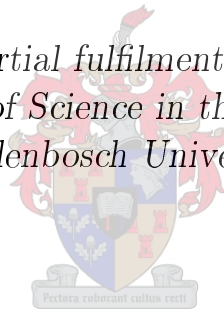


Translocation of a polymer chain under geometric confinement

by

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Declaration

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Abstract

The advent of the synthesis or manufacturing of controlled structures on sub-micron scales as well as experimental developments enabling the investigation of physics in specific biological systems at extremely small length scales underlines the need for dealing with the statistical physics of small systems which are geometrically confined. A typical example of a system for which physical questions can be answered by means of theoretical modelling is the virus, where polymer genetic material is encapsulated in a protein shell.

In this project the role of confinement on polymer chains will be investigated. We investigate how the translocation of polymer from one region to another through a small opening depends on various electrolytic, polymer concentration and wall interaction conditions. This is an extension of the simple, purely entropic, picture in that the interaction terms enter the picture. We employ a variational scheme in deriving our results.

Opsomming

Sowel die moontlikheid van beheerbare sintese of vervaardiging van strukture op sub-mikrometer lengteskale asook die koms van eksperimentele metodes vir die ondersoek van biologiese stelsels op baie klein lengteskale onderstreep hoe nodig dit is om die statistiese fisika van klein stelsels met geometriese beperkings te verstaan. 'n Tipiese voorbeeld waar teoretiese metodes vir fisiese vrae aangewend word is 'n virus, waar die polimeriese genetiese materiaal in 'n proteïen skil beweeg.

In die huidige projek word die rol van 'n spesifieke geometriese beperking op polimeerkettings ondersoek. Ons ondersoek hoe die oorplasing van 'n polimeer deur 'n klein opening van een gebied na die ander deur verskillende elektrolietiese, polimeer-konsentrasie en wandinteraksie eienskappe afhang. Dit is 'n uitbreiding van die eenvoudige, volledig entropiese beeld vir oorplasing deurdat wisselwerkings ingesluit word. 'n Variasiebeginsel word aangewend om die resultate af te lei.

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Chapter 1

Introduction

Polymer theory has become a well developed subject since when S. F. Edwards formulated the problem of a self-avoiding polymer in a continuous model of a Hamiltonian with two terms (13). The first term giving a description of the segments connectivity and the second being the repulsive pseudo potential between segments. This model is a basis of theoretical polymer physics. It is closely linked to the path integral formalism of Quantum Mechanics (19; 22). Thus it enables the application of sophisticated techniques already developed in high energy physics and condensed matter.

P.G. de Gennes took the subject further when he introduced scaling methods in analog to phase transitions. He showed that the self-avoiding polymer problem is a critical phenomenon when the polymer length becomes infinitely long (7).

1.1 Polymer theory

1.1.1 The single phantom polymer

An ensemble of Brownian particles performing a random walk with steps of finite size l is equivalent to the ensemble of random chains (22). We mention this remark to bring the notations and the formal mathematical representation of polymers and their connection with the classical process of diffusion.

The probability density $G(\mathbf{R}(s), \mathbf{R}(s'), s, s')$ for a N step unrestricted random walk is well known to satisfy the Fokker-Planck-Smoluchowski equation

$$\begin{aligned} \partial_s G(\mathbf{R}(s), \mathbf{R}(s'), s, s') - \frac{l^2}{6} \nabla^2 G(\mathbf{R}(s), \mathbf{R}(s'), s, s') \\ = \delta(\mathbf{R}(s) - \mathbf{R}(s')) \delta(s - s') \end{aligned} \quad (1.1)$$

with the solution given by

$$G(\mathbf{R}(s), \mathbf{R}(s'), s, s') = \mathcal{N} \exp \left(-\frac{3}{2l^2} \frac{(\mathbf{R} - \mathbf{R}')^2}{(s - s')} \right). \quad (1.2)$$

Alternatively, this solution can be written in the path integral language using the Feynman-Kac theorem (19) as

$$G(\mathbf{R}(s), \mathbf{R}(s'), s, s') = \mathcal{N} \exp \left\{ -\frac{3}{2l} \int_s^{s'} ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\} \quad (1.3)$$

Our object of interest the free energy functional can then be derived from the partition function

$$Z = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R}(s) \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\} \quad (1.4)$$

where $\int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R}(s)$ denotes the summation over all possible paths of length L . This expression is in the view of a polymer where $L = Nl$ is the chain contour length and l is the Kuhn length, the effective length accounting correlations between chain segments. This corresponds to the phantom polymer since two segments can occupy a single point in space which is an unphysical scenario. However it serves as a good model for chains in certain solvent conditions. Formally

$$\beta H_0 = \frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \quad (1.5)$$

can be taken to represent the Hamiltonian for the phantom chain.

1.1.2 The self-avoiding polymer

In the preceding section we have described random polymers by their counterpart of free Brownian motion. However, polymers should be at the very least be described by self-avoiding random walks. This constraint of self-avoidance ensures that the trajectories do not cross themselves. Accounting for self-avoidance requires a modification of the Hamiltonian H_0 by including an appropriate potential $\int_0^L \int_0^L ds ds' V(\mathbf{R}(s) - \mathbf{R}(s'))$. The choice of a two-body interaction potential as opposed to higher order interaction is due to the physics of these systems. The scenario whereby the segment density is very high such that three segments get close enough to interact is infrequent. This potential must always be repulsive when two segments of the chain come to close contact. It has been realized that (13)

$$\int_0^L \int_0^L ds ds' V(\mathbf{R}(s) - \mathbf{R}(s')) = \frac{v}{2} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \quad (1.6)$$

is a good approximation for this type of interaction. Including this term in the Halmitonian the partition function for a single self-avoiding polymer is

$$Z = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R}(s) \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{v}{2} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right\} \quad (1.7)$$

where we have set $\beta = 1$. This innocent expression turns out to be difficult to evaluate and field theory methods have to be invoked in order to make progress. Without going to great detail we highlight some aspects of the recipe employed (13; 8).

The Hubbard-Stratonovich transformation (21; 8)

$$\begin{aligned} & \exp \left(\frac{v}{2} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right) \\ &= \int \mathcal{D}\phi \exp \left\{ -\frac{i}{l} \int_0^L ds \phi[\mathbf{R}(s)] - \frac{v}{2} \int d\mathbf{r} \phi(\mathbf{r})\phi(\mathbf{r}) \right\} \end{aligned} \quad (1.8)$$

is applied such that the partition function becomes

$$Z = \int \mathcal{D}\phi \int \mathcal{D}\mathbf{R}(s) \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \phi[\mathbf{R}(s)] - \frac{v}{2} \int d\mathbf{r} \phi(\mathbf{r})\phi(\mathbf{r}) \right\}. \quad (1.9)$$

Defining

$$K(\mathbf{R}_i, \mathbf{R}_f; \phi, L) = \int \mathcal{D}\mathbf{R}(s) \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \phi[\mathbf{R}(s)] \right\} \quad (1.10)$$

then this partition function can be written as

$$Z = \int \mathcal{D}\phi K(\mathbf{R}_i, \mathbf{R}_f; \phi, L) \exp \left\{ -\frac{v}{2} \int d\mathbf{r} \phi(\mathbf{r})\phi(\mathbf{r}) \right\}. \quad (1.11)$$

$K(\mathbf{R}_i, \mathbf{R}_f; \phi, L)$ corresponds to the propagator of a particle in an imaginary potential $i\phi$. Therefore it must satisfy (22)

$$\left[\frac{\partial}{\partial s} - \frac{l^2}{6} \nabla^2 + i\phi(\mathbf{R}(s)) \right] K(\mathbf{R}(s), \mathbf{R}(s'); \phi, L) = \delta(\mathbf{R}(s) - \mathbf{R}(s'))\delta(s - s'). \quad (1.12)$$

1.1.3 Collective system – melts and solutions

More often than not polymers exist as a collective thereby forming a polymer solution in a presence of a solvent. Depending on the polymer segment density ρ polymer solutions are usually classified into three regimes, namely, dilute, semidilute and concentrated polymer solutions. Dilute regime is defined by $\rho < \rho^*$, for which ρ^* is the overlap concentration. The overlap concentration is reached when the average bulk density exceeds overlap density inside a polymer coil (31). Since the polymer end-to-end distance R is approximated by the scaling relation $R \sim lN^\nu$. The characteristic concentration ρ^* can then be estimated as

$$\rho^* \approx \frac{N}{R^3} = l^{-3}N^{1-3\nu}. \quad (1.13)$$

This shows that the overlap concentration decreases much more rapidly with increasing chain length and even more so for self-avoiding(swollen) chain in contrast to the flexible (ideal) chain since ν is larger. The crossover to the concentrated regime occurs when the density reaches the local density ρ^{**} inside a Gaussian blob, which is for good solvent conditions given by (31)

$$\rho^{**} \simeq \frac{v}{l^6} \quad (1.14)$$

where v is the second virial coefficient. The semidilute regime falls into the range $\rho^* < \rho < \rho^{**}$.

In this collective many chain system excluded volume interactions are now not only taking place within one single chain, but at an increasing number of contact points from other chains, that is, increasing polymer concentration gives rise to additional excluded volume. On the other hand, the correlations within one chain become more and more destroyed (4). The partition function is no longer dominated by all the self-avoiding paths but by the remaining density fluctuations. It is thus useful to introduce collective variables (4; 43; 42), such as collective densities and construct free energy functionals which contain the collective properties.

We shall now extend the formulation of the preceding section to that of dense monodisperse chain system. Taking into account the multiplicity of the chains the partition function now becomes

$$Z[\mathbf{R}] = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \prod_{\alpha=1}^n \mathcal{D}\mathbf{R}_\alpha(s) \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_\alpha}{\partial s} \right)^2 - \frac{v}{2} \sum_{\alpha, \beta} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')) \right\}. \quad (1.15)$$

This partition function is difficult to evaluate and approximation methods have to be employed. This is done by transforming the problem from chain variables to chains segment density variables also known as collective variables.

1.1.3.1 Defining collective variables

As noted above it is now traditional to transform such a problem formulation to microscopic density variables

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^n \int_0^L ds \delta(\mathbf{r} - \mathbf{R}_\alpha(s)). \quad (1.16)$$

It is convenient to work with the Fourier transform counterpart $\rho_{\mathbf{k}}$. This we define from

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^n \int_0^L ds \int d\mathbf{k} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_\alpha(s))} \quad (1.17)$$

where we have substituted the Fourier representation of the delta function to the last expression (1.16). Switching between continuous and discrete representation under the rule $\int d\mathbf{k} \rightarrow \frac{1}{V} \sum_{\mathbf{k}}$ leads to

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{\alpha=1}^n \int_0^L ds \frac{1}{V} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_\alpha(s))} \\ \rho(\mathbf{r}) &= \sum_{\mathbf{k}} \sum_{\alpha=1}^n \frac{1}{V} \int_0^L ds e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s)} e^{-i\mathbf{k}\cdot\mathbf{r}} \end{aligned} \quad (1.18)$$

of which the final result is

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{\mathbf{k}} \rho_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} \\ \rho_{\mathbf{k}} &\equiv \sum_{\alpha=1}^n \frac{1}{V} \int_0^L ds e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s)}. \end{aligned} \quad (1.19)$$

1.1.3.2 Transformation of the partition function

Our principal goal is to evaluate or at least approximate the generating function Z and as such we want to perform the following transformation

$$Z[\mathbf{R}] \mapsto Z[\rho(\mathbf{r})] = Z[\rho_{\mathbf{k}}]. \quad (1.20)$$

The intent of transforming to the reciprocal space \mathbf{k} is because of the notation and the benefits of Fourier methods. This we achieve by performing a passive transformation

$$Z[\rho_{\mathbf{k}}] = Z[\mathbf{R}] \underbrace{\int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \delta \left(\rho_{\mathbf{k}} - \sum_{\alpha=1}^n \frac{1}{V} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s)} \right)}_{=1} \quad (1.21)$$

which effectively transforms the partition function to density variables. Reminding ourselves that

$$Z[\mathbf{R}] = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \prod_{\alpha=1}^n \mathcal{D}\mathbf{R}_{\alpha}(s) \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{v}{2} \sum_{\alpha, \beta} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s')) \right\}. \quad (1.22)$$

According to equations (1.16)–(1.19) the interaction component of the Hamiltonian is transformed to the density variables as follows

$$\begin{aligned} & \frac{v}{2} \sum_{\alpha, \beta} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s')) \\ &= \frac{v}{2} \sum_{\alpha, \beta} \int_0^L \int_0^L ds ds' \left(\frac{1}{V} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot (\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s'))} \right) \\ &= \frac{v}{2} \sum_{\mathbf{k}} \left(\sum_{\alpha} \frac{1}{V} \int_0^L ds e^{i(-\mathbf{k}) \cdot \mathbf{R}_{\alpha}(s)} \right) \left(\sum_{\beta} \int_0^L ds' e^{i\mathbf{k} \cdot \mathbf{R}_{\beta}(s')} \right) \\ &= \frac{v}{2} V \sum_{\mathbf{k}} \left(\sum_{\alpha} \frac{1}{V} \int_0^L ds e^{i(-\mathbf{k}) \cdot \mathbf{R}_{\alpha}(s)} \right) \left(\sum_{\beta} \frac{1}{V} \int_0^L ds' e^{i\mathbf{k} \cdot \mathbf{R}_{\beta}(s')} \right). \end{aligned} \quad (1.23)$$

Thus the transformed interaction potential is

$$\frac{v}{2} \sum_{\alpha, \beta} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s')) = \frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}}. \quad (1.24)$$

As we shall see later that the recipe that we are following expresses quantities in terms of averages over the Gaussian distribution

$$\int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \prod_{\alpha=1}^n \mathcal{D}\mathbf{R}_\alpha(s) \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_\alpha}{\partial s} \right)^2 \right\}. \quad (1.25)$$

We now turn our attention to transform the delta functional in (1.21) to a more useful form (43)

$$\begin{aligned} & \delta \left(\rho_{\mathbf{k}} - \sum_{\alpha=1} \frac{1}{V} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right) \\ &= \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \exp \left\{ i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \left(\rho_{\mathbf{k}} - \sum_{\alpha=1} \frac{1}{V} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right) \right\} \\ &= \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \exp \left\{ i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{i}{V} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \sum_{\alpha=1} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right\} \end{aligned} \quad (1.26)$$

taking a quadratic order approximation we have

$$\begin{aligned} & \delta \left(\rho_{\mathbf{k}} - \sum_{\alpha=1} \frac{1}{V} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right) \\ & \simeq \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left[1 - \frac{i}{V} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \sum_{\alpha=1} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right. \\ & \quad \left. + \frac{1}{2} \left(\frac{i}{V} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \sum_{\alpha=1} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right)^2 \right] \exp \left\{ i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{\mathbf{k}} \right\} \\ &= \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left[1 - \frac{i}{V} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \sum_{\alpha=1} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s)} \right. \\ & \quad \left. - \frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha, \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' e^{i\mathbf{k} \cdot \mathbf{R}_\alpha(s) + i\mathbf{k}' \cdot \mathbf{R}_\beta(s')} \right] \exp \left\{ i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{\mathbf{k}} \right\}. \end{aligned} \quad (1.27)$$

With this crucial result the partition function can be expressed as

$$\begin{aligned}
 Z[\mathbf{R}] & \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \delta \left(\rho_{\mathbf{k}} - \sum_{\alpha=1} \frac{1}{V} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s)} \right) \\
 & = \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} + i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} \\
 & \quad \left(\int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\} \right. \\
 & \quad \left. - \int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} \left[\frac{i}{V} \sum_{\mathbf{k}, \alpha} \phi_{\mathbf{k}} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s)} \right] \right. \\
 & \quad \left. \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\} \right. \\
 & \quad \left. - \int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} \left[\frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha, \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s) + i\mathbf{k}' \cdot \mathbf{R}_{\beta}(s')} \right] \right. \\
 & \quad \left. \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\} \right) \tag{1.28}
 \end{aligned}$$

$$\begin{aligned}
 & = \mathcal{N} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left[1 - \frac{i}{V} \sum_{\mathbf{k}, \alpha} \phi_{\mathbf{k}} \int_0^L ds \langle e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s)} \rangle_0 \right. \\
 & \quad \left. - \frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha, \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \langle e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}(s) + i\mathbf{k}' \cdot \mathbf{R}_{\beta}(s')} \rangle_0 \right] \\
 & \quad \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} + i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{-\mathbf{k}} \right\}. \tag{1.29}
 \end{aligned}$$

The angular brackets denotes averaging as follows

$$\langle \dots \rangle_0 \equiv \frac{\int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} [\dots] \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\}}{\int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\}} \tag{1.30}$$

where \mathcal{N} is the Gaussian distribution function given by equation (1.25).

Perhaps it is well suited to evaluate \mathcal{N} here. The evaluation follows from the standard result (19) in path integral methods, namely

$$\int_{\mathbf{R},s_0}^{\mathbf{R},s} \mathcal{D}\mathbf{R}(s) e^{-\frac{1}{4D} \int_{s_0}^s ds \dot{\mathbf{R}}^2(s)} = \frac{1}{\sqrt{4\pi D(s-s_0)}} e^{-\frac{(\mathbf{R}-\mathbf{R}_0)^2}{4D(s-s_0)}}. \quad (1.31)$$

It then follows from this result that

$$\begin{aligned} & \int \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \right\} \\ &= \left(\frac{1}{\sqrt{\frac{2}{3}\pi l L}} \right)^{3n} \exp \left\{ -\frac{3}{2lL} \sum_{\alpha} (\mathbf{R}_{\alpha}(L) - \mathbf{R}_{\alpha}(0))^2 \right\}. \end{aligned} \quad (1.32)$$

The next step to complete the evaluation of the generating function Z is then to perform the sums I_1 and I_2 , which we define below, in order to integrate out the ρ and ϕ variables. This is done by rewriting \mathbf{R} in terms of the centre of mass coordinates \mathbf{R}_0 .

$$I_1 \equiv \frac{i}{V} \sum_{\mathbf{k},\alpha} \phi_{\mathbf{k}} \int_0^L ds \langle e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha}(s)} \rangle_0 \quad (1.33)$$

and

$$I_2 \equiv \frac{1}{2V^2} \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \alpha,\beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \langle e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha}(s) + i\mathbf{k}'\cdot\mathbf{R}_{\beta}(s')} \rangle_0. \quad (1.34)$$

As for I_1 in these new relative coordinates we have

$$I_1 = \frac{i}{V} \sum_{\mathbf{k},\alpha} \phi_{\mathbf{k}} \int_0^L ds \langle e^{i\mathbf{k}\cdot(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s))} \rangle_0 \quad (1.35)$$

which is equivalent to

$$\frac{i}{V} \sum_{\mathbf{k},\alpha} \phi_{\mathbf{k}} \int_0^L ds \frac{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} e^{i\mathbf{k}\cdot(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s))} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}$$

$$\begin{aligned}
 &= \frac{i}{V} \sum_{\mathbf{k}, \alpha} \phi_{\mathbf{k}} \int_0^L ds \frac{\int d\mathbf{R}_0 e^{i\mathbf{k} \cdot \mathbf{R}_0} \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} e^{i\mathbf{k} \cdot \mathbf{Y}_{\alpha}(s)} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}} \\
 &= \frac{i}{V} \sum_{\mathbf{k}, \alpha} \phi_{\mathbf{k}} \int_0^L ds \frac{\delta(\mathbf{k}) \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} e^{i\mathbf{k} \cdot \mathbf{Y}_{\alpha}(s)} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}} \\
 &= \frac{i}{V} \sum_{\alpha} \phi_{\mathbf{0}} \int_0^L ds \frac{\int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}} \\
 &= \frac{i \sum_{\alpha} \phi_{\mathbf{0}} \int_0^L ds}{\int d\mathbf{R}_0} \\
 I_1 &= \frac{i nL \phi_{\mathbf{0}}}{V}.
 \end{aligned} \tag{1.36}$$

Then as for I_2 we have

$$I_2 = \frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha, \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k}(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s)) + i\mathbf{k}'(\mathbf{R}_0 + \mathbf{Y}_{\beta}(s'))} \right\rangle_0 \tag{1.37}$$

which we split into two sums one for $\alpha = \beta$ and the other for $\alpha \neq \beta$, that is,

$$\begin{aligned}
 &\frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k}(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s)) + i\mathbf{k}'(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s'))} \right\rangle_0 \\
 &+ \frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha \neq \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k}(\mathbf{R}_{0,\alpha} + \mathbf{Y}_{\alpha}(s)) + i\mathbf{k}'(\mathbf{R}_{0,\beta} + \mathbf{Y}_{\beta}(s'))} \right\rangle_0
 \end{aligned} \tag{1.38}$$

The first sum

$$\begin{aligned}
 & \frac{1}{2V^2} \sum_{\mathbf{k}, \mathbf{k}'_{\alpha}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k}(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s)) + i\mathbf{k}'(\mathbf{R}_0 + \mathbf{Y}_{\alpha}(s'))} \right\rangle_0 \\
 &= \frac{1}{2V^2} \sum_{\mathbf{k}, \mathbf{k}'_{\alpha}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i(\mathbf{k} + \mathbf{k}')\mathbf{R}_0} e^{i\mathbf{k} \cdot \mathbf{Y}_{\alpha}(s) + i\mathbf{k}' \cdot \mathbf{Y}_{\alpha}(s')} \right\rangle_0 \\
 &= \frac{1}{2V^2} \sum_{\mathbf{k}, \mathbf{k}'_{\alpha}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \\
 & \quad \times \frac{\delta(\mathbf{k} + \mathbf{k}') \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} e^{i\mathbf{k} \cdot \mathbf{Y}_{\alpha}(s) + i\mathbf{k}' \cdot \mathbf{Y}_{\alpha}(s')} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}} \\
 &= \frac{1}{2V^2} \sum_{\mathbf{k}_{\alpha}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' \\
 & \quad \times \left[\frac{\int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} e^{i\mathbf{k}(\mathbf{Y}_{\alpha}(s) - \mathbf{Y}_{\alpha}(s'))} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}}{\int d\mathbf{R}_0 \int \prod_{\alpha} \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \sum_{\alpha} \int_0^L ds \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial s} \right)^2 \right\}} \right]. \tag{1.39}
 \end{aligned}$$

If we split the expression inside the parantheses such that it can be expressed in manner as follows

$$\langle K(0, s) \rangle_0 \langle K(s', s) \rangle_0 \langle K(s, L) \rangle_0 \tag{1.40}$$

then the last line then simplifies to

$$\begin{aligned}
 &= \frac{1}{2V^2} \sum_{\mathbf{k}_{\alpha}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' \\
 & \quad \times \frac{\int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial \sigma} \right)^2 + i\mathbf{k}(\mathbf{Y}_{\alpha}(s) - \mathbf{Y}_{\alpha}(s')) \right\}}{\int d\mathbf{R}_0 \int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial \sigma} \right)^2 \right\}} \\
 &= \frac{1}{2V^2} \sum_{\mathbf{k}_{\alpha}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' \frac{\int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left[\left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial \sigma} \right)^2 - i\frac{2l}{3} \mathbf{k} \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial \sigma} \right) \right] \right\}}{\int d\mathbf{R}_0 \int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left(\frac{\partial \mathbf{Y}_{\alpha}}{\partial \sigma} \right)^2 \right\}} \\
 &= \frac{1}{2V^2} \sum_{\mathbf{k}_{\alpha}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' \frac{\int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left[\left(\dot{\mathbf{Y}}_{\alpha} - i\frac{l}{3} \mathbf{k} \right)^2 + \frac{l^2}{9} \mathbf{k}^2 \right] \right\}}{\int d\mathbf{R}_0 \int \mathcal{D}\mathbf{Y}_{\alpha} \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \dot{\mathbf{Y}}_{\alpha}^2 \right\}}. \tag{1.41}
 \end{aligned}$$

Performing a transformation

$$\begin{aligned}\mathbf{X}_\alpha &= \mathbf{Y}_\alpha - i\frac{l}{3}\mathbf{k}\sigma \\ \dot{\mathbf{X}}_\alpha &= \dot{\mathbf{Y}}_\alpha - i\frac{l}{3}\mathbf{k}\end{aligned}\quad (1.42)$$

thereby leading to

$$\begin{aligned}& \frac{1}{2V^2} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' \frac{\int \mathcal{D}\mathbf{X}_\alpha \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \left[\dot{\mathbf{X}}_\alpha^2 + \frac{l^2}{9} \mathbf{k}^2 \right] \right\}}{\int d\mathbf{R}_0 \int \mathcal{D}\mathbf{Y}_\alpha \exp \left\{ -\frac{3}{2l} \int_{s'}^s d\sigma \dot{\mathbf{Y}}_\alpha^2 \right\}} \\ &= \frac{1}{2V^3} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \int_0^L ds \int_0^L ds' e^{-\frac{l}{6} \mathbf{k}^2 |s-s'|} \\ &\approx \frac{n}{2V^3} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \left[\frac{L^2}{1 + \frac{\mathbf{k}^2 L l}{12}} \right].\end{aligned}\quad (1.43)$$

The final step comes from the approximation which reduces the double integral to

$$\int_0^L ds \int_0^L ds' e^{-\frac{l}{6} \mathbf{k}^2 |s-s'|} \simeq \frac{L^2}{1 + \frac{\mathbf{k}^2 L l}{12}} \quad (1.44)$$

the details of which are given in appendix A. Then the second sum is evaluated to

$$\begin{aligned}& \frac{1}{2V^2} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \alpha \neq \beta}} \phi_{\mathbf{k}} \phi_{\mathbf{k}'} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k}(\mathbf{R}_{0,\alpha} + \mathbf{Y}_\alpha(s)) + i\mathbf{k}'(\mathbf{R}_{0,\beta} + \mathbf{Y}_\beta(s'))} \right\rangle_0 \\ &= \frac{1}{2V^2} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \int_0^L ds \left\langle e^{i\mathbf{k}(\mathbf{R}_{0,\alpha} + \mathbf{Y}_\alpha(s))} \right\rangle_0 \sum_{\mathbf{k}'} \phi_{\mathbf{k}'} \int_0^L ds' \left\langle e^{i\mathbf{k}'(\mathbf{R}_{0,\beta} + \mathbf{Y}_\beta(s'))} \right\rangle_0 \\ &= \frac{n^2 - n}{2V^2} \left(\frac{L\phi_0}{V} \right)^2\end{aligned}\quad (1.45)$$

which leads to the conclusion

$$I_2 = \frac{1}{2V^2} \left(\frac{nL\phi_0}{V} \right)^2 + \frac{n}{2V^3} \sum_{\mathbf{k}} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \left[\frac{L^2}{1 + \frac{\mathbf{k}^2 L l}{12}} \right] \quad (1.46)$$

where we approximated $n^2 - n \simeq n^2$ at large n limit. Combining these results

the generating function (1.28) becomes

$$\begin{aligned}
 Z[\rho_{\mathbf{k}}] &= \mathcal{N} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left[1 - \frac{i}{V} \left(\frac{n\phi_{\mathbf{0}}L}{V} \right) - \frac{1}{2V^2} \left(\frac{n\phi_{\mathbf{0}}L}{V} \right)^2 \right. \\
 &\quad \left. - \frac{1}{2V^3} \sum_{\alpha} \phi_{\mathbf{k}} \phi_{-\mathbf{k}} \left[\frac{L^2}{1 + \frac{\mathbf{k}^2 L l}{12}} \right] \right] \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} + i \sum_{\mathbf{k}} \phi_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} \\
 &= \mathcal{N} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left[-\frac{i}{V} \left(\frac{n\phi_{\mathbf{0}}L}{V} \right) - \frac{1}{2V^2} \left(\frac{n\phi_{\mathbf{0}}L}{V} \right)^2 \right] \\
 &\quad \times \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} - \frac{1}{2} \sum_{\mathbf{k}} \left[\left(\frac{nL^2}{V^3} \left(\frac{1}{1 + \frac{\mathbf{k}^2 L l}{12}} \right) \right) \phi_{-\mathbf{k}} \phi_{\mathbf{k}} - i \rho_{-\mathbf{k}} \phi_{\mathbf{k}} \right] \right\}
 \end{aligned} \tag{1.47}$$

where $\mathbf{k} \neq 0$. If we now define the bare structure function as

$$S^0(\mathbf{k}) = \frac{nL^2}{V} \left(\frac{1}{1 + \frac{\mathbf{k}^2 L l}{12}} \right) \tag{1.48}$$

we can then express the generating function as

$$\begin{aligned}
 Z[\rho_{\mathbf{k}}] &= \mathcal{C} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \\
 &\quad \times \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} |\rho_{\mathbf{k}}|^2 - \frac{1}{2} \sum_{\mathbf{k}} \left[\frac{1}{V^2} S^0(\mathbf{k}) |\phi_{\mathbf{k}}|^2 - i \rho_{-\mathbf{k}} \phi_{\mathbf{k}} \right] \right\} \\
 &= \mathcal{C} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \right\} \\
 &\quad \times \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\frac{1}{V^2} S^0(\mathbf{k}) \phi_{-\mathbf{k}} \phi_{\mathbf{k}} - i (\rho_{-\mathbf{k}} \phi_{\mathbf{k}} + \rho_{\mathbf{k}} \phi_{-\mathbf{k}}) \right] \right\}
 \end{aligned} \tag{1.49}$$

where symmetry has been employed in the last line. We are then now in a

position to complete the square and perform the $\phi_{\mathbf{k}}$ integral, that is,

$$\begin{aligned}
 Z[\rho_{\mathbf{k}}] &= \mathcal{C} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left\{ -\frac{v}{2} V \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \right\} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \\
 &\quad \times \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\left(\phi_{\mathbf{k}} - i \frac{V^2}{S^0(\mathbf{k})} \rho_{\mathbf{k}} \right)^* \frac{S^0(\mathbf{k})}{V^2} \left(\phi_{\mathbf{k}} - i \frac{V^2}{S^0(\mathbf{k})} \rho_{\mathbf{k}} \right) + V^2 \frac{\rho_{-\mathbf{k}} \rho_{\mathbf{k}}}{S^0(\mathbf{k})} \right] \right\}
 \end{aligned} \tag{1.50}$$

$$\begin{aligned}
 &= \mathcal{C} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left\{ -\frac{V^2}{2} \sum_{\mathbf{k}} \left[\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right] \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \right\} \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \\
 &\quad \times \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}} \left[\left(\phi_{\mathbf{k}} - i \frac{V^2}{S^0(\mathbf{k})} \rho_{\mathbf{k}} \right)^* \frac{S^0(\mathbf{k})}{V^2} \left(\phi_{\mathbf{k}} - i \frac{V^2}{S^0(\mathbf{k})} \rho_{\mathbf{k}} \right) + V^2 \frac{\rho_{-\mathbf{k}} \rho_{\mathbf{k}}}{S^0(\mathbf{k})} \right] \right\}
 \end{aligned} \tag{1.51}$$

$$\begin{aligned}
 &= \mathcal{C} \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left\{ -\frac{V^2}{2} \sum_{\mathbf{k}} \left[\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right] \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \right\} \\
 &\quad \times \int \prod_{\mathbf{k}} d\tilde{\phi}_{\mathbf{k}} \exp \left\{ -\frac{1}{2V^2} \sum_{\mathbf{k}} S^0(\mathbf{k}) \tilde{\phi}_{-\mathbf{k}} \tilde{\phi}_{\mathbf{k}} \right\}
 \end{aligned} \tag{1.52}$$

$$\begin{aligned}
 &= \mathcal{C}' \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left\{ -\frac{V^2}{2} \sum_{\mathbf{k}} \left[\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right] \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \right\} \\
 Z[\rho_{\mathbf{k}}] &= \mathcal{C}'' \frac{1}{\sqrt{\det \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)}}
 \end{aligned} \tag{1.53}$$

where \mathcal{C}' and \mathcal{C}'' contains the infinite prefactors and factors we are not interested in from the evaluation of the integrals. We have used the identity

$$\int_{\mathbf{R}^N} d\mathbf{y} \exp \left\{ -\frac{1}{2} \mathbf{y}^T \mathbf{A} \mathbf{y} \right\} = \frac{\sqrt{2\pi}^N}{\sqrt{\det(\mathbf{A})}}, \tag{1.54}$$

further upon (1.53) we apply the identity

$$\det \mathbf{B} = \exp \text{Tr} \ln \mathbf{B} \tag{1.55}$$

and finally obtain

$$F \simeq F_0 + \frac{k_B T}{2} \sum_{\mathbf{k}} \ln \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right). \tag{1.56}$$

1.1.3.3 The effective screened potential

The important result of the preceding calculation is the description of the screening phenomenon of the interactions on a single chain that takes place in the system of sufficiently many chains. This result was first formally obtained by Edwards (13). We shall outline its derivation here. This is done by rewriting the interaction term such that we tag one of the chains with a label 1 and apply the so called Random Phase Approximation again. Thus we have

$$\begin{aligned}
 & \frac{v}{2} \sum_{\alpha, \beta}^n \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')) \\
 &= \frac{v}{2} \left[\sum_{\alpha, \beta}^{n-1} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')) + \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) \right. \\
 & \quad \left. + \sum_{\alpha}^{n-1} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_1(s) - \mathbf{R}_\alpha(s')) \right]
 \end{aligned} \tag{1.57}$$

employing the transformation as before in (1.16) and (1.19) results in

$$\begin{aligned}
 Z[\rho_{\mathbf{k}}] \sim & \int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \exp \left[-\frac{V^2}{2} \sum_{\mathbf{k}} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right) \rho_{\cdot\mathbf{k}} \rho_{\mathbf{k}} - \frac{v}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_1(s)} \right. \\
 & \quad \left. - \frac{v}{2} \int_0^L \int_0^L ds ds' \delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) \right]
 \end{aligned} \tag{1.58}$$

employing symmetry we have

$$\begin{aligned}
 & -\frac{V^2}{2} \sum_{\mathbf{k}} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right) \rho_{\cdot\mathbf{k}} \rho_{\mathbf{k}} - \frac{v}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_1(s)} \\
 &= -\frac{V^2}{2} \sum_{\mathbf{k}} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right) \rho_{\cdot\mathbf{k}} \rho_{\mathbf{k}} \\
 & \quad - \frac{v}{4} \left(\sum_{\mathbf{k}} \rho_{\mathbf{k}} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_1(s)} + \rho_{\cdot\mathbf{k}} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_1(s)} \right)
 \end{aligned} \tag{1.59}$$

enabling us to completing a square for the first two terms which then become equivalent to

$$\begin{aligned}
 &= -\frac{V^2}{2} \sum_{\mathbf{k}} \left[\left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{1/2} \rho_{\mathbf{k}} - \frac{v}{2} \left(\left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{-1/2} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_1(s)} \right) \right] \\
 &\quad \times \left[\left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{1/2} \rho_{\mathbf{k}} - \frac{v}{2} \left(\left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{-1/2} \int_0^L ds e^{i\mathbf{k} \cdot \mathbf{R}_1(s)} \right) \right]^* \\
 &\quad + \sum_{\mathbf{k}} \frac{V^2 v^2}{8} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{-1} \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))}.
 \end{aligned} \tag{1.60}$$

Therefore, the first two terms are reduced to

$$\begin{aligned}
 &-\frac{V^2}{2} \sum_{\mathbf{k}} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right) \rho_{-\mathbf{k}} \rho_{\mathbf{k}} - \frac{v}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \int_0^L ds e^{-i\mathbf{k} \cdot \mathbf{R}_1(s)} \\
 &= -\frac{V^2}{2} \sum_{\mathbf{k}} \tilde{\rho}_{-\mathbf{k}} \tilde{\rho}_{\mathbf{k}} + \sum_{\mathbf{k}} \left[\frac{V^2 v^2}{8} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{-1} \right] \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))}.
 \end{aligned} \tag{1.61}$$

This shows that the interactions within the single chain are no longer

$$\sum_{\mathbf{k}} \frac{v}{2} \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))} \tag{1.62}$$

but they become reduced or screened to

$$\sum_{\mathbf{k}} \left[\frac{v}{2} - \frac{V^2 v^2}{8} \left(\frac{v}{V} + \frac{1}{S^0(\mathbf{k})} \right)^{-1} \right] \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))} \tag{1.63}$$

due to the presence of other chains in a melt. Substituting for $S^0(\mathbf{k})$ as given in (1.48) we have the approximation

$$\begin{aligned}
 \Delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) &= \sum_{\mathbf{k}} \left[\frac{v}{2} - \frac{v^2 V^2 / 8}{\frac{v}{V} + \frac{\mathbf{k}^2 l^2}{12\rho}} \right] \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))} \\
 \Delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) &= \sum_{\mathbf{k}} \left[\frac{v}{2} - \frac{v^2 V^2 / 8}{\frac{l^2}{12\rho} (\mathbf{k}^2 + \xi^{-2})} \right] \int_0^L ds ds' e^{i\mathbf{k} \cdot (\mathbf{R}_1(s) - \mathbf{R}_1(s'))}
 \end{aligned} \tag{1.64}$$

where we have set the L dependent term to zero and defined $\rho = nL/V$. If we transform this result back to real space variables we have

$$\begin{aligned} \Delta = & \frac{v}{2} \int_0^L ds ds' \delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) \\ & - \frac{v^2}{8} \left(\frac{12\rho V^2}{l^2} \right) \left(\frac{V}{(2\pi)^3} \right) \int_0^L ds ds' \int d\mathbf{k} \frac{e^{i\mathbf{k}\cdot(\mathbf{R}_1(s) - \mathbf{R}_1(s'))}}{\mathbf{k}^2 + \xi^{-2}}. \end{aligned} \quad (1.65)$$

The Fourier transformation relationship (44).

$$\int d\mathbf{r} \frac{e^{-|\mathbf{R}(s) - \mathbf{R}(s')|/\xi}}{|\mathbf{R}(s) - \mathbf{R}(s')|} e^{i\mathbf{k}\cdot(\mathbf{R}(s) - \mathbf{R}(s'))} = \frac{4\pi}{k^2 + \xi^{-2}} \quad (1.66)$$

allows us to finally obtain,

$$\begin{aligned} \Delta = & \frac{v}{2} \int_0^L ds ds' \delta(\mathbf{R}_1(s) - \mathbf{R}_1(s')) \\ & - \frac{v^2}{8} \left(\frac{12\rho}{l^2} \right) \int_0^L ds \int_0^L ds' \frac{e^{-|\mathbf{R}_1(s) - \mathbf{R}_1(s')|/\xi}}{|\mathbf{R}_1(s) - \mathbf{R}_1(s')|} \end{aligned} \quad (1.67)$$

where $\xi = \xi(\rho^{-1/2})$ is the Edwards screening length which determines the length scale or concentration at which the interactions are important. Beyond this length the chain can progressively be treated as a Gaussian chain.

1.1.4 Adsorption

Generally, polymers exist in confining environments of one form or the other. These environments can be membranes, for example, which can interact with the chain in a variety of ways. In the context of this thesis we shall be interested in adsorption type of interaction in conjunction with polymer translocation under constriction. Under certain physical conditions, polymers can adsorb spontaneously from solution onto a confining surface if the interaction between the polymer and the surface is more favourable than that of a solvent with the surface. In equilibrium, adsorption increases the concentration of the polymers near the surface. The knowledge of conformational states of the polymer at the surface and the polymer monomer density profile near the surface enables the evaluation of physical quantities such as the surface tension (39).

In the literature various models have been reported for equilibrium adsorption. In these models effects of either the nature (liquid or solid) or the geometry of the interface are studied. These are coupled to the nature of the interactions whether they are short or long ranged interactions.

In cases of weak adsorption fluctuations of monomer concentration are of central importance (31). It has been shown (7) that the thickness t of the adsorbed polymer layer is characterized by a divergent power law

$$t \sim (T - T_c)^{-1}$$

However, in the cases of strong adsorption and long ranged attractive surface potentials mean field theory (30) suffices in describing adsorption behavior.

An interesting example of adsorption is that of a polyelectrolyte chain confined into a vesicle. This study well illustrates the physics of adsorption phenomena. When the pH of the solution in the vesicle is altered the vesicle undergoes rupture (41).

1.1.5 Translocation

As mentioned earlier, our study will evolve around translocation upon constriction. We shall briefly review here the background of our study we find relevant. Starting with the definition. Polymer translocation is a stochastic process whereby a chain threads through a pore with a size comparable to the segment of the chain crossing from one side of a membrane under the free energy barrier determined by the configuration partition function (38).

Due to various potential technological applications such as rapid DNA sequencing, gene therapy and controlled drug delivery, polymer translocation has received considerable experimental and theoretical interest in the last decade (38).

The research efforts have increasingly been investigating quantitatively the force driving translocation on physical grounds. Amongst the investigated driving mechanisms is the effect of asymmetry in the solution concentrations on both sides of the membrane (3), and selective adsorption of the membrane (38) and the Brownian ratchet mechanism (37).

The theoretical treatment normally reduces this problem to a one dimensional diffusion process. The translocation coordinate s is considered the only relevant dynamical variable. The central difficulty is to find an appropriate expression for the probability current that correctly reflects the correlated motion of the whole polymer (25). A simplified model is usually adopted upon the assumption that the polymer progression is slow compared to the equilibration period for both polymer strands on both sides of the membrane. Thus the force acting on the translocating segment is taken to be only due to the free energy $F(s)$ barrier of an entropic nature. The dynamics of the translocation coordinate s then follows standard Brownian motion. The Smoluchowski (34) equation can be used with the free energy $F(s)$ playing the role of an external potential.

Under the above mentioned assumption the average passage time τ is found to scale as $\tau \sim \frac{l^2 N^2}{D}$ where l is the Kuhn length and D is the diffusion constant (6). There is controversy around the diffusion constant D . Sung and

Park (38) chose $D \propto N^{-1}$ in analogy to reptation dynamics of a Rouse chain, thus yielding $\tau \propto N^3$ whilst Muthukumar (29) argued that D is not the diffusion coefficient for the whole chain but rather that of the individual segment threading through the pore thus $D \neq D(N)$. On the other hand the equilibration time scales as $\tau \propto N^{2\nu+1}$ (6) where ν is the Flory exponent. This then raises questions on the foundation of the entire approach since the equilibration time in this picture is larger than the translocation time. On the basis of these inconsistencies Metzler and coworker then suggested that anomalous diffusion should be a more suitable description (24). Sakaue (40) took another approach and formulated the problem in the framework of tension propagation dynamics (40; 20).

1.2 Thesis organization

In Chapter 2 we shall study the translocation of a single polymer confined to a semi-infinite space. We first start by a very simplified picture of a phantom polymer to outline the program we will be applying. We model this process by applying the method of images (5) in order to compute the force driving the translocation. Thereafter we introduce the short range interactions of excluded volume type between the polymer segments. In the study of this translocation scenario we introduce a variational calculation to compute the renormalized Kuhn length (17) which we shall further employ in the rest of the chapters. Effectively our scheme is to compute the renormalized Kuhn length of the polymer such that the polymer is viewed as a Markov chain in order to follow the same method as in the phantom polymer to compute the driving force. We apply the afore mentioned methods to a scenario of a charged polymer chain under various solvent conditions. These electrolyte conditions are chosen to be dissimilar on the either side of the wall. We have derived the translocation force under various of these solvent conditions. This force we used to determined how far would the chain thread to a zero force.

In contrast to the hardwall confinement in Chapter 5 we model a scenario whereby one of the walls has an attractive long range potential. We limit the wall interactions to be such that the polymer on the other half of the partition does not interact with the strand on the other side of the wall. We similarly determine how far does the translocation progress under various regimes.

Finally we present the summary of the results and highlight the possible further investigations that we would like to undertake for this long standing problem.

Chapter 2

Phantom chain under hard wall confinement

In this section we shall formulate the ideas that we shall be using later for non-phantom chain models we are interested in. Here we describe the phantom chain model of contour length L translocating through a pore under wall confinement by studying the statistical force f on the segment at the transition point. This force is a function of the free energy F of the chain.

We shall account for electrolytic conditions by using the method of effective step length developed by Edwards and Singh (17). That is the polymer chain is modelled by a Gaussian chain of a renormalized Kuhn length. This effective step length is computed by variational methods. In this chapter we shall not formulate this variational scheme but assume the validity of the approach. We will demonstrate how the role of the effective step length affects the free energy of the chain.

2.1 The free energy

We shall simplify our model by assuming that part of the chain, with contour length L_- , has already threaded to the left side (cis-side) of the confining wall thereby we shall not consider the initial pore targeting process. The total free energy F is given by the combination of the cis-side free energy $F_-(L_-)$ and the trans-side free energy $F_+(L_+)$

$$F = F_-(L - L_+) + F_+(L_+). \quad (2.1)$$

The trans-side free energy F_+ is given by the partition function Z_+ through the relationship

$$F_+ = -k_B T \ln Z_+ \quad (2.2)$$

where Z_+ is given by

$$Z_+ = \int d\mathbf{r} d\mathbf{r}' G_+(\mathbf{r}, \mathbf{r}'; L_+). \quad (2.3)$$

$G_+(\mathbf{r}, \mathbf{r}'; L_+)$ is a probability distribution function satisfying (1.1). The solution for the unconfined chain is given by

$$G(\mathbf{r}, \mathbf{r}'; L_+) = \left(\frac{3}{2\pi N_+ l_+^2} \right)^{\frac{3}{2}} \exp \left(-\frac{3}{2N_+ l_+^2} (\mathbf{r} - \mathbf{r}') \right). \quad (2.4)$$

with the reminder that $L = Nl$. In this model, analogous to the free random flight, we can apply the method of images (5) to determine our probability distribution function $G_+(\mathbf{r}, \mathbf{r}'; L_+)$ for the semi-infinite space confinement. That is,

$$G_+(\mathbf{r}, \mathbf{r}'; L_+) = G(\mathbf{r}, \mathbf{r}'; L_+) - G(\mathbf{r}, -\mathbf{r}'; L_+). \quad (2.5)$$

Setting the starting anchor vector point \mathbf{r}' to $\mathbf{r}' = \langle 0, 0, \epsilon \rangle$ near the wall. The probability distribution function $G_+(\mathbf{r}, \mathbf{r}'; L_+)$ is

$$\begin{aligned} G_+(\mathbf{r}, \mathbf{r}'; L_+) &= [G_z(z, \epsilon; L_+) - G_z(z, -\epsilon; L_+)] G_x(x, 0; L_+) G_y(y, 0; L_+) \\ &= \left(\frac{3}{2\pi N_+ l_+^2} \right) e^{\left(-\frac{3}{2N_+ l_+^2} (x^2 + y^2) \right)} \left[e^{\left(-\frac{3}{2N_+ l_+^2} (z - \epsilon)^2 \right)} - e^{\left(-\frac{3}{2N_+ l_+^2} (z + \epsilon)^2 \right)} \right]. \end{aligned} \quad (2.6)$$

This distribution function inserted in (2.5) then results in (2.3) becoming

$$\begin{aligned} Z_+ &= \left(\frac{3}{2\pi N_+ l_+^2} \right) \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \exp \left(-\frac{3}{2N_+ l_+^2} (x^2 + y^2) \right) \\ &\quad \int_{\epsilon}^{\infty} dz \left[\exp \left(-\frac{3}{2N_+ l_+^2} (z - \epsilon)^2 \right) - \exp \left(-\frac{3}{2N_+ l_+^2} (z + \epsilon)^2 \right) \right] \\ Z_+ &= \sqrt{\frac{\pi l_+^2 N_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{N_+ l_+^2}} \right) \end{aligned} \quad (2.7)$$

or rather in terms of length we have

$$Z_+ = \sqrt{\frac{\pi l_+ L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right). \quad (2.8)$$

Therefore the free energy F_+ of the trans-side follow as

$$F_+ = -k_B T \ln \left[\sqrt{\frac{\pi l_+ L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \right]. \quad (2.9)$$

2.2 Effect of electrolytic conditions on the force

We shall account for electrolytic conditions by using the method of effective step length developed by Edwards and Singh (17). That is the polymer chain is modelled by Gaussian chain of a renormalized Kuhn length. The implicit assumption we shall make is that the wall has no effect on the renormalized step length. This might not be completely accurate.

The second law of thermodynamics (33)

$$F = U - TS \quad (2.10)$$

where U , S and T are the internal energy, temperature and the entropy of the system respectively allows us to calculate the statistical force f as

$$f = -\frac{\partial F}{\partial L}. \quad (2.11)$$

2.2.1 Similar electrolytic conditions

The partition function Z_- of the cis-side is essentially similar in form to that of the trans-side

$$Z_- = \sqrt{\frac{\pi l_-(L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L - L_+)l_-}} \right) \quad (2.12)$$

and thus the cis-side free energy

$$F_- = -k_B T \ln \left\{ \sqrt{\frac{\pi l_-(L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L - L_+)l_-}} \right) \right\} \quad (2.13)$$

with the emphasis on the effective Kuhn length. The partition function of the whole chain is given by the product of the generating function of the polymer strand on the trans and cis-side, with the note that $l = l_+$ under similar electrolytic conditions, is

$$Z = \frac{\pi l_+}{6} \sqrt{L_+(L - L_+)} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+L_+}} \right) \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+(L - L_+)}} \right). \quad (2.14)$$

Therefore the total free energy F follows from this generating function as

$$\begin{aligned}
 F &= -k_B T \ln \left\{ \frac{\pi l_+}{6} \sqrt{L_+(L-L_+)} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+(L-L_+)}} \right) \right\} \\
 F &= -k_B T \ln \left[\frac{\pi l_+}{6} \sqrt{L_+(L-L_+)} \right] \\
 &\quad - k_B T \ln \left[\operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+(L-L_+)}} \right) \right].
 \end{aligned} \tag{2.15}$$

The driving force f follows from (2.11) and is given by

$$\begin{aligned}
 f &= \frac{k_B T}{2} \left\{ \frac{L-2L_+}{L_+(L-L_+)} \right\} \\
 &\quad + k_B T \epsilon \sqrt{\frac{6l_+}{\pi}} \left(\frac{\exp \left\{ -\frac{6\epsilon^2}{l_+(L-L_+)} \right\}}{(L-L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+(L-L_+)}} \right)} - \frac{\exp \left\{ -\frac{6\epsilon^2}{l_+ L_+} \right\}}{L_+^{3/2} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right)} \right).
 \end{aligned} \tag{2.16}$$

The profile of such a force is shown below in Figure 2.1

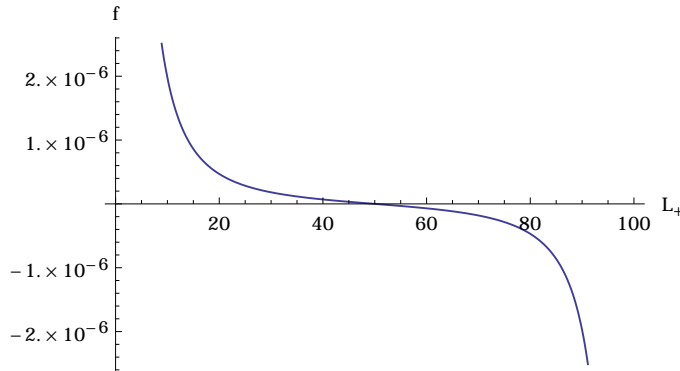


Figure 2.1: Force profile for the phantom chain where the Kuhn lengths are set to 1 unit.

2.2.2 Different electrolytic conditions

We shall now demonstrate in a simple perturbation of the effective step length from the case of equivalent Kuhn lengths how the force profile changes due to such a perturbation. This consequently demonstrates how the translocation is biased. This is essentially the manner we shall be incorporating the effect of solvent conditions on the translocation.

We have seen above that the translocation force is zero when the chain strands are of equivalent length on either side of the partition. We shall determine on this basis, $f(L_+ = \frac{L}{2}) = 0$ when $l_+ = l$, what will be the new chain length distribution on either side of the partition that achieves this. We shall also derive the rates of translocation at least from the force profile gradients. We let the new Kuhn lengths be defined by

$$\begin{aligned} l'_+ &= l_+ + \lambda \\ l'_- &= l_+ - \lambda \end{aligned} \quad (2.17)$$

and we want to determine the length L_+ such that the translocation force is equivalent to zero, that is,

$$f(L_+^0 + \alpha\lambda, l_+ + \lambda, l_+ - \lambda) = f\left(\frac{L}{2} + \alpha\lambda, l_+ + \lambda, l_+ - \lambda\right) = 0 \quad (2.18)$$

which reduces this to the problem of calculating α . Performing a Taylor expansion to the first order produces the constraint that determines α , namely

$$\frac{df\left(\frac{L}{2} + \alpha\lambda, l_+ + \lambda, l_+ - \lambda\right)}{d\lambda} = 0 \quad (2.19)$$

where the function $f(L_+, l, l_+; L)$ is given by

$$\begin{aligned} f(L_+, l, l_+; L) &= \frac{k_B T}{2} \left\{ \frac{L - 2L_+}{L_+(L - L_+)} \right\} \\ &\quad + k_B T \epsilon \sqrt{\frac{6}{\pi}} \left(\frac{\sqrt{l} \exp\left\{-\frac{6\epsilon^2}{l(L-L_+)}\right\}}{(L - L_+)^{3/2} \operatorname{erf}\left(\frac{\sqrt{6}\epsilon}{\sqrt{l(L-L_+)}}\right)} - \frac{\sqrt{l_+} \exp\left\{-\frac{6\epsilon^2}{l_+L_+}\right\}}{L_+^{3/2} \operatorname{erf}\left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+L_+}}\right)} \right) \end{aligned} \quad (2.20)$$

The length distribution is then given by the α equivalent to

$$\begin{aligned} \alpha &= \frac{2L\epsilon \left(\sqrt{3\pi} e^{\frac{12\epsilon^2}{l^2L}} (l^2L - 24\epsilon^2) \operatorname{erf}\left(\frac{2\sqrt{3}\epsilon}{l\sqrt{L}}\right) - 12l\sqrt{L}\epsilon \right)}{l \left(6\sqrt{3\pi}\epsilon e^{\frac{12\epsilon^2}{l^2L}} (8\epsilon^2 - l^2L) \operatorname{erf}\left(\frac{2\sqrt{3}\epsilon}{l\sqrt{L}}\right) + \pi l^3 L^{3/2} e^{\frac{24\epsilon^2}{l^2L}} \operatorname{erf}\left(\frac{2\sqrt{3}\epsilon}{l\sqrt{L}}\right)^2 + 24l\sqrt{L}\epsilon^2 \right)} \end{aligned} \quad (2.21)$$

so that the zero force will be attained when the length distribution is

$$L_+ = L/2 + \alpha\lambda. \quad (2.22)$$

An illustration for $L = 100$ is shown in Figure 2.2. The profile depicting this translocation force for a different Kuhn length is shown in Figure 2.3. This graphical result illustrates the bias on translocation due to the difference in effective step length. Also from this profile we get insight on the rate of translocation due to the bias.

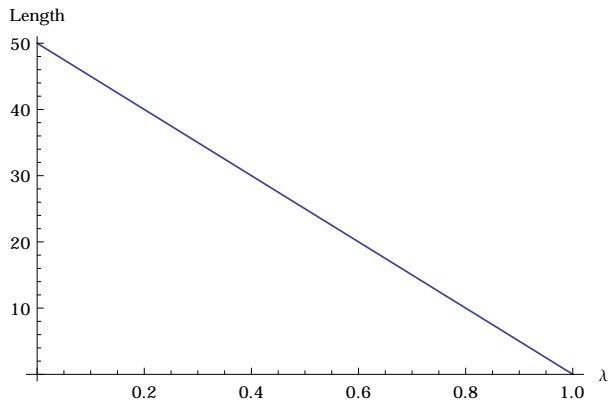


Figure 2.2: The variation of the length that corresponds to the zero force.

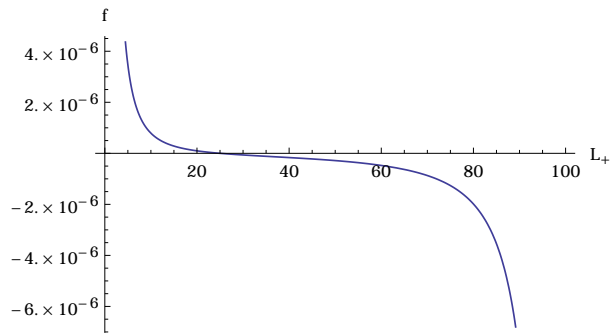


Figure 2.3: Force profile for the phantom chain where the Kuhn lengths for are varied by 0.5 units each set to 1.5 and 0.5 units.

Chapter 3

Self avoiding chain under hard wall confinement

In this chapter we shall further develop what we started with in the last section of the previous chapter. We shall account for the chain interactions on the effective Kuhn length such that we can treat the chain as a Markov chain. This effective Kuhn length is derived by applying a variational method. We shall model a chain in a good solvent translocating under similar geometric confinement introduced earlier to the cis-side with a theta solvent.

3.1 Formulation

The strategy we are following here was pioneered in (17; 15). We will largely be borrowing from this work. We have mentioned in section (1.1.2) that the probability distribution of the self-avoiding polymer, corresponding to good solvent conditions, is of the form

$$G(\mathbf{R}, \mathbf{R}_0; L) = \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - v \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right\}. \quad (3.1)$$

We shall use this distribution to pursue a simpler alternative method to model interacting polymer chains by introducing an effective step length l_1 such that

$$\langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle = Ll_1. \quad (3.2)$$

Hence the task is reduced to calculating this effective Kuhn length. The average square end-to-end distance of the chain on the trans-side is given by

$$\begin{aligned}
 & \langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle \\
 &= \frac{1}{\mathcal{N}} \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 \\
 & \quad \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - v \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right\}
 \end{aligned} \tag{3.3}$$

where

$$\mathcal{N} = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - v \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right\}. \tag{3.4}$$

Introducing the effective Kuhn length l_1 as follows

$$\begin{aligned}
 & \langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle \\
 &= \frac{1}{\mathcal{N}} \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 \\
 & \quad \exp \left\{ -\underbrace{\frac{3}{2l_1} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2}_{H_a} - \overbrace{\left[\frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 + v \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right]}^{H_b} \right\}
 \end{aligned} \tag{3.5}$$

and replacing e^{-H_b} with its series representation

$$e^{-H_b} = 1 - H_b + \frac{H_b^2}{2} + \dots \tag{3.6}$$

where we shall limit ourselves to first order approximation

$$\begin{aligned}
 & \langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle \\
 & \approx \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 e^{-H_a}}{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a}} \\
 & \quad - \frac{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 H_b e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\
 & \quad + \frac{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} H_b e^{-H_a} \right]}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\
 & = Ll_1 + \mathcal{O}(H_b).
 \end{aligned} \tag{3.7}$$

We have used the approximation

$$\frac{1}{1 - H_b} \simeq 1 + H_b + H_b^2 \quad (3.8)$$

to obtain the result in (3.7). Now, in order for (3.2) to be fulfilled we have the constraint $\mathcal{O}(H_b)$ must be equivalent to 0, that is,

$$\begin{aligned} & \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 H_b e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a}}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\ &= \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} H_b e^{-H_a}}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \end{aligned} \quad (3.9)$$

which effectively determines the effective step length l_1 . Splitting H_b to two terms (see expression (3.5)) the first term integral on the left hand side of the above expression is equivalent to

$$\begin{aligned} & \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 H_b^i e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a}}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\ &= \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \left[\frac{\partial}{\partial \lambda} \frac{\int \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 \exp \left\{ \lambda \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ \lambda \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\}} \right]_{\lambda = -3/2l_1} \\ & \quad + \left(\frac{\int \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\}}{\left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\} \right]^2} \right) \\ & \quad \times \int \mathcal{D}\mathbf{R} \left[\int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right] \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right\} \end{aligned} \quad (3.10)$$

$$\begin{aligned} &= \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \frac{\partial}{\partial \lambda} \left(-\frac{3L}{2\lambda} \right) \Big|_{\lambda = 3/2l_1} \\ & \quad + \langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle_1 \left\langle \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \left[\int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right] \right\rangle_1 \\ &= Ll_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) + \langle \mathbf{R}^2 \rangle_1 \left\langle \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \dot{\mathbf{R}}^2 \right\rangle_1. \end{aligned} \quad (3.11)$$

The second term integral on the left hand side of (3.9) with the second term of H_b , H_b^{ii} , is equivalent to

$$\begin{aligned}
 & \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 H_b^{ii} e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a}}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\
 &= v \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} \left[\mathbf{R}^2 \left(\int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \right) \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \dot{\mathbf{R}}^2 \right\} \right] \\
 & \quad \times \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \dot{\mathbf{R}}^2 \right\} \\
 &= \frac{v}{(2\pi)^3} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} \mathbf{R}^2 \int_0^L ds \int_0^L ds' \int d\mathbf{k} \\
 & \quad \times \exp \left\{ i\mathbf{k} \cdot (\mathbf{R}(s) - \mathbf{R}(s')) - \frac{3}{2l_1} \int_0^L ds \dot{\mathbf{R}}^2 \right\} \\
 & \quad \times \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \dot{\mathbf{R}}^2 \right\} \tag{3.12}
 \end{aligned}$$

where we omitted the normalization factor from the second line. Applying the same arguments as in (1.39) and (1.40) and transforming the \mathbf{k} integral to spherical coordinates

$$\int_{\Omega} d\mathbf{k} = \int_0^\pi \int_0^\pi \int_{-\infty}^\infty k^2 \sin \theta d\theta d\phi dk = 4\pi \int_{-\infty}^\infty k^2 dk \tag{3.13}$$

we have (3.11) becoming

$$\begin{aligned}
 & \frac{v}{2\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^\infty dk k^2 e^{\frac{k^2 l_1 |s-s'|}{6}} \left[\langle \mathbf{R}^2 \rangle_1 - \frac{k^2 l_1^2 |s-s'|^2}{9} \right] \\
 &= \frac{v}{2\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^\infty dk k^2 e^{\frac{k^2 l_1 |s-s'|}{6}} \langle \mathbf{R}^2 \rangle_1 \\
 & \quad - \frac{v l_1^2}{18\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^\infty dk k^4 e^{\frac{k^2 l_1 |s-s'|}{6}} |s-s'|^2. \tag{3.14}
 \end{aligned}$$

Therefore, the left hand side of (3.9) is equivalent to

$$\begin{aligned}
 & Ll_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) + \langle \mathbf{R}^2 \rangle_1 \left\langle \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \dot{\mathbf{R}}^2 \right\rangle_1 \\
 & \quad + \frac{v}{2\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^\infty dk k^2 e^{\frac{k^2 l_1 |s-s'|}{6}} \langle \mathbf{R}^2 \rangle_1 \\
 & \quad - \frac{v l_1^2}{18\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^\infty dk k^4 e^{\frac{k^2 l_1 |s-s'|}{6}} |s-s'|^2. \tag{3.15}
 \end{aligned}$$

Similarly, we evaluate the right hand side of (3.9)

$$\begin{aligned}
 & \frac{\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} [\mathbf{R}(L) - \mathbf{R}(0)]^2 e^{-H_a} \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} H_b e^{-H_a}}{\left[\int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R} e^{-H_a} \right]^2} \\
 &= \langle \mathbf{R}^2 \rangle_1 \left[\left\langle \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \dot{\mathbf{R}}^2 \right\rangle_1 \right. \\
 & \quad \left. + \frac{v}{(2\pi)^3} \int_0^L ds \int_0^L ds' \int d\mathbf{k} \left\langle e^{i\mathbf{k} \cdot (\mathbf{R}(s) - \mathbf{R}(s'))} \right\rangle_1 \right] \\
 &= \langle \mathbf{R}^2 \rangle_1 \left\langle \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \dot{\mathbf{R}}^2 \right\rangle_1 \\
 & \quad + \frac{v}{2\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^{\infty} dk k^2 e^{-\frac{k^2 l_1 |s-s'|}{6}} \langle \mathbf{R}^2 \rangle_1.
 \end{aligned} \tag{3.16}$$

Equating between (3.14) and (3.15) results in the cancellation of similar terms and leaves us with

$$\begin{aligned}
 Ll_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) &= \frac{vl_1^2}{18\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^{\infty} dk k^4 e^{-\frac{k^2 l_1 |s-s'|}{6}} |s-s'|^2 \\
 Ll_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) &= 2v \sqrt{\frac{6}{\pi^3}} \sqrt{\frac{L^3}{l_1}}.
 \end{aligned} \tag{3.17}$$

The final step is a result from

$$\begin{aligned}
 & \frac{vl_1^2}{18\pi^2} \int_0^L ds \int_0^L ds' \int_{-\infty}^{\infty} dk k^4 e^{-\frac{k^2 l_1 |s-s'|}{6}} |s-s'|^2 \\
 &= \frac{vl_1^2}{18\pi^2} \int_0^L ds \int_0^L ds' \frac{\partial^2}{\partial \alpha^2} \int_{-\infty}^{\infty} dk e^{-\alpha k^2 |s-s'|} \Big|_{\alpha=l_1/6} \\
 &= \frac{vl_1^2}{18\pi^2} \frac{3\sqrt{\pi}}{4} \left(\frac{6}{l_1} \right)^{5/2} \int_0^L ds \int_0^L ds' |s-s'|^{-1/2} \\
 &= \frac{vl_1^2}{18\pi^2} \frac{3\sqrt{\pi}}{4} \left(\frac{6}{l_1} \right)^{5/2} \int_0^L ds \left[\int_0^s ds' (s-s')^{-1/2} + \int_s^L ds' (s-s')^{-1/2} \right] \\
 &= \frac{vl_1^2}{18\pi^2} \frac{3\sqrt{\pi}}{4} \left(\frac{6}{l_1} \right)^{5/2} \left(\frac{4}{3} \right) L^{3/2} = v \sqrt{\frac{6}{\pi^3}} \sqrt{\frac{L^3}{l_1}}
 \end{aligned} \tag{3.18}$$

Investigating different limits of (3.17), we have in the limit of small v , l_1 approximately equivalent to l . A more interesting limit is when $v < L^{\frac{1}{2}}$ such

that

$$l_1^{\frac{5}{2}} \left(\frac{1}{l} - \frac{1}{l_1} \right) = 2\sqrt{\frac{6}{\pi^3}} v L^{\frac{1}{2}} \quad (3.19)$$

thereby leading to the conclusion that

$$l_1 = 2^{\frac{2}{5}} \left(\frac{6}{\pi^3} \right)^{\frac{1}{5}} l^{\frac{2}{5}} v^{\frac{2}{5}} L^{\frac{1}{5}}.$$

3.2 The free energy

We then approximate from the above results the total free energy of our translocating polymer with a strand on the cis-side having the effective step length $l^{\text{eff}} = l_+$ and corresponding cis-side free energy

$$F_- = -k_B T \ln \left[\sqrt{\frac{\pi l_+(L-L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L-L_+)l_+}} \right) \right]. \quad (3.20)$$

The free energy of the strand on the trans-side having the effective step length

$$l_+^{\text{eff}} = 2^{\frac{2}{5}} \left(\frac{6}{\pi^3} \right)^{\frac{1}{5}} l_+^{\frac{2}{5}} v^{\frac{2}{5}} L^{\frac{1}{5}} \quad (3.21)$$

is approximated as

$$F_+ = -k_B T \ln \left[\sqrt{\frac{\pi l_+^{\text{eff}} L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+^{\text{eff}} L_+}} \right) \right]. \quad (3.22)$$

Therefore the approximate total free energy is

$$F = -k_B T \left\{ \ln \left[\sqrt{\frac{\pi l_+(L-L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L-L_+)l_+}} \right) \right] - \ln \left[\sqrt{\left(\frac{2\pi l_+ v}{6^2} \right)^{2/5} L_+ L^{1/5}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\left(\frac{6}{\pi^3} \right)^{1/5} (2\pi v l_+)^{2/5} L_+ L^{1/5}}} \right) \right] \right\}. \quad (3.23)$$

3.3 The force driving translocation

The force that that will be experienced by the chain segment at the pore follows from (2.11) and is given by

$$f = \frac{1}{2} \left(-\frac{2\alpha\epsilon \exp\left(-\frac{\beta\sqrt[5]{\pi}\epsilon^2}{\sqrt[5]{L}L_+(l_+v)^{2/5}}\right)}{\pi^{2/5}L_+\sqrt{\sqrt[5]{L}L_+(l_+v)^{2/5}}\operatorname{erf}\left(\frac{\alpha\sqrt[10]{\pi}\epsilon}{\sqrt{\sqrt[5]{L}L_+(l_+v)^{2/5}}}\right)} + \frac{2\sqrt{\frac{6}{\pi}}l_+\epsilon e^{\frac{6\epsilon^2}{l_+(L_+-L)}}}{(l_+(L-L_+))^{3/2}\operatorname{erf}\left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+(L-L_+)}}\right)} + \frac{2L_+-L}{L_+(L_+-L)} \right) \quad (3.24)$$

where $\alpha = \sqrt[5]{2}3^{2/5}$ and $\beta = 2^{2/5}3^{4/5}$. This force has the profile depicted in Figure 3.1

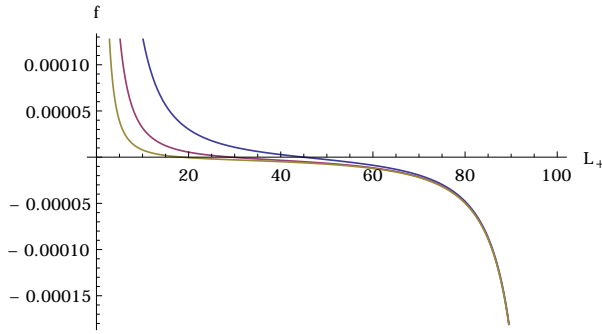


Figure 3.1: The force profile where the strength v is varied from 0.1 represented by the leftmost profile to 60 units represented by the rightmost profile.

Figure 3.1, shows that the chain will thread further upon the increase of the excluded volume strength from 0.1 units to 30 and 20 units for an increased volume strength to respectively, 3 and 60 units. This we find interesting since it demonstrates somewhat the complex relationship between the translocation force and excluded volume interaction strength and hence the translocation time. It is also worthwhile to note the rates of translocation for the different regimes depicted in the same figure.

Chapter 4

Polyelectrolyte chain under hard wall confinement

In this chapter we shall again outline an approximation scheme presented by Muthukumar (28), somewhat similar to that of the preceding chapter, that provides us with limiting laws and analytical interpolation formulas for the renormalized step length for various polyelectrolyte concentrations. We then use these to model the translocation of a single polyelectrolyte chain under similar geometric constraints that we have introduced.

4.1 Collective chain system

The calculation here is built on what we presented in section 1.1.2-3. Our ideal is to determine the effective interaction and effective step length. In order to achieve that we need to undergo the following constructs since these quantities of interest are interrelated. We have already seen that the free energy of the polymer solution takes the following form

$$e^{-\beta F_p} = \frac{1}{n!} \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \prod_{\alpha} \mathcal{D}\mathbf{R}_{\alpha}(s) \exp \left\{ -\frac{3}{2l} \sum_{\alpha}^n \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{1}{2l^2} \sum_{\alpha, \beta}^n \int_0^L \int_0^L ds ds' V(\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s')) \right\} \quad (4.1)$$

where $V(\mathbf{R}_{\alpha}(s) - \mathbf{R}_{\beta}(s'))$ for this model contains not only the excluded volume interactions but also the long range interactions of Coulomb type. The strategy pursued here requires that we perform a Hubbard-Stratonovich transformation as before by introducing an auxiliary field ϕ such that

$$\begin{aligned}
 & \exp \left(\frac{1}{2l^2} \sum_{\alpha, \beta}^n \int_0^L \int_0^L ds ds' V(\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s')) \right) \\
 &= \frac{\int \mathcal{D}\phi \exp \left\{ -\frac{i}{l} \sum_\alpha^n \int_0^L ds \phi[\mathbf{R}_\alpha(s)] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}}{\int \mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}}
 \end{aligned} \tag{4.2}$$

where the operator $V^{-1}(\mathbf{r} - \mathbf{r}')$ is defined such that

$$\int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') V^{-1}(\mathbf{r}' - \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}''). \tag{4.3}$$

The result of this transformation is that the free energy expression (4.1) becomes

$$\begin{aligned}
 e^{-\beta F_p} &= \frac{\mathcal{M}^{-1}}{n!} \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \prod_\alpha \mathcal{D}\mathbf{R}_\alpha(s) \mathcal{D}\phi \left[\exp \left\{ -\frac{3}{2l} \sum_\alpha^n \int_0^L ds \left(\frac{\partial \mathbf{R}_\alpha}{\partial s} \right)^2 \right. \right. \\
 &\quad \left. \left. + \left(-\frac{i}{l} \sum_\alpha^n \int_0^L ds \phi[\mathbf{R}_\alpha(s)] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right) \right\} \right]
 \end{aligned} \tag{4.4}$$

where

$$\mathcal{M} = \int \mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}. \tag{4.5}$$

Proceeding in a similar manner as we did in (1.9) we have

$$K(\mathbf{R}_i, \mathbf{R}_f; \phi, L) \equiv \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \phi[\mathbf{R}(s)] \right\} \tag{4.6}$$

which we shall write in shorthand as $K(\phi)$. This reduces the free energy expression to

$$e^{-\beta F_p} = \frac{1}{n!} \frac{\int \mathcal{D}\phi [K(\phi)]^n \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}}{\int \mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}}. \tag{4.7}$$

If we apply the identity (16)

$$[K(\phi)]^n = n! \int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu K(\phi)] \tag{4.8}$$

where the closed contour C encloses the origin once in the complex plane. The free energy expression becomes

$$e^{-\beta F_p} = \mathcal{M}^{-1} \int \mathcal{D}\phi \left[\int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu K(\phi)] \right] \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}. \quad (4.9)$$

We now introduce an effective distribution function for a labelled chain in order to evaluate these integrals. Let \bar{K} represents this distribution with any pair of its segments undergoing an effective interaction through the field created by all other chains. We denote this effective interaction by Δ which combines both screened Coulomb and excluded volume interactions. Hence \bar{K} can be written as

$$\begin{aligned} \bar{K} &= \frac{\int \mathcal{D}\phi K(\phi) \exp \left\{ \mu K(\phi) - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}}{\int \mathcal{D}\phi \exp \left\{ \mu K(\phi) - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}} \\ &\equiv \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \Delta(\mathbf{R}(s) - \mathbf{R}(s')) \right\}. \end{aligned} \quad (4.10)$$

This then enables the computation of the effective interaction and the related quantities of interest as we see in the next section when we implement this to the free energy expression.

4.1.1 The free energy

The effective distribution function of a labelled chain \bar{K} can be introduced by adding and subtracting $\mu \bar{K}$ in (4.9) yielding

$$\begin{aligned} e^{-\beta F_p} &= \mathcal{M}^{-1} \int \mathcal{D}\phi \left\{ \int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu K(\phi)] \right\} \exp [\mu \bar{K} - \mu \bar{K}] \\ &\quad \times \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\} \\ &= \mathcal{M}^{-1} \int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu \bar{K}] \\ &\quad \times \int \mathcal{D}\phi \exp \left\{ \mu [K(\phi) - \bar{K}] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\}. \end{aligned} \quad (4.11)$$

It is useful to rewrite the auxillary field variable $\phi(\mathbf{r})$ by its Fourier representation

$$\phi(\mathbf{r}) = \phi_0 + \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (4.12)$$

such that the pair interaction term becomes

$$\begin{aligned}
 & \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r})V^{-1}(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r}') \\
 &= \phi_0^2 \int d\mathbf{r} d\mathbf{r}' V^{-1}(\mathbf{r} - \mathbf{r}') \\
 &\quad + \frac{1}{(2\pi)^6} \int d\mathbf{k}' d\mathbf{k} \phi_{\mathbf{k}}\phi_{\mathbf{k}'} \int d\mathbf{r} d\mathbf{r}' V^{-1}(\mathbf{r} - \mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}'} \\
 &= \phi_0^2\Omega V_0^{-1} + \frac{1}{(2\pi)^6} \int d\mathbf{k}' d\mathbf{k} \phi_{\mathbf{k}}\phi_{\mathbf{k}'} \int d\mathbf{r} d\mathbf{r}' V^{-1}(\mathbf{r} - \mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}'} \\
 &= \phi_0^2\Omega V_0^{-1} + \frac{1}{(2\pi)^6} \int d\mathbf{k}' d\mathbf{k} \phi_{\mathbf{k}}\phi_{\mathbf{k}'} \int d\mathbf{r} d\Delta V^{-1}(\Delta)e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}+i\mathbf{k}'\cdot\Delta}
 \end{aligned} \tag{4.13}$$

and finally

$$\int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r})V^{-1}(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r}') = \phi_0^2\Omega V_0^{-1} + \frac{1}{(2\pi)^3} \int d\mathbf{k} \phi_{\mathbf{k}}\phi_{\mathbf{k}}V_k^{-1} \tag{4.14}$$

where we have employed (4.3) to obtain the first term and \mathbf{r} transformed to $\mathbf{r}' + \Delta$. The volume is now represented by Ω . Hence,

$$\begin{aligned}
 & \exp\left\{-F_p + \frac{\Omega V_0 \phi_0^2}{2}\right\} \\
 &= \int_C \frac{d\mu}{2\pi i} \exp[-(n+1)\ln\mu + \mu\bar{K}] \\
 &\quad \times \frac{\int \prod_{\mathbf{k}\neq 0} d\phi_{\mathbf{k}} \exp\left\{\mu[K(\phi) - \bar{K}] - \frac{1}{2} \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \phi_{\mathbf{k}}^2 V_k^{-1}\right\}}{\int \prod_{\mathbf{k}\neq 0} d\phi_{\mathbf{k}} \exp\left(-\frac{1}{2} \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \phi_{\mathbf{k}}^2 V_k^{-1}\right)}.
 \end{aligned} \tag{4.15}$$

This transformation also affects \bar{K} so that it becomes

$$\begin{aligned}
 \bar{K} &= \int \prod_{\mathbf{k}\neq 0} d\phi_{\mathbf{k}} \int \mathcal{D}\mathbf{R} \exp\left\{-\frac{3}{2l} \int_0^L ds \left(\frac{\partial\mathbf{R}}{\partial s}\right)^2\right. \\
 &\quad \left.- \frac{i}{l} \int_0^L ds \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{R}(s)) + \mu K(\phi) - \frac{1}{2} \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \phi_{\mathbf{k}}^2 V_k^{-1}\right\} \\
 &\quad \div \int \prod_{\mathbf{k}\neq 0} d\phi_{\mathbf{k}} \exp\left\{\mu K(\phi) - \frac{1}{2} \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \phi_{\mathbf{k}}^2 V_k^{-1}\right\}.
 \end{aligned} \tag{4.16}$$

In order to turn \bar{K} into a Gaussian function that is amenable to evaluation we need to redefine $K(\phi)$ in a suitable manner. The choice

$$\mu K(\phi) \equiv \mu K(0) - \frac{1}{2} \int_{\mathbf{k}\neq 0} \frac{d^3k}{(2\pi)^3} \mathcal{E}_{\mathbf{k}} V_k^{-1} \phi_{\mathbf{k}}^2 \tag{4.17}$$

fulfills this requirement, where \mathcal{E}_k is an undefined quantity. As a result \bar{K} becomes

$$\begin{aligned} \bar{K} &= \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \int \mathcal{D}\mathbf{R} \\ &\times \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}(s)) \right. \\ &\quad \left. - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} \phi_k^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right\} \\ &\div \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} \phi_k^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right\} \end{aligned} \quad (4.18)$$

where the $\mu K(0)$ terms have cancelled out. Combination of the quadratic terms give us

$$\begin{aligned} \bar{K} &= \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \int \mathcal{D}\mathbf{R} \\ &\times \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}(s)) \right. \\ &\quad \left. - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} (\mathcal{E}_k + 1) V_k^{-1} \phi_k^2 \right\} \\ &\div \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} (\mathcal{E}_k + 1) V_k^{-1} \phi_k^2 \right\}. \end{aligned} \quad (4.19)$$

If we complete the square and evaluate the $\phi_{\mathbf{k}}$ integrals in the similar fashion as in (1.49)-(1.52) we have

$$\begin{aligned} \bar{K} &= \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right. \\ &\quad \left. - \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp(i\mathbf{k}[\mathbf{R}(s) - \mathbf{R}(s')]) \right\} \end{aligned} \quad (4.20)$$

where the Gaussian integrals cancelled out with those of the denominator. It is befitting to define the quantity resulting from the completion of the square in (4.19)

$$\Delta_k \equiv [V_k^{-1} (1 + \mathcal{E}_k)]^{-1} \quad (4.21)$$

or equivalently

$$\Delta_k = V_k (1 + \mathcal{E}_k)^{-1} \quad (4.22)$$

and importantly Edwards and Anderson showed that (12)

$$\Delta_k = \frac{1}{\Omega} \langle \phi_k^2 \rangle \quad (4.23)$$

These two equations are of central importance in the calculation of the quantities we are interested in, namely, the renormalized step length and the effective interaction. The connection to the free energy expression (4.15) follows from the average of (4.17) with the substitution of (4.22)

$$\begin{aligned} \mu \langle K(\phi) \rangle &= \left\langle \mu K(0) - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} \phi_k^2 \right\rangle \\ &= \mu K(0) - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} \langle \phi_k^2 \rangle \\ \mu \langle K(\phi) \rangle &= \mu K(0) - \frac{\Omega}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} \Delta_k. \end{aligned} \quad (4.24)$$

Therefore $\mu [K(\phi) - \langle K(\phi) \rangle]$ in the free energy expression can be expressed as

$$\mu [K(\phi) - \langle K(\phi) \rangle] = -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} (\phi_k^2 - \Omega \Delta_k) \quad (4.25)$$

such that the exponential of the free energy expression is equivalent to

$$\begin{aligned} &\exp \left\{ -F_p + \frac{\Omega V_0 \phi_0^2}{2} \right\} \\ &= \int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu \bar{K}] \\ &\quad \times \frac{\int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \mathcal{E}_k V_k^{-1} (\phi_k^2 - \Omega \Delta_k) - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right\}}{\int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right)} \\ &= \int_C \frac{d\mu}{2\pi i} \exp[-(n+1) \ln \mu + \mu \bar{K}] \\ &\quad \times \frac{\int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} [(\mathcal{E}_k + 1) V_k^{-1} \phi_k^2 - \Omega \mathcal{E}_k V_k^{-1} \Delta_k] \right\}}{\int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right)}. \end{aligned} \quad (4.26)$$

Applying the identity (4.8) again we have

$$\begin{aligned}
 & \exp \left\{ -F_p + \frac{\Omega V_0 \phi_0^2}{2} \right\} \\
 &= \frac{\bar{K}^n \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \left[\frac{\phi_{\mathbf{k}}^2}{\Delta_{\mathbf{k}}} - \Omega \left(1 - \frac{\Delta_{\mathbf{k}}}{V_{\mathbf{k}}} \right) \right] \right\}}{n! \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}}^2 V_{\mathbf{k}}^{-1} \right)} \\
 &= \frac{\bar{K}^n \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \left[\frac{\phi_{\mathbf{k}}^2}{\Delta_{\mathbf{k}}} - \Omega \left(1 - \frac{\Delta_{\mathbf{k}}}{V_{\mathbf{k}}} \right) \right] \right\}}{n! \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \phi_{\mathbf{k}}^2 V_{\mathbf{k}}^{-1} \right)} \quad (4.27)
 \end{aligned}$$

Taking the natural logarithm on both sides gives the free energy expression as

$$\begin{aligned}
 -\beta F_p &= -\frac{\Omega V_0 \phi_0^2}{2} \\
 &+ \ln \left[\frac{\bar{K}^n \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \left[\frac{\phi_{\mathbf{k}}^2}{\Delta_{\mathbf{k}}} - \Omega \left(1 - \frac{\Delta_{\mathbf{k}}}{V_{\mathbf{k}}} \right) \right] \right\}}{n! \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \phi_{\mathbf{k}}^2 V_{\mathbf{k}}^{-1} \right)} \right] \\
 -\beta F_p &= -\frac{\Omega V_0 \phi_0^2}{2} + \ln \left[\frac{\bar{K}^n}{n!} \right] \\
 &+ \ln \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left\{ -\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \left[\frac{\phi_{\mathbf{k}}^2}{\Delta_{\mathbf{k}}} - \Omega \left(1 - \frac{\Delta_{\mathbf{k}}}{V_{\mathbf{k}}} \right) \right] \right\} \\
 &- \ln \int \prod_{\mathbf{k} \neq 0} d\phi_{\mathbf{k}} \exp \left(-\frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \phi_{\mathbf{k}}^2 V_{\mathbf{k}}^{-1} \right) \quad (4.28)
 \end{aligned}$$

evaluating the Gaussian integrals in a similar manner for (1.53) and recombining the logarithm terms gives us

$$\beta F_p = \frac{\Omega V_0 \phi_0^2}{2} - \ln \left[\frac{\bar{K}^n}{n!} \right] - \frac{1}{2} \sum_{\mathbf{k} \neq 0} \left[1 - \frac{\Delta_{\mathbf{k}}}{V_{\mathbf{k}}} \right] - \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \ln \left[\frac{V_{\mathbf{k}}}{\Delta_{\mathbf{k}}} \right]^{-1} \quad (4.29)$$

the free energy from various contributions, namely, the background contribution, the n many effective chains contribution and the fluctuation contribution. This free energy expression takes the similar form to that derived by Vilgis and Borsali (42).

4.2 Isolated polyelectrolyte chain

4.2.1 The Effective interaction

We shall determine the effective interaction Δ by the method of effective step length which we have seen already in Chapter 3. The actual distribution function of the n many chain system

$$G(\phi, \mathbf{R}) = \prod_{\alpha} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_{\alpha}) - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} \right\} \quad (4.30)$$

is approximated by an effective Gaussian distribution

$$G_0(\phi, \mathbf{R}) = \prod_{\alpha} \exp \left\{ -\frac{3}{2} \int_0^L \frac{ds}{l_1} \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\} \\ \equiv \exp[-H_0] \quad (4.31)$$

where l_1 is an effective step length, such that

$$\langle [\mathbf{R}_{\alpha}(L) - \mathbf{R}_{\alpha}(0)]^2 \rangle = Ll_1. \quad (4.32)$$

In a similar construction, as in the previous chapter, we add and subtract the Hamiltonian H_0 to the argument of the exponent of the actual distribution. This gives us

$$G(\phi, \mathbf{R}) = \prod_{\alpha} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{i}{l} \int_0^L ds \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_{\alpha}) - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 V_k^{-1} + \frac{3}{2} \int_0^L \frac{ds}{l_1} \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} - \frac{3}{2} \int_0^L \frac{ds}{l_1} \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 + \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\} \\ G(\phi, \mathbf{R}) \equiv \exp[-H_0 - H_{11} - H_{12} - iH_2] \quad (4.33)$$

where the different terms in the exponent are defined below, namely

$$H_{11} = \frac{3}{2} \sum_{\alpha} \int_0^L ds \left(\frac{1}{l} - \frac{1}{l_1} \right) \left(\frac{\partial \mathbf{R}_{\alpha}}{\partial s} \right)^2 \quad (4.34)$$

$$H_{12} = \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_k^2 (V_k^{-1} - \Delta_k^{-1}) \quad (4.35)$$

$$H_2 = \frac{1}{l} \sum_{\alpha} \int_0^L ds \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \phi_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_{\alpha}). \quad (4.36)$$

The definition of the effective interaction Δ_k was established in (4.23) as

$$\Delta_k = \frac{1}{\Omega} \langle \phi_k^2 \rangle. \quad (4.37)$$

According to the distribution function (4.33) we have

$$\begin{aligned} \Delta_k &= \frac{1}{\Omega} \frac{\int \mathcal{D}\phi \mathcal{D}\mathbf{R} \phi_k^2 P(\phi, \mathbf{R})}{\int \mathcal{D}\phi \mathcal{D}\mathbf{R} P(\phi, \mathbf{R})} \\ &= \langle \phi_k^2 \rangle_0 + \left\{ \langle \phi_k^2 (-H_{11} - H_{12} + h) \rangle_0 \right. \\ &\quad \left. - \langle \phi_k^2 \rangle_0 \langle \phi_k^2 (-H_{11} - H_{12} + h) \rangle_0 + \dots \right\} \end{aligned} \quad (4.38)$$

$$(4.39)$$

where the identity we employed in (3.8) has been invoked. One should perhaps stress that the averaging is over the effective (renormalized step length) Gaussian distribution of (4.31). Further, h is defined as

$$h \equiv \sum_{j=2,4}^{\infty} \frac{(-1)^{\frac{j}{2}} H_2^j}{j!}. \quad (4.40)$$

If we approximate Δ_k by the zeroth term $\langle \phi_k^2 \rangle_0$ then we have the constraint from the next two terms in (4.39)

$$\langle \phi_k^2 (-H_{11} - H_{12} + h) \rangle_0 - \langle \phi_k^2 \rangle_0 \langle \phi_k^2 (-H_{11} - H_{12} + h) \rangle_0 = 0 \quad (4.41)$$

resulting in

$$\langle \phi_k^2 (H_{12} - h) \rangle_0 = \langle \phi_k^2 \rangle_0 \langle \phi_k^2 (H_{12} - h) \rangle_0 \quad (4.42)$$

since H_{11} is independent of ϕ_k as listed in (4.32). The derivation of the effective interaction Δ_k essentially rests upon this constraint. The problem is then reduced to the evaluation of the above expression.

We start by evaluating the left hand $\langle \phi_k^2(H_{12} - h) \rangle_0$.

$$\begin{aligned}
 & \langle \phi_k^2(H_{12} - h) \rangle_0 \\
 &= \frac{\int \mathcal{D}\phi \mathcal{D}\mathbf{R} \phi_k^2(H_{12} - h) \exp[-H_0]}{\mathcal{D}\phi \mathcal{D}\mathbf{R} \exp[-H_0]} \\
 &= \int \mathcal{D}\phi \mathcal{D}\mathbf{R} \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 (V_\mu^{-1} - \Delta_\mu^{-1}) - h \right] \\
 & \quad \times \exp \left\{ -\frac{3}{2} \sum_\alpha \int_0^L \frac{ds}{l_1} \left(\frac{\partial \mathbf{R}_\alpha}{\partial s} \right)^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\} \\
 & \quad \div \mathcal{D}\phi \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \sum_\alpha \int_0^L \frac{ds}{l_1} \left(\frac{\partial \mathbf{R}_\alpha}{\partial s} \right)^2 - \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}
 \end{aligned} \tag{4.43}$$

factoring the chain variable components leaves us with

$$\begin{aligned}
 & \langle \phi_k^2(H_{12} - h) \rangle_0 \\
 &= \frac{1}{\Omega} \frac{\int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 (V_\mu^{-1} - \Delta_\mu^{-1}) - h \right] \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}}{\mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}}
 \end{aligned} \tag{4.44}$$

Without going to the details of pictorial representation of h , the contribution from all terms of h upon configurational average is defined to be (28)

$$h \rightarrow -\frac{1}{2}\rho \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 \zeta_\mu \tag{4.45}$$

where

$$\zeta_\mu = g(\mu) - \beta g(\mu) \int \frac{d^3\nu}{(2\pi)^3} \zeta_{\mu+\nu} \Delta_{-\nu} g(\nu) \tag{4.46}$$

with $g(\mu)$ given by

$$g(\mu) \equiv \frac{6}{\mu^2 l_1 l}. \tag{4.47}$$

Applying the fundamental result (4.45) to (4.44) then we have

$$\begin{aligned}
 & \langle \phi_k^2(H_{12} - h) \rangle_0 \\
 &= \frac{\mathcal{W}^{-1}}{\Omega} \int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 (V_\mu^{-1} - \Delta_\mu^{-1}) + \frac{1}{2} \rho \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 \zeta_\mu \right] \\
 & \quad \times \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\} \\
 &= \frac{\mathcal{W}^{-1}}{\Omega} \int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 (V_\mu^{-1} - \Delta_\mu^{-1} + \rho \zeta_\mu) \right] \\
 & \quad \times \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}
 \end{aligned} \tag{4.48}$$

where

$$\mathcal{W}^{-1} = \mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}. \tag{4.49}$$

A shorthand definition of the quantity in braces

$$F_\mu = V_\mu^{-1} - \Delta_\mu^{-1} + \rho \zeta_\mu \tag{4.50}$$

allows us to turn the integral into a generating function as we outline below

$$\begin{aligned}
 & \langle \phi_k^2(H_{12} - h) \rangle_0 \\
 &= \frac{1}{\Omega} \frac{\int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 F_\mu \right] \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}}{\mathcal{D}\phi \exp \left\{ -\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 \Delta_k^{-1} \right\}} \\
 &= \left[\frac{1}{\Omega} \frac{\int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 F_\mu \right] \times}{\mathcal{D}\phi \exp \left\{ -\left[\frac{\lambda}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 F_k + \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} - F_k) \right] \right\}} \right. \\
 & \quad \left. \exp \left\{ -\left[\frac{\lambda}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 F_k + \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} - F_k) \right] \right\} \right]_{\lambda=1}.
 \end{aligned} \tag{4.52}$$

Now, defining

$$z(\lambda) = \left[\frac{\lambda}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 F_k + \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} - F_k) \right] \tag{4.53}$$

$$z(\lambda) = \frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} + (\lambda - 1)F_k). \tag{4.54}$$

The expression (4.52), in a similar fashion to (3.10), simplifies to the desired result

$$\begin{aligned}
 & \langle \phi_k^2(H_{12} - h) \rangle_0 \\
 &= \left[\frac{1 \int \mathcal{D}\phi \phi_k^2 \left[\frac{1}{2} \int_{\mu \neq 0} \frac{d^3\mu}{(2\pi)^3} \phi_\mu^2 F_\mu \right] e^{-z(\lambda)}}{\int \mathcal{D}\phi e^{-z(\lambda)}} \right]_{\lambda=1} \\
 &= -\partial_\lambda \left[\frac{1 \int \mathcal{D}\phi \phi_k^2 e^{-z(\lambda)}}{\int \mathcal{D}\phi e^{-z(\lambda)}} \right] + \langle \phi_k^2 \rangle_0 \langle \phi_k^2(H_{12} - h) \rangle_0. \quad (4.55)
 \end{aligned}$$

The quantity in the brackets is given by

$$\begin{aligned}
 & \frac{1 \int \mathcal{D}\phi \phi_k^2 e^{-\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} + (\lambda-1)F_k)}}{\int \mathcal{D}\phi e^{-\frac{1}{2} \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \phi_k^2 (\Delta_k^{-1} + (\lambda-1)F_k)}} \\
 &= \frac{1}{\Omega} \frac{\frac{\delta}{\delta \mu_{\mathbf{k}}} \int \mathcal{D}\phi e^{-\frac{1}{2} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \mu_{k'} \phi_{k'}^2}}{\int \mathcal{D}\phi e^{-\frac{1}{2} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \mu_{k'} \phi_{k'}^2}} \\
 & \quad (4.56)
 \end{aligned}$$

following the same procedure as in (1.50), (4.56) reduces to

$$\begin{aligned}
 & \frac{1}{\Omega} \frac{\frac{\delta}{\delta \mu_{\mathbf{k}}} e^{-\frac{\Omega}{2} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \ln \mu_{k'}}}{e^{-\frac{\Omega}{2} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \ln \mu_{k'}}} \\
 &= -\frac{1}{2} \frac{\delta}{\delta \mu_{\mathbf{k}}} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \ln \mu_{k'} \\
 &= -\frac{1}{2} \int_{\mathbf{k}' \neq 0} \frac{d^3k'}{(2\pi)^3} \mu_{k'}^{-1} \delta(k' - k) \\
 &= -\frac{1}{2} [\Delta_k^{-1} + (\lambda - 1)F_k]^{-1}. \quad (4.57)
 \end{aligned}$$

Therefore,

$$\langle \phi_k^2(H_{12} - h) \rangle_0 - \langle \phi_k^2 \rangle_0 \langle \phi_k^2(H_{12} - h) \rangle_0 = \partial_\lambda [\Delta_k^{-1} + (\lambda - 1)F_k]^{-1} \quad (4.58)$$

where λ is set to unity thereafter. Equation (4.41) requires that the right hand side is equated to zero which implies $F_k = 0$. According to (4.50) we have

$$V_k^{-1} - \Delta_k^{-1} + \rho \zeta_k = 0 \quad (4.59)$$

giving us the quantity of interest

$$\Delta_k = \frac{V_k}{1 + \rho V_k \zeta_k(\Delta_k, l_1)}. \quad (4.60)$$

Vilgis and Borsali (42) showed that for the system under consideration

$$V_k = \left(w + \frac{w_c}{k^2 + \kappa^2} \right) \quad (4.61)$$

where w, w_c and κ are respectively the excluded volume strength, Coulomb strength and the Debye screening length. Thus the effective interaction is given by

$$\Delta_k = \frac{\left(w + \frac{w_c}{k^2 + \kappa^2} \right)}{1 + \rho \left(w + \frac{w_c}{k^2 + \kappa^2} \right) \zeta_k(\Delta_k, l_1)}. \quad (4.62)$$

4.2.2 The Effective step length

Our primary goal has been to determine the renormalized step length under various salt and concentration regimes. This we pursue in this section with a construction closely similar to that of Chapter 3 but for more general type of interactions presented in (26). The distribution function of the labeled chain

$$\bar{K} = \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp(i\mathbf{k}[\mathbf{R}(s) - \mathbf{R}(s')]) \right\}$$

as in (3.5) then becomes

$$\begin{aligned} \bar{K} = \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2l_1} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_1} \right) \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp(i\mathbf{k}[\mathbf{R}(s) - \mathbf{R}(s')]) \right\}. \end{aligned} \quad (4.63)$$

Writing $\mathbf{R}(s)$ in its Fourier representation

$$\mathbf{R}(s) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q \exp(iqs) \quad (4.64)$$

leads to

$$\begin{aligned}
 & \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \\
 &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \int_0^L ds i^2 q q' \mathbf{R}_q \mathbf{R}_{q'} \exp(i(q+q')s) \\
 &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} \int_{-\infty}^{\infty} dq' i^2 q q' \mathbf{R}_q \mathbf{R}_{q'} \delta(q+q') \\
 &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} q^2 \mathbf{R}_q \mathbf{R}_{-q} = \int_{-\infty}^{\infty} \frac{dq}{2\pi} q^2 \mathbf{R}_q \mathbf{R}_q^* \\
 &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} q^2 \mathbf{R}_q^2.
 \end{aligned} \tag{4.65}$$

Therefore, the generating function becomes

$$\begin{aligned}
 \bar{K} &= \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right. \\
 &\quad - \left. \left\{ \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right. \right. \\
 &\quad \left. \left. + \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \Delta_k \right. \right. \\
 &\quad \left. \left. \times \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q \exp(iqs) - \exp(iqs') \right] \right\} \right\} \\
 \bar{K} &= \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - X \right\}
 \end{aligned} \tag{4.66}$$

where $g(q) \equiv l_1/q^2$ and X is defined by

$$\begin{aligned}
 X &\equiv \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \\
 &\quad + \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3k}{(2\pi)^3} \Delta_k \\
 &\quad \times \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q \exp(iqs) - \exp(iqs') \right].
 \end{aligned} \tag{4.67}$$

In order to make progress from this point onward we employ the maximum entropy condition (33)

$$\frac{1}{k_B T} \frac{\delta S}{\delta g(q)} = 0 \quad \text{where} \quad S = k_B \ln \bar{K} \tag{4.68}$$

at equilibrium. A key construct to this program is the inequality relation

$$\langle \exp(-x) \rangle \geq \exp \langle -x \rangle \tag{4.69}$$

that we apply to the generating function (4.66) with the consequence

$$\begin{aligned} & \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - X \right\} \\ & \geq \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - \langle X \rangle_g \right\} \end{aligned} \quad (4.70)$$

where

$$\langle X \rangle_g = \frac{\int \mathcal{D}\mathbf{R} X \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}. \quad (4.71)$$

The entropy function is obtained by taking the logarithm on both sides such that

$$\begin{aligned} & k_B \ln \left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - X \right\} \right] \\ & \geq k_B \ln \left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - \langle X \rangle_g \right\} \right] \end{aligned} \quad (4.72)$$

or rather

$$S \geq k_B \ln \left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - \langle X \rangle_g \right\} \right]. \quad (4.73)$$

Now, applying the extremum condition (4.68) we have

$$\begin{aligned} \frac{\delta}{\delta g(q)} k_B \ln \left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} - \langle X \rangle_g \right\} \right] &= 0 \\ \frac{\delta}{\delta g(q)} \ln \left[\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \right] &= \frac{\delta}{\delta g(q)} \langle X \rangle_g \end{aligned} \quad (4.74)$$

this forms the principal construct in the derivation of the renormalized step length equation. The task remaining is to evaluate this expression. Beginning

with the left hand side we have

$$\begin{aligned} & \frac{\delta}{\delta g(q)} \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \\ & \frac{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}} \\ & = \frac{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \frac{\delta}{\delta g(q)} \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}} \end{aligned} \quad (4.75)$$

$$= \frac{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \mathbf{R}_{q'}^2 \frac{\delta}{\delta g(q)} [g(q')]^{-1} \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}} \quad (4.76)$$

$$= \frac{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \left\{ \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \mathbf{R}_{q'}^2 [g(q')]^{-2} \delta(q' - q) \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}} \quad (4.77)$$

$$= \frac{\int \prod_k d\mathbf{r}_k \left[\frac{3}{2} \frac{\mathbf{R}_q^2}{g^2(q)} \right] \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\mathbf{R}_k^2}{g(k)} \right\}}{\int \prod_q d\mathbf{r}_q \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}. \quad (4.78)$$

Discretization of the integral in the exponent where now $q \rightarrow \frac{2\pi p}{L}$ and performing the Gaussian integrals we have

$$\frac{\int d\mathbf{r}_q \left[\frac{\mathbf{R}_q^2}{g^2(q)} \right] \exp \left\{ -\frac{\mathbf{R}_p^2}{Lg(p)} \right\}}{\int d\mathbf{r}_{q'} \exp \left\{ -\frac{3}{2} \frac{\mathbf{R}^2(\frac{2\pi p}{L})}{Lg(p)} \right\}} = \frac{L}{g(q)}. \quad (4.79)$$

Our next focus is the evaluation of the right hand side of (4.74)

$$\begin{aligned} & \frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right. \\ & \quad \left. + \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q \exp(iqs) - \exp(iqs') \right] \right\rangle_g \\ & = \frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right\rangle_g \\ & \quad + \frac{\delta}{\delta g(q)} \left\langle \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q \exp(iqs) - \exp(iqs') \right] \right\rangle_g. \end{aligned} \quad (4.80)$$

The first term is computed as follows

$$\begin{aligned} & \frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right\rangle_g \\ &= \frac{\delta}{\delta g(q)} \left[\frac{\int \mathcal{D}\mathbf{R} \left\{ \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \left(\frac{1}{g_0(q')} - \frac{1}{g(q')} \right) \mathbf{R}_{q'}^2 \right\} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}}{\int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\}} \right] \end{aligned} \quad (4.81)$$

discretization of the term in the exponent leaves us with standard multiple Gaussian integrals

$$\begin{aligned} & \frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right\rangle_g \\ &= \frac{\delta}{\delta g(q)} \left[\frac{\int \prod_p d\mathbf{r}_p \left\{ \frac{3}{2L} \sum_{-\infty}^{\infty} \left(\frac{1}{g_0(p')} - \frac{1}{g(p')} \right) \mathbf{R}_{p'}^2 \right\} \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\}}{\int \prod_p d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \right] \end{aligned} \quad (4.82)$$

$$= \frac{\delta}{\delta g(q)} \left[\frac{\sum_{-\infty}^{\infty} \int \prod_p d\mathbf{r}_p \left\{ \frac{3}{2L} \left(\frac{1}{g_0(p')} - \frac{1}{g(p')} \right) \mathbf{R}_{p'}^2 \right\} \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\}}{\int \prod_p d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \right] \quad (4.83)$$

$$= \frac{\delta}{\delta g(q)} \left[\frac{\sum_{-\infty}^{\infty} \int d\mathbf{r}_p \left\{ \frac{3}{2L} \left(\frac{1}{g_0(p)} - \frac{1}{g(p)} \right) \mathbf{R}_p^2 \right\} \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}}{\int d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \right] \quad (4.84)$$

$$(4.85)$$

where we use the Gaussian integral as the generator to get

$$\begin{aligned} & \frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right\rangle_g \\ &= \frac{\delta}{\delta g(q)} \sum_{-\infty}^{\infty} \left[\frac{g(p)}{g_0(p)} - 1 \right] \end{aligned} \quad (4.86)$$

$$= \frac{\delta}{\delta g(q)} L \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \left[\frac{g(q')}{g_0(q')} - 1 \right] \quad (4.87)$$

$$= L \int_{-\infty}^{\infty} \frac{dq'}{2\pi} \left[\frac{\delta(q' - q)}{g_0(q')} \right] \quad (4.88)$$

$$\frac{\delta}{\delta g(q)} \left\langle \frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \left(\frac{1}{g_0(q)} - \frac{1}{g(q)} \right) \mathbf{R}_q^2 \right\rangle_g = \frac{L}{g_0(q)}. \quad (4.89)$$

Then as for the second term of (4.80) we have

$$\begin{aligned}
 & \frac{\delta}{\delta g(q)} \left\langle \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q [\exp(iqs) - \exp(iqs')] \right] \right\rangle_g \\
 &= \frac{\delta}{\delta g(q)} \left[\int \mathcal{D}\mathbf{R} \left\{ \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \right. \right. \\
 & \quad \times \exp \left[i\mathbf{k} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \mathbf{R}_q [\exp(iqs) - \exp(iqs')] \right] \left. \right\} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \\
 & \quad \div \int \mathcal{D}\mathbf{R} \exp \left\{ -\frac{3}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{\mathbf{R}_q^2}{g(q)} \right\} \right] \tag{4.90}
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{\delta}{\delta g\left(\frac{2\pi p}{L}\right)} \left[\int \prod_p d\mathbf{r}_p \left\{ \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \right. \right. \\
 & \quad \times \exp \left[\frac{i}{L} \mathbf{k} \cdot \sum_{-\infty}^{\infty} \mathbf{R}_p \left[\exp\left(\frac{2\pi ips}{L}\right) - \exp\left(\frac{2\pi ips'}{L}\right) \right] \right] \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\} \\
 & \quad \div \int \prod_p d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \sum_{-\infty}^{\infty} \frac{\mathbf{R}_p^2}{g(p)} \right\} \right] \tag{4.91}
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{\delta}{\delta g\left(\frac{2\pi p}{L}\right)} \left[\prod_p \frac{\int d\mathbf{r}_p \left\{ \frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \right\} \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}}{\int d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \right. \\
 & \quad \times \exp \left[\frac{i}{L} \mathbf{k} \cdot \mathbf{R}_p \left[\exp\left(\frac{2\pi ips}{L}\right) - \exp\left(\frac{2\pi ips'}{L}\right) \right] \right] \left. \right] \\
 &= \frac{\delta}{\delta g\left(\frac{2\pi p}{L}\right)} \left[\frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \prod_p \frac{\int d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}}{\int d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \right. \\
 & \quad \times \exp \left[\frac{i}{L} \mathbf{k} \cdot \mathbf{R}_p \left[\exp\left(\frac{2\pi ips}{L}\right) - \exp\left(\frac{2\pi ips'}{L}\right) \right] \right] \left. \right] \\
 &= \frac{\delta}{\delta g\left(\frac{2\pi p}{L}\right)} \left[\frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \right. \\
 & \quad \times \prod_p \frac{\int d\mathbf{r}_p \exp \left[\frac{i}{L} \mathbf{k} \cdot \mathbf{R}_p \left[\exp\left(\frac{2\pi ips}{L}\right) - \exp\left(\frac{2\pi ips'}{L}\right) \right] - \frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right]}{\int d\mathbf{r}_p \exp \left\{ -\frac{3}{2L} \frac{\mathbf{R}_p^2}{g(p)} \right\}} \left. \right]. \tag{4.92}
 \end{aligned}$$

After completing the square for the \mathbf{R}_p variable to evaluate the Gaussian in-

tegrals we have (4.92) equivalent to

$$\begin{aligned} & \frac{\delta}{\delta g\left(\frac{2\pi p}{L}\right)} \left[\frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \times \prod_p \exp \left\{ -\frac{gk^2}{6L} \left(e^{i\sigma s} - e^{i\sigma s'} \right)^2 \right\} \right] \\ &= \frac{\delta}{\delta g(q)} \left[\frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \exp \left\{ -\frac{k^2}{6L} \sum_q g(q) \left(e^{iqs} - e^{iqs'} \right)^2 \right\} \right] \end{aligned} \quad (4.93)$$

$$\begin{aligned} &= \frac{\delta}{\delta g(q)} \left[\frac{1}{2l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k \right. \\ & \quad \left. \times \exp \left\{ -\frac{k^2}{6} \int \frac{dq'}{2\pi} g(q') \left(e^{iq's} - e^{iq's'} \right)^2 \right\} \right] \end{aligned} \quad (4.94)$$

$$\begin{aligned} &= -\frac{1}{12l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k k^2 \left(e^{iqs} - e^{iqs'} \right)^2 \\ & \quad \times \exp \left\{ -\frac{k^2}{6} \int \frac{dq'}{2\pi} g(q') \left(e^{iq's} - e^{iq's'} \right)^2 \right\} \\ &= -\frac{1}{12l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k k^2 \sin^2 \left(\frac{q'(s-s')}{2} \right) \\ & \quad \times \exp \left\{ -\frac{k^2}{6} \int \frac{dq'}{2\pi} g(q') \sin^2 \left(\frac{q'(s-s')}{2} \right) \right\} \\ &= -\frac{1}{12l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k k^2 \sin^2 \left(\frac{q'(s-s')}{2} \right) \\ & \quad \times \exp \left\{ -\frac{k^2}{6} \int \frac{dq'}{2\pi} \frac{l_1(q')}{q^2} \sin^2 \left(\frac{q'(s-s')}{2} \right) \right\}. \end{aligned} \quad (4.95)$$

Combining this result and (4.79) as well as (4.89) we therefore arrive at the integral expression that one has to solve to determine the approximate renormalized step length given here

$$\begin{aligned} & Lq^2 \left(\frac{1}{l} - \frac{1}{l_1(q)} \right) \\ &= \frac{1}{12l^2} \int_0^L \int_0^L ds ds' \int_{\mathbf{k} \neq 0} \frac{d^3 k}{(2\pi)^3} \Delta_k k^2 \sin^2 \left(\frac{q'(s-s')}{2} \right) \\ & \quad \times \exp \left\{ -\frac{k^2}{6} \int \frac{dq'}{2\pi} \frac{l_1(q')}{q^2} \sin^2 \left(\frac{q'(s-s')}{2} \right) \right\}. \end{aligned} \quad (4.96)$$

Evaluating this expression require numerical methods in general except in some limits. At this point we shall quote the analytic results given in the reference paper (28) for different salt and polymer concentration limits.

4.2.2.1 High salt limit

The approximate analytic results for high salt condition where the effective interaction takes the form of (1.67) with a slight modification

$$\Delta(r) = \left(w + \frac{w_c}{\kappa} \right) \left[\delta(r) - \frac{1}{4\pi r \xi_1^2} e^{-r/\xi_1} \right] \quad (4.97)$$

where w, w_c and κ are respectively the excluded volume, Coulomb strength and the inverse Debye screening length a parameter depending on the charge density of counterions and salt ions. ξ_1 is the exclude volume screening length depending on polymer segments concentration ρ and $w + \frac{w_c}{\kappa^2}$.

- Infinitely dilute solution

Within this salt limit when the polymer concentration $\rho \rightarrow 0$ which corresponds to $\xi_1 \rightarrow \infty$ we have

$$l_1^{\frac{5}{2}} \left(\frac{1}{l} - \frac{1}{l_1} \right) = \frac{1}{l^2} \sqrt{\frac{6}{\pi^3}} \left(w + \frac{w_c}{\kappa^2} \right) L^{\frac{1}{2}}. \quad (4.98)$$

- Approaching the overlap density

When the polymer concentration ρ approaches the overlap concentration ρ^* we have

$$\begin{aligned} l_1 &= \frac{1}{2^{\frac{1}{4}}} \sqrt{\frac{6}{\pi}} \beta^{\frac{1}{4}} \left(w + \frac{w_c}{\kappa^2} \right)^{\frac{1}{4}} \rho^{-\frac{1}{4}} l^{-\frac{1}{2}} \\ \xi_1 &= \frac{1}{2^{\frac{5}{4}}} \sqrt{\frac{3}{\pi}} \beta^{\frac{3}{4}} \left(w + \frac{w_c}{\kappa^2} \right)^{-\frac{1}{4}} \rho^{-\frac{3}{4}} l^{-\frac{1}{2}}. \end{aligned} \quad (4.99)$$

- Concentrated regime

Above the overlap concentration we have

$$\begin{aligned} l_1 &= l + \mathcal{O} \left(\frac{w + \frac{w_c}{\kappa^2}}{\rho l^4} \right)^{1/2} \\ \xi_1 &= l \left(6\rho \left(w + \frac{w_c}{\kappa^2} \right) \right)^{-1/2}. \end{aligned} \quad (4.100)$$

4.2.2.2 Low salt limit

The approximate analytic results for low salt condition where the effective interaction is given by both screened and oscillatory expression

$$\Delta(r) = \frac{w_c}{4\pi r} \cos \left(-\frac{r}{\sqrt{2}\xi_2} \right) e^{-r/\sqrt{2}\xi_2}. \quad (4.101)$$

ξ_2 is the correlation length depending on polymer segments concentration ρ and Coulomb strength w_c .

- Infinitely dilute solution

Within this salt limit when the polymer concentration $\rho \rightarrow 0$ which corresponds to $\xi_2 \rightarrow \infty$ we have

$$l_1^{\frac{3}{2}} \left(\frac{1}{l} - \frac{1}{l_1} \right) = \frac{1}{\sqrt{3}\pi^{\frac{5}{2}}l^2} \left(w + \frac{w_c}{\kappa^2} \right) L^{\frac{3}{2}}. \quad (4.102)$$

- Approaching the overlap density

When the polymer concentration ρ approaches the overlap concentration ρ^* we have

$$\begin{aligned} l_1 &= \sqrt{\frac{\beta}{8}} \left(\frac{6\sqrt{2}}{\pi} \right)^{2/3} \left(\frac{w_c}{l} \right)^{1/6} (\rho l)^{-1/2} \\ \xi_2 &= \sqrt{\frac{\beta}{8}} \left(\frac{6\sqrt{2}}{\pi} \right)^{1/3} \left(\frac{w_c}{l} \right)^{-1/6} (\rho l)^{-1/2}. \end{aligned} \quad (4.103)$$

- Concentrated regime

Above the overlap concentration we have

$$\begin{aligned} l_1 &= l + \mathcal{O} \left(\frac{w_c^{1/4}}{l^{3/2}} \rho^{-3/4} \right) \\ \xi_2 &= \left(\frac{6\rho w_c}{l^2} \right)^{-1/4}. \end{aligned} \quad (4.104)$$

4.3 The force driving translocation

We shall discuss translocation upon three regimes, namely, translocation between high and low salt in infinitely dilute solution, again translocation between high and low salt, however, for semidilute solution and finally translocation between concentrated and infinitely dilute solutions in both salt limits.

4.3.1 High and low salt limit – infinitely dilute solution

In this section we shall investigate the translocation from a high salt to a low salt solvent conditions for infinitely dilute concentration. We shall do this, as before, by determining an approximate force driving translocation.

High salt case on the trans-side

The renormalized Kuhn length from (4.96) is given by

$$l_1^{\frac{5}{2}} \left(\frac{1}{l_+} - \frac{1}{l_1} \right) = \frac{1}{l_+^2} \sqrt{\frac{6}{\pi^3}} \left(w + \frac{w_c}{\kappa^2} \right) L_+^{\frac{1}{2}} \quad (4.105)$$

which shows the $l_1 \sim L_+^{\frac{1}{5}}$ scaling relationship. We write the solution to this expression as

$$l_1 \simeq \gamma L_+^{\frac{1}{5}} \quad (4.106)$$

thereby resulting in the trans-side free energy, with the new renormalized step length accounting for the chain interactions in high salt conditions, given by

$$F_+ = -k_B T \ln \left[\sqrt{\frac{\pi \gamma L_+^{6/5}}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\gamma L_+^{6/5}}} \right) \right]. \quad (4.107)$$

Low salt case on the cis-side

If, in contrast to the trans-side, we have low salt conditions such that the renormalized step length of the chain is given by (4.102)

$$l_1^{\frac{3}{2}} \left(\frac{1}{l_-} - \frac{1}{l_1} \right) = \frac{1}{\sqrt{3}\pi^{\frac{5}{2}} l_-^2} \left(w + \frac{w_c}{\kappa^2} \right) L_-^{\frac{3}{2}} \quad (4.108)$$

which shows the $l_1 \sim L - L_+$ scaling relationship. We write the solution to this expression as

$$l_1 \simeq \eta (L - L_+). \quad (4.109)$$

Therefore the cis-side free energy follows from (2.13) as

$$F_- = -k_B T \ln \left[\sqrt{\frac{\pi \eta (L - L_+)^2}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\eta (L - L_+)^2}} \right) \right]. \quad (4.110)$$

The total free energy is thus given by

$$F(L_+) = -k_B T \ln \left[\sqrt{\frac{\pi \gamma L_+^{6/5}}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\gamma L_+^{6/5}}} \right) \right] - k_B T \ln \left[\sqrt{\frac{\pi \eta (L - L_+)^2}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\eta (L - L_+)^2}} \right) \right]. \quad (4.111)$$

The force driving translocation then follows as

$$f = \frac{1}{5}kT \left(-\frac{6\sqrt{\frac{6}{\pi}}\epsilon e^{-\frac{6\epsilon^2}{\gamma L_+^{6/5}}}}{L_+ \sqrt{\gamma L_+^{6/5}} \operatorname{erf}\left(\frac{\sqrt{6}\epsilon}{\sqrt{\gamma L_+^{6/5}}}\right)} + \frac{10\sqrt{\frac{6}{\pi}}\eta(L-L_+) \epsilon e^{-\frac{6\epsilon^2}{\eta(L-L_+)^2}}}{(\eta(L-L_+)^2)^{3/2} \operatorname{erf}\left(\frac{\sqrt{6}\epsilon}{\sqrt{\eta(L-L_+)^2}}\right)} + \frac{3L-8L_+}{(L-L_+)L_+} \right). \quad (4.112)$$

The force profile corresponding to this modelled situation is shown in Figure 4.1.

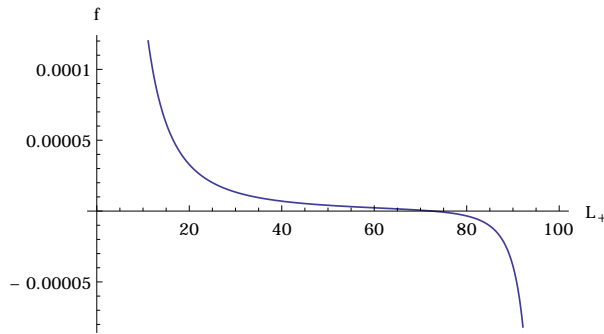


Figure 4.1: The force profile for translocation between high and low salt conditions in infinitely dilute solution.

In this scenario of infinitely dilute polymer density between high and low salt the threading traverses till 70 units towards the high salt side. The rate of translocation is also enhanced as depicted in Figure 4.1.

4.3.2 High and low salt limit – semidilute solution

In this section we shall investigate the translocation again from a high salt to a low salt solvent condition, however, for semidilute concentration. We shall do this, as before, by determining an approximate force driving translocation.

High salt case on the trans-side

The renormalized Kuhn length from (4.99) is given by

$$\begin{aligned} l_1 &= \frac{1}{2^{\frac{1}{4}}} \sqrt{\frac{6}{\pi}} \beta^{\frac{1}{4}} \left(w + \frac{w_c}{\kappa^2} \right)^{\frac{1}{4}} \rho_+^{-\frac{1}{4}} l_+^{-\frac{1}{2}} \\ l_1 &= \delta l^{-\frac{1}{2}} \end{aligned} \quad (4.113)$$

and a screening length relationship

$$\xi_1 = \frac{1}{2^{\frac{5}{4}}} \sqrt{\frac{3}{\pi}} \beta^{\frac{3}{4}} \left(w + \frac{w_c}{\kappa^2} \right)^{-\frac{1}{4}} \rho_+^{-\frac{3}{4}} l^{-\frac{1}{2}} \quad (4.114)$$

thereby resulting in the trans-side free energy, with the new renormalized step length accounting for the chain interactions in high salt conditions, given by

$$F_+ = -k_B T \ln \left[\sqrt{\frac{\pi \delta l^{-\frac{1}{2}} L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{\delta l^{-\frac{1}{2}} L_+}} \right) \right]. \quad (4.115)$$

Low salt case on the cis-side

If, in contrast to the trans-side, we have low salt conditions such that the renormalized step length of the chain from (4.103) is given by

$$\begin{aligned} l_1 &= \left(\frac{6\sqrt{2}}{\pi} \right)^{\frac{2}{3}} \sqrt{\frac{\tilde{\beta}}{8}} (\tilde{w}_c)^{\frac{1}{6}} \tilde{\rho}_-^{-\frac{1}{2}} l_-^{-\frac{2}{3}} \\ l_1 &= \mu l^{-\frac{2}{3}} \end{aligned} \quad (4.116)$$

and the screening length relationship

$$\xi_1 = \left(\frac{6\sqrt{2}}{\pi} \right)^{\frac{1}{3}} \sqrt{\frac{\tilde{\beta}}{8}} \left(\frac{\tilde{w}_c}{l_-} \right)^{-\frac{1}{6}} \tilde{\rho}_-^{-\frac{1}{2}} l_-^{-\frac{1}{2}}. \quad (4.117)$$

Therefore the cis-side free energy follows from (2.13) as

$$F_- = -k_B T \ln \left\{ \sqrt{\frac{\pi \mu l^{-\frac{2}{3}} (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{\mu l^{-\frac{2}{3}} (L - L_+)}} \right) \right\}. \quad (4.118)$$

The total free energy is thus given by

$$\begin{aligned}
 F(L_+) = & -k_B T \ln \left[\sqrt{\frac{\pi \delta l^{-\frac{1}{2}} L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6\epsilon}}{\sqrt{\delta l^{-\frac{1}{2}} L_+}} \right) \right] \\
 & -k_B T \ln \left\{ \sqrt{\frac{\pi \mu l^{-\frac{2}{3}} (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6\epsilon}}{\sqrt{\mu l^{-\frac{2}{3}} (L - L_+)}} \right) \right\}.
 \end{aligned} \tag{4.119}$$

The force driving translocation then follows as

$$\begin{aligned}
 f = & \frac{1}{2} k_B T \left(\frac{2\sqrt{6}\mu\sqrt[3]{l}\epsilon e^{-\frac{6l^{2/3}\epsilon^2}{\mu L - \mu L_+}}}{\sqrt{\pi} (\mu (L - L_+))^{3/2} \operatorname{erf} \left(\frac{\sqrt{6}\sqrt[3]{l}\epsilon}{\sqrt{\mu(L-L_+)}} \right)} \right. \\
 & \left. - \frac{2\sqrt{6}\delta\sqrt[4]{l}\epsilon e^{-\frac{6\sqrt{l}\epsilon^2}{\delta L_+}}}{\sqrt{\pi} (\delta L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6}\sqrt[4]{l}\epsilon}{\sqrt{\delta L_+}} \right)} + \frac{L - 2L_+}{(L - L_+) L_+} \right).
 \end{aligned} \tag{4.120}$$

The force profile corresponding to this modelled situation is shown in Figure 4.2.

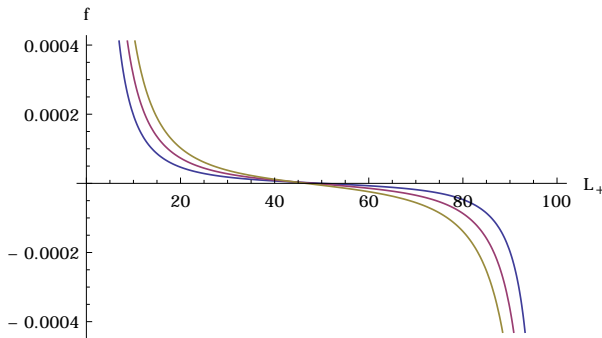


Figure 4.2: The force profile of varying l from small to large for high-low salt translocation in semi dilute concentration.

In the semidilute regime electrolytic conditions asymmetry do not seem to have any significant bias on the translocation force bias as shown in Figure 4.2 except for the steepening of the force profile.

4.3.3 Infinitely dilute and concentrated solutions

We have seen that in the concentrated regime for both salt limits the renormalized step length is essentially reflecting Gaussian chain statistics and it is given by $l_1 = l_+$. Therefore the free energy expression of the trans-side is given by

$$F_+ = -k_B T \ln \left[\sqrt{\frac{\pi l_+ L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \right] \quad (4.121)$$

On the other hand we have already determined the free energies of infinitely dilute concentration for both salt limits as shown in equations (4.107) in the high salt and (4.111) in the low salt. Combining the free energies for either salt concentration for dense polymer regime and high salt infinitely dilute solution and for either salt concentration for dense polymer regime and low salt infinitely dilute solutions we, respectively, have

$$F(L_+) = \begin{cases} -k_B T \ln \left[\sqrt{\frac{\pi l_+ L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \right] \\ -k_B T \ln \left[\sqrt{\frac{\pi \gamma (L-L_+)^{6/5}}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\gamma (L-L_+)^{6/5}}} \right) \right] \\ -k_B T \ln \left[\sqrt{\frac{\pi l_+ L_+}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l_+ L_+}} \right) \right] \\ -k_B T \ln \left[\sqrt{\frac{\pi \eta (L-L_+)^2}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\eta (L-L_+)^2}} \right) \right]. \end{cases} \quad (4.122)$$

The force expressions then follow from this equation as as

$$f(L_+) = \begin{cases} \frac{1}{10} kT \left(-\frac{10\sqrt{\frac{6}{\pi}}\epsilon e^{-\frac{6\epsilon^2}{lL_+}}}{\sqrt{lL_+^{3/2}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l}\sqrt{L_+}} \right)} \right. \\ \left. + 6 \left(\frac{2\sqrt{\frac{6}{\pi}}\epsilon e^{-\frac{6\epsilon^2}{\gamma(L-L_+)^{6/5}}}}{\sqrt{\gamma(L-L_+)^{8/5}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\gamma(L-L_+)^{3/5}}} \right)} \right) + \frac{5L-11L_+}{L-L_+} \right) \\ \frac{1}{2} kT \left(2\sqrt{\frac{6}{\pi}}\epsilon \left(\frac{2e^{-\frac{6\epsilon^2}{\eta(L-L_+)^2}}}{\sqrt{\eta(L-L_+)^2} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{\eta(L-L_+)}} \right)} - \frac{e^{-\frac{6\epsilon^2}{lL_+}}}{\sqrt{lL_+^{3/2}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{l}\sqrt{L_+}} \right)} \right) \right. \\ \left. + \frac{L-3L_+}{(L-L_+)L_+} \right). \end{cases} \quad (4.123)$$

The accompanying force profiles are shown below in Figure 4.3

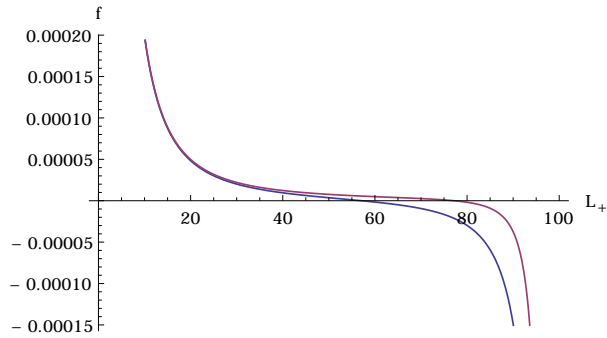


Figure 4.3: The force profiles for concentrated to high and low salt in semi dilute concentration with high salt on the left.

The translocation to the infinitely dilute polymer concentration in the high salt limit does not show any significant bias. However, when in the low salt limit the bias is clearly illustrated where the chain progresses 75% to the concentrated side at a slower rate contrast to the case of both sides being of infinitely dilute concentrations. Thus the density asymmetry is manifested through the rate of translocation.

Chapter 5

Polyelectrolyte chain under attractive wall confinement

Short range adsorption behavior of Gaussian chain models has been investigated to a large extent (31) with experimental results achieved. When interactions such as excluded volume interactions are present the description of the adsorption behavior becomes difficult to determine (2). In this chapter we shall model the polyelectrolyte chain translocation in the presence of an attractive wall of uniform charge density σ in the regime where the effects due to counterion condensation on the chain and on the surface respectively obtained by Manning and Gouy-Chapman theory (31) will not be taken into account. This is an initial investigation where the role of the length variation upon the adsorption is not considered. We will do this by again employing the approximate method of effective step length to account for other interactions excluding the surface chain interactions. This enables the separation of variables, that is, the probability distribution function can be written as the product of three functions, each of single real space co-ordinate. The result of this is the two dimensional diffusion equation with a renormalized Kuhn length and a one dimensional diffusion equation, of renormalized step length, with a surface chain potential.

5.1 Formulation

The strategy we are pursuing here closely follows the work of Wiegler (45). We have discussed in the preceding chapter the effective Hamiltonian of a collective system of charged polymers. That is, the probability distribution for the polyelectrolyte chain interacting with an attractive potential can be

modelled as

$$G(\mathbf{R}, L) = \int_{\mathbf{R}_i(0)}^{\mathbf{R}_f(L)} \mathcal{D}\mathbf{R}(s) \exp \left\{ -\frac{3}{2l} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - \int_0^L \int_0^L ds ds' \Delta(\mathbf{R}(s) - \mathbf{R}(s')) - \beta \int_0^L d^2S \frac{\sigma Q}{\epsilon r l} e^{-\kappa r} \right\}. \quad (5.1)$$

The last term represents the surface-chain segment interaction where r is the distance between chain segment $\mathbf{R}(s)$ and the wall, κ is the inverse Debye screening length, d^2S is the surface element area, ϵ is the dielectric constant and Q is charge of each monomer segment and finally r is the distance from the wall to the segment $\mathbf{R}(s)$ of the chain. The renormalized step length approximation method and Feynman-Kac theorem allow us to map the problem to (27)

$$\left[\frac{\partial}{\partial L} - \frac{l_1}{6} \nabla^2 + \beta \frac{2\pi\sigma Q}{\epsilon\kappa l} e^{-\kappa z} \right] G(\mathbf{R}(s), \mathbf{R}_0; L) = \delta(\mathbf{R}(s) - \mathbf{R}(s')) \delta(s - s') \quad (5.2)$$

where the chain-chain and chain-solvent interactions are encapsulated in the effective step length l_1 with the exclusion of the surface-chain interaction. Fortunately, we have already computed this effective step length using a variational method approximation in Chapter 4. Upon the separability assumption the solution can be written as

$$G(\mathbf{R}(s), \mathbf{R}_0; L) = G(x, x_0; L)G(y, y_0; L)G(z, z_0; L) \quad (5.3)$$

where $\mathbf{R}_0 = \langle 0, 0, \epsilon \rangle$. The solution can then be derived from the two dimensional diffusion equation in x and y , of renormalized step length, together with the eigenvalue problem

$$\left[-\frac{l_1}{6} \frac{d^2}{dz^2} - \beta \frac{2\pi\sigma Q}{\epsilon\kappa l} e^{-\kappa z} \right] \psi_m(z) = E_m \psi_m(z) \quad (5.4)$$

for the z coordinate which has the boundary conditions

$$\psi_m(z = 0) = \psi_m(z \rightarrow \infty) = 0. \quad (5.5)$$

The z -component of the Green function can be expressed as the expansion (44)

$$G(z, z_0; L) = \sum_m \psi_m(z) \psi_m^*(z_0) e^{-E_m L}. \quad (5.6)$$

The transformation of this equation, see below, produces a Bessel differential equation which has Bessel function solutions $J_\nu(\xi)$. The x and y Green's function component is

$$G(\mathbf{R}_{x,y}, \mathbf{R}_{0x,y}; L) = \frac{3}{2\pi L l_1} \exp \left\{ -\frac{3}{2L l_1} [x^2 + y^2] \right\} \quad (5.7)$$

Then the remaining task is to determine the eigenfunctions and their corresponding eigenvalues for the z component.

5.2 Adsorption Behaviour

An analogy to the quantum mechanical problem of a particle in a box with the potential (35)

$$\beta V(z) = -\frac{2\pi|\sigma Q|}{k_B T \varepsilon \kappa l} e^{-\kappa z} \quad (5.8)$$

suggests two regimes of different characteristics. The regime where $\beta < \beta_c$ the potential has no bound states(adsorbed states). Where β_c is a certain critical value. As for the case where $\beta > \beta_c$ the potential has at least one bound state. That is for $T < T_c$ there is a bound state with a ground state energy E_0 . In the limit $L \rightarrow \infty$ (8)

$$\begin{aligned} G(z, z_0; L) &= \sum_m \psi_m(z) \psi_m^*(z_0) e^{-E_m L} \\ G(z, z_0; L) &\approx \psi_0(z) \psi_0^*(z_0) e^{-E_0 L} \end{aligned} \quad (5.9)$$

where the sum is then dominated by the ground state term where

$$\psi_0(z) \approx J_{\nu_0} \left(\left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa z}{2}} \right) \quad (5.10)$$

as will be discussed shortly. ν_0 is the value corresponding to the ground state energy, (see (5.19) below). This eigenfunction is derived from the transformation of (5.4) by

$$\phi(\xi) = \psi(z) \quad (5.11)$$

$$\xi = \left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa z}{2}} \quad (5.12)$$

since

$$\frac{d^2}{dz^2} = \frac{d^2 \xi}{dz^2} \frac{d}{d\xi} + \left(\frac{d\xi}{dz} \right)^2 \frac{d^2}{d\xi^2} \quad (5.13)$$

and

$$\left(\frac{d\xi}{dz} \right)^2 = \left\{ \left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} \left[-\frac{\kappa}{2} e^{-\frac{\kappa z}{2}} \right] \right\}^2 = \frac{\kappa^2}{4} \xi^2 \quad (5.14)$$

while

$$\frac{d^2 \xi}{dz^2} = \left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} \left[\frac{\kappa^2}{4} e^{-\frac{\kappa z}{2}} \right] = \frac{\kappa^2}{4} \xi \quad (5.15)$$

therefore

$$\begin{aligned}
 & \left[-\frac{l_1}{6} \frac{d^2}{dz^2} - \beta \frac{2\pi\sigma Q}{\varepsilon\kappa l} e^{-\kappa z} \right] \phi(\xi) \\
 &= \left[-\frac{l_1}{6} \left(\frac{d^2\xi}{dz^2} \frac{d}{d\xi} + \left(\frac{d\xi}{dz} \right)^2 \frac{d^2}{d\xi^2} \right) - \beta \frac{2\pi\sigma Q}{\varepsilon\kappa l} e^{-\kappa z} \right] \phi(\xi) \\
 &= -\frac{\kappa^2 l_1 \xi^2}{24} \left[\frac{1}{\xi} \frac{d}{d\xi} + \frac{d^2}{d\xi^2} - \beta \frac{48\pi\sigma Q}{\xi^2 \varepsilon \kappa^3 l l_1} e^{-\kappa z} \right] \phi(\xi)
 \end{aligned} \tag{5.16}$$

which eventually transforms (5.4) the eigenvalue expression to the Bessel equation (44)

$$\frac{d^2\phi}{d\xi^2} + \frac{1}{\xi} \frac{d\phi}{d\xi} + \left(1 + \frac{\lambda}{\xi^2} \right) \phi = 0 \tag{5.17}$$

upon the definition

$$\lambda = \frac{24E}{\kappa^2 l_1}$$

with the boundary conditions

$$\phi(0) = 0 \tag{5.18}$$

$$\phi \left(\left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} \right) = 0. \tag{5.19}$$

The regime that has a bound state (adsorb) is a solution to the differential equation when $\lambda < 0$. The solutions to this equation is given by Bessel functions of the first kind (45) that is

$$\phi(\xi) = \text{Const} \times J_\nu(\xi) \tag{5.20}$$

where ν is determined by solving (45)

$$J_\nu \left(\left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} \right) = 0 \tag{5.21}$$

$$\tag{5.22}$$

upon the condition that

$$\lambda = -\nu^2, \quad \nu > 0. \tag{5.23}$$

This expression shows that the ground state energy E_0 corresponds to the case where $\nu = \nu_{max} =: \nu_0$. This value is obtained for the first time when (45)

$$\left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} = j_{0,1} = 2.4048. \tag{5.24}$$

The solution(s) which corresponds to the bound state (s) to this algebraic expression thus exists only when

$$\left(\frac{48\pi|\sigma Q|}{k_B T \varepsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} > j_{0,1} = 2.4048. \quad (5.25)$$

The critical temperature T_c between the adsorbed and unadsorbed state then follows as

$$T_c = \frac{48\pi|\sigma Q|}{j_{0,1}^2 k_B \varepsilon \kappa^3 l l_1}. \quad (5.26)$$

This equation determines the critical point between the state of adsorption and unadsorption to the surface. In the limits of low and high salt we have shown the values of the renormalized step length l_1 at infinitely dilute solutions so that the critical temperature is determined by

$$T_c \sim \begin{cases} \frac{|\sigma Q|}{\varepsilon \kappa^3 l L} & \kappa \rightarrow 0 \\ \frac{|\sigma Q|}{\varepsilon \kappa^{\frac{1}{5}} l L^{1/5}} & \kappa (L l_1)^{\frac{1}{2}} \rightarrow \infty. \end{cases} \quad (5.27)$$

This illustrates that in the strong screening case, which corresponds to the flexible chain, achieving adsorption would require greater temperature reduction when compared to the rod-like chain limit of low salt. This expressed differently, when the excluded volume interaction dominates the electrostatic interactions the critical temperature scales as

$$T_c \sim L^{-\frac{1}{5}}. \quad (5.28)$$

5.3 The force driving translocation–adsorbing trans-side and hard wall cis-side

Here we approximate the free energy in a scenario where the trans-side has an attractive wall contrast to the cis-side which has the hard wall. The free energy of the cis-side is given by equation (2.13)

$$F_-(L_+) = -k_B T \ln \left\{ \sqrt{\frac{\pi l (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{(L - L_+) l}} \right) \right\}. \quad (5.29)$$

We can now estimate the free energy F_+ of the trans-side from equation (2.3), (5.7) and (5.9) as follows

$$\begin{aligned}
 Z_+ &= \int d\mathbf{r} \int d\mathbf{R}_0 G(\mathbf{R}, \mathbf{R}_0, L_+) \\
 Z_+ &= \int_{-\infty}^{\infty} dx dy \left(\frac{3}{2\pi L_+ l_1} \right) \exp \left\{ \frac{3}{2L_+ l_1} [x^2 + y^2] \right\} \\
 &\quad \times \int_{\epsilon}^{\infty} dz \psi_0(z) \psi_0^*(z_0) e^{-E_0 L_+} \\
 Z_+ &= e^{-E_0 L_+} \int_{\epsilon}^{\infty} dz J_{\nu_0} \left(\left(\frac{48\pi |\sigma Q|}{k_B T \epsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa z}{2}} \right) J_{\nu_0}^* \left(\left(\frac{48\pi |\sigma Q|}{k_B T \epsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa \epsilon}{2}} \right)
 \end{aligned} \tag{5.30}$$

substituting E_0 from (5.17) and (5.23) we have

$$\begin{aligned}
 Z_+ &= \exp \left\{ -\frac{\kappa^2 l_1 \nu_0^2}{24} L_+ \right\} J_{\nu_0}^* \left(\left(\frac{48\pi |\sigma Q|}{k_B T \epsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa \epsilon}{2}} \right) \\
 &\quad \times \int_{\epsilon}^{\infty} dz J_{\nu_0} \left(\left(\frac{48\pi |\sigma Q|}{k_B T \epsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa z}{2}} \right). \tag{5.31}
 \end{aligned}$$

The integral of J_{ν_0} above, in the limit where L is large such that the argument is small, is divergent. However, since our interest is on the logarithm of this expression we then conclude that

$$F_+ \simeq k_B T \alpha \left(\frac{\kappa^2 l_1 \nu_0^2}{24} \right) L_+ \tag{5.32}$$

where

$$\alpha = J_{\nu_0}^* \left(\left(\frac{48\pi |\sigma Q|}{k_B T \epsilon \kappa^3 l l_1} \right)^{\frac{1}{2}} e^{-\frac{\kappa \epsilon}{2}} \right). \tag{5.33}$$

In the following sections we shall determine the full approximate translocation force expressions using the combination of these free energies (5.31), (5.34) and the derived renormalized Kuhn lengths.

5.3.1 High and low salt limits – infinitely dilute solution

- High salt

In a similar token as in (4.106) the renormalized step length of the attractive wall side is given by

$$l_1 = \gamma L^{1/5}. \tag{5.34}$$

Therefore, by combining (5.31) and (5.34), the total free energy is given by

$$\begin{aligned}
 F_-(L_+) &= k_B T \alpha \left(\frac{\kappa^2 l_1 \nu_0^2}{24} \right) L_+ \\
 &\quad - k_B T \ln \left\{ \sqrt{\frac{\pi l_-(L-L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L-L_+)l_-}} \right) \right\} \\
 &= k_B T \alpha \left(\frac{\kappa^2 \gamma \nu_0^2}{24} \right) L_+^{6/5} \\
 &\quad - k_B T \ln \left\{ \sqrt{\frac{\pi l_-(L-L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{\sqrt{(L-L_+)l_-}} \right) \right\}.
 \end{aligned} \tag{5.35}$$

We then deduce the force that drives translocation as

$$\begin{aligned}
 f &= -\frac{1}{20} k T \alpha \gamma \kappa^2 \sqrt[5]{L_+} \nu_0^2 \\
 &\quad + \frac{1}{10} k T \left(\frac{2 \sqrt{\frac{6}{\pi}} \epsilon e^{\frac{6\epsilon^2}{l^2(L_+-L)}}}{l(L-L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6}\epsilon}{l\sqrt{L-L_+}} \right)} + \frac{1}{L_+-L} \right).
 \end{aligned} \tag{5.36}$$

This force is depicted in Figure 5.1 below

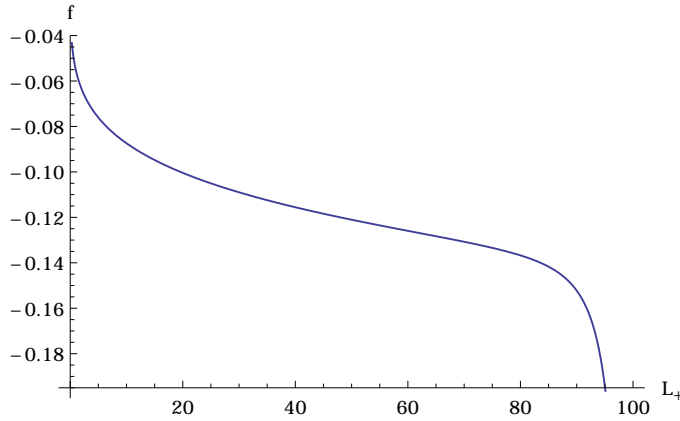


Figure 5.1: Force profile for translocation between the attractive wall for infinitely dilute high salt limit side and theta conditions.

- Low salt

In a similar token as in (4.109) the renormalized step length of the at-

tractive wall side is given by

$$l_1 = \eta L. \quad (5.37)$$

Therefore, by combining (5.31) and (5.34), the total free energy is given by

$$F_-(L_+) = k_B T \alpha \left(\frac{\kappa^2 \eta \nu_0^2}{24} \right) L_+^2 - k_B T \ln \left\{ \sqrt{\frac{\pi l (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{(L - L_+) l}} \right) \right\}. \quad (5.38)$$

We then deduce the force that drives translocation as

$$f = \frac{1}{12} k T \left(\frac{12 \sqrt{\frac{6}{\pi}} \epsilon e^{-\frac{6 \epsilon^2}{l^2 (L - L_+)}}}{l (L - L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{l \sqrt{L - L_+}} \right)} - \alpha \kappa^2 \eta L_+ \nu^2 + \frac{6}{L_+ - L} \right). \quad (5.39)$$

This force is depicted in Figure 5.2 below

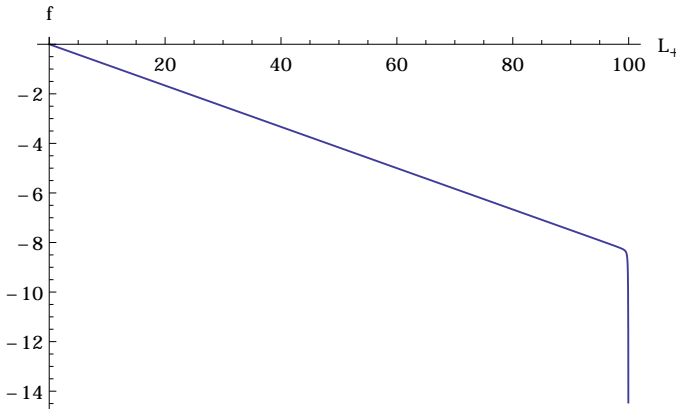


Figure 5.2: Force profile for translocation between the attractive wall for infinitely dilute low salt limit side and theta conditions.

5.3.2 High and low salt limits – semidilute solution

- High salt

In a similar token as in (4.113) the renormalized step length of the attractive wall side is given by

$$l_1 = \delta l^{-1/2}. \quad (5.40)$$

Therefore, by combining (5.31) and (5.34), the total free energy is given by

$$F_-(L_+) = k_B T \alpha \left(\frac{\kappa^2 \delta l^{-1/2} \nu_0^2}{24} \right) L_+ - k_B T \ln \left\{ \sqrt{\frac{\pi l (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{(L - L_+) l}} \right) \right\}. \quad (5.41)$$

We then deduce the force that drives translocation as

$$f = \frac{1}{24} k T \left(\frac{24 \sqrt{\frac{6}{\pi}} \epsilon e^{-\frac{6\epsilon^2}{l^2(L-L_+)}}}{l (L - L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{l \sqrt{L-L_+}} \right)} - \frac{\alpha \delta \kappa^2 \nu^2}{\sqrt{l}} + \frac{12}{L_+ - L} \right). \quad (5.42)$$

This force is depicted in Figure 5.3 below

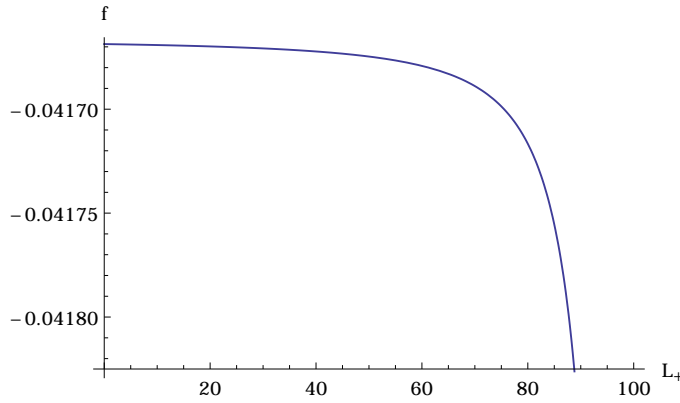


Figure 5.3: Force profile for translocation between the attractive wall for semi-dilute high salt limit side and theta conditions.

- Low salt

In a similar token as in (4.113) the renormalized step length of the attractive wall side is given by

$$l_1 = \mu l^{-2/3}. \quad (5.43)$$

Therefore, by combining (5.31) and (5.34), the total free energy is given by

$$F_-(L_+) = k_B T \alpha \left(\frac{\kappa^2 \mu l^{-2/3} \nu_0^2}{24} \right) L_+ - k_B T \ln \left\{ \sqrt{\frac{\pi l (L - L_+)}{6}} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{\sqrt{(L - L_+) l}} \right) \right\}. \quad (5.44)$$

We then deduce the force that drives translocation as

$$f = \frac{1}{24} k T \left(\frac{24 \sqrt{\frac{6}{\pi}} \epsilon e^{-\frac{6\epsilon^2}{l^2(L-L_+)}}}{l (L - L_+)^{3/2} \operatorname{erf} \left(\frac{\sqrt{6} \epsilon}{l \sqrt{L-L_+}} \right)} - \frac{\alpha \kappa^2 \mu \nu^2}{l^{2/3}} + \frac{12}{L_+ - L} \right) \quad (5.45)$$

This force is depicted in Figure 5.4 below

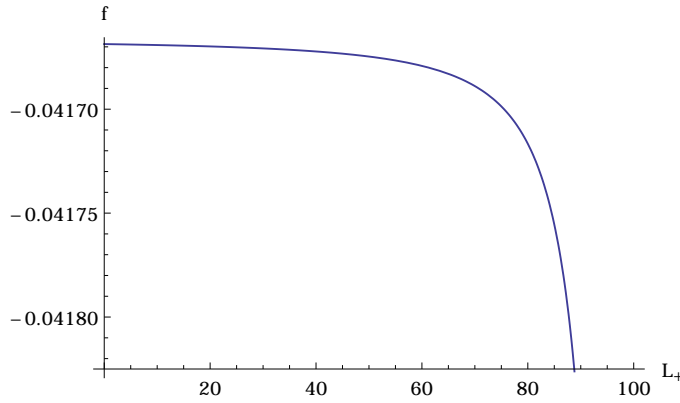


Figure 5.4: Force profile for translocation between the attractive wall for semi-dilute low salt limit side and theta conditions.

The result from the profiles derived above is that the active wall enhances the translocation in general. In the infinitely dilute density condition the role of salt concentration is depicted in Figure 5.1 and Figure 5.2. The semidilute case displays a nearly constant rate of translocation. In both scenarios above 95% of the chain thread through.

Chapter 6

Summary and outlook

6.1 Summary of results

Our discussion is mainly based on the force profiles we have derived. We have computed the force that drives translocation under various conditions on the basis of the method of images. The implementation of this method is only limited to Markov chains. Thus we followed the renormalization of the step length approximation. In the second chapter we illustrated this strategy for the phantom chain. As intuitively expected, the translocation force reaches a minimum when the chain has threaded half of its length. We then numerically shown in Figure 2.3 how far would the chain translocate to reach the minimum force. This was illustrated by varying the Kuhn lengths by 0.5 units in each side as a reflection of different solvent conditions. In this figure we understand the gradient of the force as function of length L as well. In contrast to the symmetric case the chain threads to by 25 units of length in this particular example with the length chosen to be 100 units. That is, the chain will further thread a 25 units to the side of 0.5 units step length.

In the following chapter we analytically estimate the renormalized Kuhn length for a chain under good solvent conditions threading to the cis-side of theta solvent conditions. We follow a similar program as before and conclude that, as shown in Figure 3.1, that the chain will thread further from the weak excluded volume strength to 30 and 20 units for an increased volume strength to respectively, 3 and 60 units. This we find interesting since it demonstrate sometime somewhat complex relationship between the translocation force and excluded volume interaction strength and hence the translocation time. It is also worthwhile to note the rates of translocation for the different regimes depicted on the same figure.

The essence of the analytic calculation of the renormalized Kuhn length that we outlined in Chapter 3 is taken a step further for the case where the electrostatic interactions play a role. There exist various regimes of salt concentration and chain densities. We considered three cases after the derivation

of the generic integral expression describing the renormalized step length. The three situations are those of translocation between high and low salt conditions for the infinitely dilute conditions on both sides of the partition and semidilute conditions on both sides of the partition. Also, the translocation between the concentrated solution condition to the high and low salt limits of infinitely dilute conditions. In the first scenario of infinitely dilute polymer density between high and low salt the threading traverses till 70 units towards the high salt side. The rate of translocation is depicted in Figure 4.1. In the semidilute regime the electrolytic conditions asymmetry do not seem to have any significant bias on the translocation as shown in Figure 4.2. The effect of polymer density asymmetry is illustrated in Figure 4.3. The translocation to the infinitely dilute polymer concentration in the high salt limit does not show any significant bias. However, when in the low salt limit the bias is clearly illustrated where the chain progresses 75% to the concentrated side at a slower rate contrast to the case of both sides being of infinitely dilute concentrations. Thus the density asymmetry is manifested through the rate of translocation.

The result from the profiles derived above is that the active wall enhances the translocation in general. In the infinitely dilute density condition the role of salt concentration is depicted in Figure 5.1 and Figure 5.2. The semidilute case displays a nearly constant rate of translocation. In both scenarios above 95% of the chain thread through.

6.2 Outlook

It would be interesting to study the role of the geometry of the confining surface such as that of a curved sphere to translocation, possibly, in conjunction with adsorption. These curved geometries are encountered in biological systems. As a motivating example, Alexander (1) found that adsorption on curved surfaces changes the density profile of the adsorbed polymer chains. A fluctuating surface would be a good model to bio-membranes.

As a further study, the hydrodynamical aspect would be a natural following step where coupled Navier-Stokes and Langevin equations would have to be solved to determine quantities such as the segment-to-segment correlation function.

Appendix A

Structure function

The integral

$$\int_0^L ds \int_0^L ds' e^{-\frac{1}{6}\mathbf{k}^2|s-s'|} \quad (\text{A.1})$$

upon the transformation

$$\sigma = \frac{s}{L} ; \sigma' = \frac{s'}{L} \text{ and } \alpha = \frac{\mathbf{k}^2 l L}{6}$$

becomes

$$\begin{aligned} & \int_0^L ds \int_0^L ds' e^{-\frac{1}{6}\mathbf{k}^2|s-s'|} \\ &= L^2 \int_0^1 d\sigma \int_0^1 d\sigma' e^{-\alpha|\sigma-\sigma'|} \end{aligned} \quad (\text{A.2})$$

and further

$$\tau = \sigma - \sigma' \text{ and } S = \frac{1}{2}(\sigma + \sigma')$$

which has the Jacobian equivalent to unity. This yields

$$\begin{aligned} & L^2 \int_0^1 d\sigma \int_0^1 d\sigma' e^{-\alpha|\sigma-\sigma'|} \\ &= 2L^2 \int_0^{1/2} dS \int_{-2S}^{2S} d\tau e^{-\alpha|\tau|} \\ &= 2L^2 \int_0^{1/2} dS \left[\int_{-2S}^0 d\tau e^{\alpha\tau} + \int_0^{2S} d\tau e^{-\alpha\tau} \right] \\ &= 4L^2 \int_0^{1/2} dS \int_0^{2S} d\tau e^{-\alpha\tau} \\ &= \frac{4L^2}{\alpha} \int_0^{1/2} dS (1 - e^{-2\alpha S}) \end{aligned} \quad (\text{A.3})$$

this results to

$$\begin{aligned}
 \int_0^L ds \int_0^L ds' e^{-\frac{1}{6}\mathbf{k}^2|s-s'|} &= L^2 \left[\frac{2}{\alpha^2} (-1 + \alpha + e^{-\alpha}) \right] \\
 &= L^2 f(\alpha) \\
 &= \frac{L^2}{1 + \alpha/2} \\
 \int_0^L ds \int_0^L ds' e^{-\frac{1}{6}\mathbf{k}^2|s-s'|} &= \frac{L^2}{1 + \frac{\mathbf{k}^2 L}{12}}
 \end{aligned} \tag{A.4}$$

where we have used the Debye function approximation (8) for $f(\alpha)$.

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