}{kb_0}\right). \tag{5.1}$$

We obtain the **force-extension relation,**

$$\frac{L_f}{L} = 1 + \frac{f}{kb_0} - \frac{k_B T}{2\sqrt{\kappa f}}\left(1 + \frac{3}{2}\frac{f}{kb_0}\right)\left(1 + \frac{b_0^2}{4}\frac{f_{eff}}{\kappa}\right)^{\frac{-1}{2}} - \frac{k_B T}{L f_{eff}}\left(1 + \frac{2f}{kb_0}\right) \tag{5.2}$$

The bond extension, finite length and discrete structure affect to the semiflexible polymer.

Inextensible Semiflexible Harmonic Chain

First, the effect from bond extension:

The relative extension in descrete SHC is $\frac{f}{kb_0}$. If $f \ll kb_0$, the chain is an inextensible polymer. The force-extension relation Eq.(5.2) shows in the inextensible limit $k \to \infty$, a rather different f^{-1} saturation of the entropic contribution at very high forces as compareed to the characteristic $f^{-1/2}$ saturation of WLC models that is seen at lower forces.

For $fb_0^2/\kappa \ll 4$, the chain will be inextensible continuous SHC due to the effect from the segment size b_0. The extension relation will be

$$\frac{L_f}{L} = 1 - \frac{k_BT}{2\sqrt{f\kappa}} - \frac{k_BT}{Lf}. \tag{5.3}$$

and for $fb_0^2/\kappa \gg 4$, the chain will be inextensible discrete SHC and the extension relation will be

$$\begin{aligned} \frac{L_f}{L} &= 1 - \frac{k_BT}{fb_0} - \frac{k_BT}{Lf} \\ &= 1 - \frac{k_BT}{f}\left(\frac{1}{b_0} + \frac{1}{L}\right). \end{aligned} \tag{5.4}$$

The behaviour at large force with the f^{-1} saturation recollection of FJC force-extensions. This is due to the fact that the correlation length becomes smaller than the bond length and the force effectively stretched independent discrete bonds as in a FJC model.

Second, the effect from finite length:

The extension relation of an inextensible continuous SHC is shown in Eq.(5.3). For the long chain, L large and $f \gg \frac{\kappa}{L^2}$, the bending rigidities are small, we can neglect the finite size effect the relation will be

$$\frac{L_f}{L} = 1 - \frac{k_BT}{2\sqrt{f\kappa}}. \tag{5.5}$$

That is the well known result of Marko and Siggia (1995)

For L small and $f \ll \frac{\kappa}{L^2}$, the contour length smaller than the correlation length. There are the finite size effect, the last term dominates. The relation will be

$$\frac{L_f}{L} = 1 - \frac{k_BT}{Lf}. \tag{5.6}$$

Therefore, we can write it as $1 - \frac{L_f}{L} \propto f^{-1}$ for strong stretching. It is memory of extension relation of FJC. That means, the chain conduct as a rigid rod. Then we can say, the force stretches a single bonds of length L.

Third, the effect from discrete structure:

The extension relation of an inextensible discrete SHC is shown in Eq.(5.4). For the long chain, $f \gg \frac{\kappa}{L^2}$, the correlation length smaller than the contour length, we can neglect the finite size effect the relation will be

$$\frac{L_f}{L} = 1 - \frac{k_B T}{b_0 f}. \tag{5.7}$$

Note that, Eq. (5.7) is as same as the extension relation of FJC in strong stretching limit. The correlation length become smaller than the bond length. That is the force stretches independent discrete bonds as same as in FJC model.

Extensible Semiflexible Harmonic Chain

The effect from bond extension:

If $f \gg kb_0$, that means the chain is an extensible polymer. The relative extension in discrete SHC $\frac{f}{kb_0}$ dominates or $\frac{L_f}{L} \simeq \frac{f}{kb_0}$.

For $f_{eff} b_0^2/\kappa \gg 4$, the extension relation will be

$$\begin{aligned} \frac{L_f}{L} &= 1 + \frac{f}{kb_0} - \frac{k_B T}{2\sqrt{\kappa f}}\left(1 + \frac{3}{2}\frac{f}{kb_0}\right)\left(\frac{b_0^2}{4}\frac{f_{eff}}{\kappa}\right)^{\frac{-1}{2}} \\ &= 1 + \frac{f}{kb_0} - \frac{k_B T}{b_0 f}\left(1 + \frac{2f}{kb_0}\right)\left(1 + \frac{f}{kb_0}\right)^{-1}. \end{aligned} \tag{5.8}$$

Therefore, we can write it as $1 + \frac{f}{kb_0} - \frac{L_f}{L} \propto f^{-1}$. Comparing with the inextensible case, the behaviour at large force with the f^{-1} saturation recollection of FJC force-extensions with new prefactor b_{eff}, where

$$\begin{aligned} b_{eff} &= b_0\left(1 + \frac{2f}{kb_0}\right)^{-1}\left(1 + \frac{f}{kb_0}\right) \\ &= b_0\left(1 - \frac{f}{kb_0}\right) \end{aligned} \tag{5.9}$$

This is due to the fact that the correlation length becomes smaller than the bond length and the force effectively stretches independent discrete bonds as in a FJC model.

For $f_{eff}b_0^2/\kappa \ll 4$, the chain is continuous extensible SHC. The extension relation will be (in absence of the finite size effect):

$$\frac{L_f}{L} = 1 + \frac{f}{kb_0} - \frac{k_BT}{2\sqrt{\kappa f}}\left(1 + \frac{3}{2}\frac{f}{kb_0}\right). \tag{5.10}$$

Comparing with the extension relation for worm-like chain by Marko and Siggia (1995) and Odijk (1995). The second term is the elastic response of chain and comparing with the inextensible case, the last term gives the reduced bending rigidity κ_{eff} :

$$\begin{aligned} \kappa_{eff} &= \kappa\left(1 + \frac{3}{2}\frac{f}{kb_0}\right)^{-2} \\ &= \kappa\left(1 - \frac{3f}{kb_0}\right) \end{aligned} \tag{5.11}$$

For the **weak stretching,** $\frac{fL_p}{2T} \ll 1$ we obtain the force-extension relation

$$\begin{aligned} \frac{L_f}{L} &= \frac{f}{3kb_0} + \frac{2}{3}\frac{f\widetilde{L}_p}{k_BT}\pounds(\widetilde{L}_p/L) \\ &= \frac{f}{3kb_0} + \begin{cases} \frac{2}{3}\frac{f\kappa}{(k_BT)^2} & \text{for } L \gg L_p \\ \frac{1}{3}\frac{fL}{k_BT} & \text{for } L \ll L_p \end{cases} \end{aligned} \tag{5.12}$$

The extension exhibits the typical linear response behaviour at low forces. The first term is the effect from the elastic bonds and the last term represents the contribution from entropic elasticity and the bending energy. The last line show that the semiflexible polymers exhibit very different behaviour at weak stretching depend on their contour length L which might explain difficulties in fitting experiment results for actin filaments (Liu and Pollack (2002)), which typically have contour lengths comparable or smaller than the persistence L_P or $L \gg L_P$

the response is mostly entropic whereas for $L \ll L_P$ it is governed by bending energy. Note that, for the weak stretching the correlation length of bonds is much larger than the bond length.

For the variational method, the strong stretching $\frac{fL_p}{2T} \gg 1$, in three dimensions, we obtain the **force-extension relation**

$$\frac{L_f}{L} = 1 + \frac{f}{kb_0} - \frac{k_B T}{2\sqrt{\kappa f}} \left[(1 + \frac{f}{kb_0})^{\frac{1}{2}} + \frac{f}{kb_0}(1 + \frac{f}{kb_0})^{\frac{-1}{2}} \right]. \tag{5.13}$$

Again, comparing with the extension relation for worm-like chain by Marko and Siggia (1995) and Odijk (1995). The second term is the elastic response of chain and comparing with the inextensible case, the last term gives the reduced bending rigidity κ_{eff} :

$$\begin{aligned} \kappa_{eff} &= \kappa \left[1 - \frac{3f}{kb_0} \right] \\ &< \kappa. \end{aligned} \tag{5.14}$$

For the **weak stretching,** $\frac{fL_p}{2T} \ll 1$ we obtain the force-extension relation is

$$\frac{L_f}{L} = \frac{f}{3kb_0} + \frac{4\kappa f}{3(k_B T)^2} \left(1 + \frac{2\kappa f^2}{15kb_0(k_B T)^2} \right). \tag{5.15}$$

The relation is linear with the external force.

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Appendices

Appendix A: The Correlation Function

We calculate the correlation function in real space $\langle \phi(s_1)\phi(s_2)\rangle$ by Fourier transforming $G(q)$,

$$
\begin{aligned}
G(s_1 - s_2) \quad : &= \langle \phi(s_1)\phi(s_2)\rangle = \frac{1}{L^2}\sum_{q_1}\sum_{q_2}\left\langle \tilde{\phi}(s_1)\tilde{\phi}(s_2)\right\rangle e^{iq_1 s_1 - iq_2 s_2} \\
&= \frac{1}{L}\sum_{q,|q|<\frac{\pi}{b_0}} G(q)e^{iq(s_1-s_2)} \qquad \text{(A.1)}
\end{aligned}
$$

Then

$$
\begin{aligned}
\left\langle (\phi(s_1) - \phi(s_2))^2 \right\rangle &= 2\langle \phi(s_1)\phi(s_1) - \phi(s_1)\phi(s_2)\rangle \\
&= \frac{1}{L}\sum_{q,|q|<\frac{\pi}{b_0}} G(q)2\left(1 - e^{iq(s_1-s_2)}\right) \\
&= \frac{1}{L}\sum_{q,|q|<\frac{\pi}{b_0}} G(q)2\left(1 - \cos\left(q(s_1 - s_2)\right)\right) \\
&\overset{L\to\infty}{\approx} \int_{\frac{-\pi}{b_0}}^{\frac{\pi}{b_0}} \frac{dq}{2\pi} G(q)2\left(1 - \cos\left(q(s_1 - s_2)\right)\right) \\
&= \int_{\frac{-\pi}{b_0}}^{\frac{\pi}{b_0}} \frac{dq}{2\pi}\frac{T}{\kappa}\frac{b_0^2}{2(1-\cos(qb_0))} 2\left(1 - \cos\left(q(s_1 - s_2)\right)\right) \\
&\overset{b_0\to 0}{=} \int_{-\infty}^{\infty} \frac{dq}{2\pi}\frac{T}{\kappa q^2} 2\left(1 - \cos\left(q(s_1 - s_2)\right)\right) \\
&= \frac{T}{\kappa}(s_1 - s_2). \qquad \text{(A.2)}
\end{aligned}
$$

Appendix B: Fourier Transform

From the fluctuation effective Hamiltonian

$$H_{flu-eff}\left\{\delta\mathbf{t}_\perp(n)\right\} = \sum_{n=1}^{N-1}\frac{\kappa}{2b_0}\left(\,\boldsymbol{\delta}\mathbf{t}_\perp(n+1)-\delta\mathbf{t}_\perp(n)\right)^2+\sum_{n=1}^{N}\frac{b_0 f_{eff}}{2}\delta t_\perp^2(n), \quad \text{(B.1)}$$

where

$$\boldsymbol{\delta}\mathbf{t}_\perp(n+1) = \frac{1}{L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\exp\left\{iq(n+1)b_0\right\}, \quad \text{(B.2)}$$

and

$$\boldsymbol{\delta}\mathbf{t}_\perp(n) = \frac{1}{L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\exp\left\{iqnb_0\right\}, \quad \text{(B.3)}$$

$$\boldsymbol{\delta}\mathbf{t}_\perp(n+1)-\boldsymbol{\delta}\mathbf{t}_\perp(n) = \frac{1}{L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\exp\left\{iqnb_0\right\}\left(\exp\left\{iqb_0\right\}-1\right). \quad \text{(B.4)}$$

Then

$$
\begin{aligned}
\tilde{H}_{flu-eff}\left\{\delta\tilde{\mathbf{t}}_\perp(q)\right\} &= \sum_{n=1}^{N-1}\frac{\kappa}{2b_0}\frac{1}{L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\exp\{iqnb_0\}\left(\exp\{iqb_0\}-1\right) \\
&\quad \frac{1}{L}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(\tilde{q})\exp\{i\tilde{q}nb_0\}\left(\exp\{i\tilde{q}b_0\}-1\right) \\
&\quad +\sum_{n=1}^{N}\frac{b_0f_{eff}}{2}\frac{1}{L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\exp\{iqnb_0\}\frac{1}{L}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(\tilde{q})\exp\{i\tilde{q}nb_0\} \\
&= \sum_{n=1}^{N-1}\frac{\kappa}{2b_0L^2}\sum_{q,|q|\prec\frac{\pi}{b_0}}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\exp\{inb_0(q+\tilde{q})\}\left(\exp\{iqb_0\}-1\right) \\
&\quad \left(\exp\{i\tilde{q}b_0\}-1\right)\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(\tilde{q}) \\
&\quad +\sum_{n=1}^{N}\frac{b_0f_{eff}}{2L^2}\sum_{q,|q|\prec\frac{\pi}{b_0}}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\exp\{inb_0(q+\tilde{q})\}\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(\tilde{q}) \\
&= \frac{\kappa L\delta_{q+\tilde{q},0}}{2b_0^2L^2}\sum_{q,|q|\prec\frac{\pi}{b_0}}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\exp\{inb_0(q+\tilde{q})\}\left(\exp\{iqb_0\}-1\right) \\
&\quad \left(\exp\{i\tilde{q}b_0\}-1\right)\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(\tilde{q}) \\
&\quad +\frac{Lf_{eff}}{2L^2}\sum_{q,|q|\prec\frac{\pi}{b_0}}\sum_{\tilde{q},|\tilde{q}|<\frac{\pi}{b_0}}\exp\{inb_0(q+\tilde{q})\}\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(\tilde{q}) \\
&= \frac{\kappa}{2b_0^2L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\left(\exp\{iqb_0\}-1\right)\left(\exp\{-iqb_0\}-1\right)\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(-q) \\
&\quad +\frac{f_{eff}}{2L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(-q) \\
&= \frac{\kappa}{2b_0^2L}\sum_{q,|q|\prec\frac{\pi}{b_0}}2(1-\cos qb_0)\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(-q) \\
&\quad +\frac{f_{eff}}{2L}\sum_{q,|q|\prec\frac{\pi}{b_0}}\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(-q) \\
&= \sum_{q,|q|\prec\frac{\pi}{b_0}}\left(\frac{\kappa}{b_0^2L}(1-\cos qb_0)+\frac{f_{eff}}{2L}\right)\delta\tilde{\mathbf{t}}_\perp(q)\delta\tilde{\mathbf{t}}_\perp(-q) \\
\tilde{H}_{flu-eff}\left\{\delta\tilde{\mathbf{t}}_\perp(q)\right\} &= \frac{\kappa}{b_0^2L}\sum_{q,|q|\prec\frac{\pi}{b_0},q>0}\left((1-\cos qb_0)+\frac{b_0^2f_{eff}}{2\kappa}\right) \\
&\quad \left(\left(\operatorname{Re}\delta\tilde{\mathbf{t}}_\perp(q)\right)^2+\left(\operatorname{Im}\delta\tilde{\mathbf{t}}_\perp(q)\right)^2\right). \qquad \text{(B.5)}
\end{aligned}
$$

Now we can rewrite every functional integral over the function $\delta\mathbf{t}_\perp(n)$ as an functional integral over the fourier modes

$$
\begin{aligned}
\int D\delta\mathbf{t}_\perp(s) f\left[\delta\mathbf{t}_\perp(s)\right] \quad : \quad &= \left(\prod_{i=1}^{N}\int d\delta\mathbf{t}_\perp(n)\right) f\left[\delta\mathbf{t}_\perp(n)\right] \\
&= \left(\prod_{q,|q|\prec\frac{\pi}{b_0},q>0}^{N}\int d\,\mathrm{Re}\,\delta\tilde{\mathbf{t}}_\perp(q) d\,\mathrm{Im}\,\delta\tilde{\mathbf{t}}_\perp(q)\right)\tilde{f}\left[\delta\tilde{\mathbf{t}}_\perp(q)\right] \\
&= \int D\delta\tilde{\mathbf{t}}_\perp(q)\tilde{f}\left[\delta\tilde{\mathbf{t}}_\perp(q)\right] \qquad \text{(B.6)}
\end{aligned}
$$

where $\tilde{f}\left[\delta\tilde{\mathbf{t}}_\perp(q)\right] = f\left[\delta\mathbf{t}_\perp(s)\right]$ or $\tilde{f}\left[\delta\tilde{\mathbf{t}}_\perp(q)\right] = f\left[\delta\mathbf{t}_\perp(n)\right]$ is the Fourier transformation of a functional f,for example f can be the Boltman-weight:

$$
f[\delta\mathbf{t}_\perp(n)] = \exp\{-H[\delta\mathbf{t}_\perp(n)/k_BT]\} = \exp\{-\tilde{H}[\delta\tilde{\mathbf{t}}_\perp(q)/k_BT]\} = \tilde{f}[\delta\tilde{\mathbf{t}}_\perp(q)] \qquad \text{(B.7)}
$$

with the Hamiltonian $\tilde{H}[\delta\tilde{\mathbf{t}}_\perp(q)]$ from Eq.(B.5). Because we have real and imaginary parts for each $\delta\tilde{\mathbf{t}}_\perp(q)$ but still have N point q for $|q| \prec \frac{\pi}{b_0}$. We will have doubles the number of degrees of freedom. But, for real $\delta\mathbf{t}_\perp(n)$ we have $\delta\tilde{\mathbf{t}}_\perp(q)^* = \delta\tilde{\mathbf{t}}_\perp(-q)$. We cannot integrate over all real and imaginary parts $\delta\tilde{\mathbf{t}}_\perp(q)$ independently. That is the restriction $q > 0$ to one half of the possible wavevectors q.

Appendix C:
The Metrix Equation

From the Hamiltonian in Eq.(4.7)

$$
\begin{aligned}
-H &= \frac{(k_BT)^2}{2\kappa}\mathbf{L}^2 + (\mathbf{f}\cdot\mathbf{t}) + \frac{(\mathbf{f}\cdot\mathbf{t}(s))^2}{2kb_0} \\
&= \frac{(k_BT)^2}{2\kappa}\mathbf{L}^2 + f\cos\theta + \frac{(f\cos\theta)^2}{2kb_0}, \qquad \text{(C.1)}
\end{aligned}
$$

and the spherical harmonics $\psi(\mathbf{t}) = \sum_{\acute{l}} \psi_{\acute{l}} Y_{\acute{l}\,0}(\mathbf{t})$ and $Y_{\acute{l}\,0} = \left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}} P_{\acute{l}}(x)$; $x = \cos\theta$, then

$$
\begin{aligned}
-E\psi(\mathbf{t}) &= -H\psi(\mathbf{t}) \\
E\sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}} P_{\acute{l}}(x) &= -\sum_{\acute{l}}\psi_{\acute{l}}\left[\frac{(k_BT)^2}{2\kappa}\mathbf{L}^2 + fx + \frac{(fx)^2}{2kb_0}\right] Y_{\acute{l}\,0} \qquad \text{(C.2)}
\end{aligned}
$$

Some important relations are

$$
\begin{aligned}
\mathbf{L}^2 Y_{\acute{l}\,0} &= -\acute{l}\left(\acute{l}+1\right) Y_{\acute{l}\,0}, \\
\int_{-1}^{1}\left[P_n^0(x)\right]^2 dx &= \frac{2}{2n+1} \quad ; \quad x = \cos\theta, \\
\int_{-1}^{1} P_n^m(x) P_l^m(x)\,dx &= \frac{\delta_{n,l}}{n+\frac{1}{2}}\frac{(n+m)!}{m\,(n-m)!} \quad , \\
(n+1)\,P_{n+1}(x) &= (2n+1)xP_n(x) - nP_{n-1}(x). \qquad \text{(C.3)}
\end{aligned}
$$

We will get,

$$E\sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}P_{\acute{l}}(x) = -\sum_{\acute{l}}\psi_{\acute{l}}\left[\frac{-(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{2\kappa}+fx+\frac{(fx)^2}{2kb_0}\right]Y_{\acute{l}}$$

$$\int_{-1}^{1}P_l^*(x)E\sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}P_{\acute{l}}(x)dx = \int_{-1}^{1}P_l^*(x)\sum_{\acute{l}}\psi_{\acute{l}}[\frac{(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{2\kappa}$$

$$-fx-\frac{(fx)^2}{2kb_0}]\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}P_{\acute{l}}(x)dx$$

$$E\sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}\int_{-1}^{1}P_l(x)P_{\acute{l}}(x)dx = \sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}\int_{-1}^{1}P_l(x)$$

$$[\frac{(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{2\kappa}-fx-\frac{(fx)^2}{2kb_0}]P_{\acute{l}}(x)dx$$

$$E\sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}\frac{2\delta_{l,\acute{l}}}{2l+1} = \sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}[\frac{(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{2\kappa}$$

$$\cdot\int_{-1}^{1}P_l(x)P_{\acute{l}}(x)dx - f\int_{-1}^{1}P_l(x)xP_{\acute{l}}(x)dx$$

$$-\frac{f^2}{2kb_0}\int_{-1}^{1}P_l(x)x^2P_{\acute{l}}(x)dx]$$

$$E\psi_l\frac{1}{(\pi(2l+1))^{\frac{1}{2}}} = \sum_{\acute{l}}\psi_{\acute{l}}\left(\frac{2\,\acute{l}+1}{4\pi}\right)^{\frac{1}{2}}[\frac{(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{2\kappa}\frac{2\delta_{l,\acute{l}}}{2l+1}$$

$$-f\int_{-1}^{1}P_l(x)\left[\frac{\left(\acute{l}+1\right)P_{\acute{l}+1}(x)}{\left(2\acute{l}+1\right)}+\frac{\acute{l}P_{\acute{l}-1}(x)}{\left(2\acute{l}+1\right)}\right]dx$$

$$-\frac{f^2}{2kb_0}\int_{-1}^{1}P_l(x)\{\frac{\left(\acute{l}+1\right)}{\left(2\acute{l}+1\right)}$$

$$\cdot\left[\frac{\left(\acute{l}+2\right)P_{\acute{l}+2}(x)}{\left(2\acute{l}+3\right)}+\frac{(\acute{l}+1)P_{\acute{l}}(x)}{\left(2\acute{l}+3\right)}\right]$$

$$+\frac{\acute{l}}{\left(2\acute{l}+1\right)}\left[\frac{\acute{l}P_{\acute{l}}(x)}{\left(2\acute{l}-1\right)}+\frac{(\acute{l}-1)P_{\acute{l}-2}(x)}{\left(2\acute{l}-1\right)}\right]\}]dx,$$

$$
\begin{aligned}
E\psi_l \;=\; & \sum_{\acute{l}} \psi_{\acute{l}} \frac{\left(2\,\acute{l}+1\right)^{\frac{1}{2}}(2l+1)^{\frac{1}{2}}}{2}\Big[\frac{(k_BT)^2\acute{l}\left(\acute{l}+1\right)}{\kappa}\frac{\delta_{l,\acute{l}}}{2l+1} \\
& -f\frac{\left(\acute{l}+1\right)}{\left(2\acute{l}+1\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}+1}(x)dx \\
& -\frac{\acute{l}f}{\left(2\acute{l}+1\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}-1}(x)dx \\
& -\frac{f^2\left(\acute{l}+1\right)\left(\acute{l}+2\right)}{2kb_0\left(2\acute{l}+1\right)\left(2\acute{l}+3\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}+2}(x)dx \\
& -\frac{f^2(\acute{l}+1)^2P_{\acute{l}}(x)}{2kb_0\left(2\acute{l}+1\right)\left(2\acute{l}+3\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}}(x)dx \\
& -\frac{f^2\acute{l}^2}{2kb_0\left(2\acute{l}+1\right)\left(2\acute{l}-1\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}}(x)dx \\
& -\frac{f^2\acute{l}(\acute{l}-1)}{2kb_0\left(2\acute{l}+1\right)\left(2\acute{l}-1\right)}\int_{-1}^{1}P_l(x)P_{\acute{l}-2}(x)dx\Big].
\end{aligned}
\tag{C.4}
$$

Finally we obtain

$$
\begin{aligned}
E\psi_l \;=\; & \sum_{l'}\psi_{l'}\Big\{\Big[\frac{(k_BT)^2}{2\kappa}l(l+1) \\
& -\frac{f^2}{2kb_0(2l+1)}\Big(\frac{(l+1)^2}{(2l+3)}+\frac{l^2}{(2l-1)}\Big)\Big]\delta_{l,l'} \\
& -\frac{f}{((2l'+1)(2l+1))^{1/2}}[(l'+1)\delta_{l,l'+1}+l'\delta_{l,l'-1}] \\
& -\frac{f^2}{2kb_0((2l'+1)(2l+1))^{1/2}}\Big[\frac{(l'+1)(l'+2)}{2l'+3}\delta_{l,l'+2}+\frac{l'(l'-1)}{2l'-1}\delta_{l,l'-2}\Big]\Big\}
\end{aligned}
\tag{C.5}
$$

Appendix D: Mathematica Program

For Figture 4.1 Variational method

```
ClearAll[f, k, Ext, fcr]
(* k is kb_0 and fcr is (k_B T)^2/κ *)
T = 1;
fcr = 1;
Ext[k_, f_] = 1 + f/k - 1/(2) *(fcr /f)^(1/2)
               *((1 + f/k)^(1/2) + (f/k)*(1 + f/k)^(-1/2));
gvFit = Plot[Ext[10000, f], {f, 10, 100}, PlotStyle -> {RGBColor[0, 0, 1]},
              Ext[100000, f], {f, 10, 100}, PlotStyle -> {RGBColor[0, 1, 0]},
              AxesLabel->{"force","extension"}];
```

For Figture 4.2 Numerical method

```
ClearAll[g,f,k,a,b,nEmin,T,kappa,i,j,d]
k=10000 (* k is kb_0*)
T=1;
kappa=1;
Dim=11
nEmin= { };
H={ };
x={ };
For[ m=-Dim+1;b={ },m<Dim,m++,
    Do[
```

g[m_,n_] := Which[n==m ,H=Append[H,($\frac{\text{m(m+1)T\^{}2}}{\text{2kappa}}$) -

$(\frac{\text{f\^{}2}}{\text{2k(2m+1)}})$ *$(\frac{\text{(m+1)\^{}2}}{\text{(2m+3)}}+\frac{\text{m\^{}2}}{\text{(2m-1)}})$],

m==n-1 ,H=Append[H,(- f) *$(\frac{\text{n}}{\text{((2n+1)(2m+1))\^{}(1/2)}})$],

m==n+1 ,H=Append[H,$\frac{\text{(-f)*(n+1)}}{\text{((2n+1)(2m+1))\^{}(1/2)}}$],

m==n-2, H=Append[H,$\frac{\text{(-f\^{}2/(2k))*n(n-1)}}{\text{(2n-1)((2n+1)(2m+1))\^{}(1/2)}}$],

m==n+2, H=Append[H,$\frac{\text{(-f\^{}2)*(n+2)(n+1)}}{\text{(2k)(2n+3)((2n+1)(2m+1))\^{}(1/2)}}$],

True , H=Append[H,0]];

g[m,n];a=H ,{n,-Dim+1,Dim-1}

];

b=Append[b,a];

H={ }

]

d=Eigenvalues[-b];

j=D[d,f];

For[f=10, f<101, f+=1, i=Chop[N[Max[j]]]; nEmin=Append[nEmin,{f,i}]];

gnEmin5=ListPlot[nEmin,AxesLabel->{"force","extension"}];

Vitae

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