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Title: The effect of thermal fluctuations on elastic instabilities of biopolymers
Issue Date: 2012-07-04

Chapter 6

Free energy of a confined worm like chain under torsion

In this chapter we lay the foundation for the extension of the mechanistic plectoneme model with thermal fluctuations, that will be the main subject of the next chapter. The plectonemes that form put the chains into a confined environment that has an important impact on the way the torsional loads get divided. We will extend the WLC model from earlier chapters to one with a finite stretch modulus and twist stretch coupling, confined in a channel with dimensions far below the persistence length of the chain, even compared to a torsion corrected persistence length. The narrowness of the channel implicates that the chain does not fold on itself, but that it is up to fluctuations stretched, the so called Odijk regime [170]. In the torsion free case an analogous calculation was performed by Burkhardt [171], but his calculation can not immediately be applied to this more complex problem. To start of we will redo the calculations of Moroz and Nelson [172] of a chain under torsion and tension below buckling. We will take a different approach, as a guideline for how to treat the more complicated cases. An analogous calculation in less detail was also done by Marko [173]

6.1 Chain under tension

The WLC Hamiltonian is easily extended to include an elastic stretch term and a twist stretch coupling. The stretch modulus, multiplying a term quadratic in the stretch, is not precisely known, but values are in the 700 pN to 1400 pN range. It is pretty large which is one of the reasons stretch is often neglected. The twist stretch coupling modulus, B, multiplies a term linear in twist and stretch, thereby breaking stretch-compress and chiral symmetries. It was recently found to be negative: when stretch increases, twist also increases. More about these quantities for DNA in the next chapter. The chain is now not only represented by its tangent and differential twist angle, but also by a local stretch scalar. The parametrization is as before, but it is to be noted that the parametrization does not anymore coincide with the contour length due to the stretch. The Hamiltonian reads, up to quadratic order:

$$\mathcal{H} = \int_0^{L_c} ds \left[\frac{P_b}{2} \left(\frac{d\mathbf{t}(s)}{ds} \right)^2 + \frac{P_c}{2} \dot{\psi}^2(s) + \frac{S}{2} u(s)^2 + B\, \dot{\psi}(s) u(s) - f\left(1 + u(s) - \frac{\mathbf{t}_\perp^2(s)}{2} \right) \right] \tag{6.1}$$

We look at fluctuations around the ground-state. The Euler Lagrange equations for the twist angle, $\dot{\psi}$, and stretch factor $u(s)$ give the obvious “classical” results:

$$\dot{\psi}_0 = \text{constant} \qquad\qquad u_0 = \frac{f - B\,\dot{\psi}_0}{S} \tag{6.2}$$

When changing to a fixed linking number ensemble we will make the natural choice $\dot{\psi}_0 = 2\pi\, \langle \text{tw} \rangle$, the expectation value of the twist density. Completing the square for $u(s)$, and assuming the fluctuations around the ground-state stretch factor to be small, they can be integrated out:

$$\mathcal{H} = \int_0^{L_c} ds \left[\frac{P_b}{2} \left(\frac{d\mathbf{t}_\perp(s)}{ds} \right)^2 + \frac{P_c}{2} \dot{\psi}^2(s) - \frac{(f - B\,\dot{\psi}(s))^2}{2\,S} - f\left(1 - \frac{\mathbf{t}_\perp^2(s)}{2} \right) \right] \tag{6.3}$$

As we have local expressions for twist, $\text{tw}(s) = \frac{\dot{\psi}(s)}{2\pi}$, and writhe ω, given by Fuller’s equation, equation (4.14) up to quadratic order:

$$\omega(s) \simeq \frac{1}{4\pi} \left(t_x(s) \frac{dt_y(s)}{ds} - \frac{dt_x(s)}{ds} t_y(s) \right), \tag{6.4}$$

we can define a linking density as $\text{lk}(s) := \text{tw}(s) + \omega(s)$. The boundary conditions we want to study are with $\text{Lk} = \int ds\, \text{lk}$ fixed. Writing $\text{lk}(s) = \text{lk} + \delta(s)$, with $\text{lk} = \text{Lk} / L_c$, allows us to integrate over the fluctuations:

$$\begin{aligned}
\mathcal{H} &= \int_0^{L_c} ds \left[\frac{P_b}{2} \left(\frac{d\mathbf{t}_\perp(s)}{ds} \right)^2 + 2\pi^2 P_c (\text{lk} - \omega(s))^2 - \frac{(f - 2\pi\, B(\text{lk} - \omega(s)))^2}{2\,S} \right. \\
&\qquad \left. - f\left(1 - \frac{\mathbf{t}_\perp^2(s)}{2} \right) \right] \\
&= \int_0^{L_c} ds \left[\frac{P_b}{2} \left(\frac{d\mathbf{t}_\perp}{ds} \right)^2 + \frac{f}{2} \mathbf{t}_\perp^2 - \left(\pi\, P_c'\, \text{lk} + \frac{B\,f}{2\,S} \right) \left(t_x \dot{t}_y - \dot{t}_x t_y \right) \right] \\
&\qquad + \left(2\pi^2 P_c\, \text{lk}^2 - \frac{(f - 2\pi\, B\, \text{lk})^2}{2\,S} - f \right) L_c
\end{aligned} \tag{6.5}$$

with $P_c' := P_c - B^2 / S$, the effective torsional persistence length renormalized by the twist stretch coupling, as introduced by Marko [173]. We rescale lengths with the deflection length, $\hat{s} = s/\lambda$:

$$\mathcal{H} = \int_0^{\hat{L_c}} d\hat{s} \left[\frac{\alpha}{2} \left(\frac{d\mathbf{t}_\perp(\hat{s})}{d\hat{s}} \right)^2 + \frac{\alpha}{2} \mathbf{t}_\perp^2(\hat{s}) - \frac{\gamma}{2}(t_x \dot{t}_y - \dot{t}_x t_y) \right] + \left(2\pi^2 P_c \, lk^2 - \frac{(f - B\, 2\pi\, lk)^2}{2S} - f \right) L_c$$

with $\alpha = \sqrt{P_b f}$, $\hat{L_c} = L_c / \lambda$, and $\gamma = 2(\pi P_c' \, lk + \frac{Bf}{2S})$ dimensionless. We take periodic boundary conditions changing to Fourier series

$$\mathbf{t}(\hat{s}) = \sum_{n=-\infty}^{\infty} \mathbf{a}_n \exp\left(\imath \frac{2\pi n}{\hat{L_c}} \right) \tag{6.6}$$

resulting in

$$\mathcal{H} = \sum_{n=1}^{\infty} \left(\mathbf{a}_n^\dagger \hat{\mathsf{T}}_n \mathbf{a}_n \right) + \left(2\pi^2 P_c \, lk^2 - \frac{(f - B\, 2\pi\, lk)^2}{2S} - f \right) L_c \tag{6.7}$$

with

$$\hat{\mathsf{T}}_n = \begin{pmatrix} \alpha \left(\frac{2\pi n}{\hat{L_c}} \right)^2 + \alpha & -\imath \gamma \frac{2\pi n}{\hat{L_c}} \\ \imath \gamma \frac{2\pi n}{\hat{L_c}} & \alpha \left(\frac{2\pi n}{\hat{L_c}} \right)^2 + \alpha \end{pmatrix}. \tag{6.8}$$

The eigenvalues are

$$\mu_{n,\pm} = \alpha \left(\frac{2\pi n}{\hat{L_c}} \right)^2 + \alpha \pm \gamma \frac{2\pi n}{\hat{L_c}} \tag{6.9}$$

The partition sum is a product of Gaussian integrals and so

$$Z = \mathcal{N} \exp\left[-\left(2\pi^2 P_c \, lk^2 - \frac{(f - B\, 2\pi\, lk)^2}{2S} - f \right) L_c \right] \prod_{n=1}^{\infty} \frac{\alpha^2 (\frac{2\pi n}{\hat{L_c}})^4}{\mu_{n,+} \mu_{n,-}} \tag{6.10}$$

In the denominator of the product we have a quadratic expression in n^2. Let η_i, $(i = 1, 2)$ be its roots. Then we can write the product as:

$$\prod_{n=1}^{\infty}(\cdots) = \prod_{i=1}^{2}\prod_{n=1}^{\infty}\frac{1}{(1-\frac{\eta_i}{n^2})} = \prod_{i=1}^{2}\frac{\pi\sqrt{\eta_i}}{\sin(\pi\sqrt{\eta_i})} \tag{6.11}$$

The complex part of the square root of these roots gives the exponential decay with increasing chain length. The roots are:

$$\eta_{1,2} = \left(\frac{\hat{\mathrm{L_c}}}{2\pi}\right)^2\left(\frac{\gamma^2}{2\alpha^2} - 1 \pm \imath\frac{\gamma}{\alpha^2}\sqrt{\alpha^2 - \frac{\gamma^2}{4}}\right) \tag{6.12}$$

Alternatively we can work all the time in the continuum limit, which will turn out to be useful for the confined case coming up soon:

$$\begin{aligned}\mathcal{F} &= \left(2\pi^2\,\mathrm{P_c}\,\mathrm{lk}^2 - \frac{(\mathrm{f}-\mathrm{B}\,2\pi\,\mathrm{lk})^2}{2\,\mathrm{S}} - \mathrm{f}\right)\mathrm{L_c} + \hat{\mathrm{L_c}}\int_0^\infty\frac{\mathrm{d}p}{2\pi}\log\left(\frac{(p^2+1)^2 - \frac{\gamma^2}{\alpha^2}p^2)}{p^4}\right)\\ &= \left(2\pi^2\,\mathrm{P_c}\,\mathrm{lk}^2 - \frac{(\mathrm{f}-\mathrm{B}\,2\pi\,\mathrm{lk})^2}{2\,\mathrm{S}} - \mathrm{f} + \frac{\sqrt{\alpha^2-\gamma^2/4}}{\alpha\lambda}\right)\mathrm{L_c}\\ &= \left(2\pi^2\,\mathrm{P_c}\,\mathrm{lk}^2 - \frac{(\mathrm{f}-\mathrm{B}\,2\pi\,\mathrm{lk})^2}{2\,\mathrm{S}} - \mathrm{f} + \frac{1}{\mathrm{P_b}}\sqrt{\mathrm{f}\,\mathrm{P_b} - \tfrac{1}{4}(2\pi\,\mathrm{P_c}'\,\mathrm{lk} + \frac{\mathrm{B\,f}}{\mathrm{S}} - \frac{\sigma}{2\pi})^2}\right)\mathrm{L_c}\end{aligned} \tag{6.13}$$

To calculate the writhe density expectation value we have added a term $\sigma\omega$ to the Hamiltonian and we find

$$\begin{aligned}\langle\omega\rangle &= \frac{1}{\mathrm{L_c}}\frac{\partial\beta\,\mathcal{F}}{\partial\sigma}\bigg|_{\sigma=0} = \frac{1}{2\pi\,\mathrm{P_b}}\frac{\frac{1}{4}\left(2\pi\,\mathrm{P_c}'\,\mathrm{lk}+\frac{\mathrm{B\,f}}{\mathrm{S}}\right)}{\sqrt{\mathrm{f}\,\mathrm{P_b} - \frac{\left(2\pi\,\mathrm{P_c}'\,\mathrm{lk}+\frac{\mathrm{B\,f}}{\mathrm{S}}\right)^2}{4}}} \Rightarrow\\ \langle\mathrm{tw}\rangle &= \mathrm{lk}\left(1 - \frac{1}{2\pi\,\mathrm{P_b}}\frac{\frac{1}{4}\left(2\pi\,\mathrm{P_c}'+\frac{\mathrm{B\,f}}{\mathrm{S\,lk}}\right)}{\sqrt{\mathrm{f}\,\mathrm{P_b} - \frac{\left(2\pi\,\mathrm{P_c}'\,\mathrm{lk}+\frac{\mathrm{B\,f}}{\mathrm{S}}\right)^2}{4}}}\right)\end{aligned} \tag{6.14}$$

The stretch factor u_0 follows from equation (6.2): $u_0 = (\mathrm{f} - \mathrm{B}\, 2\pi\, \langle \mathrm{tw} \rangle)/\, \mathrm{S}$. We obtain he relative extension of the chain by differentiating the free energy with respect to the force:

$$\begin{aligned} \rho &:= \frac{\langle \Delta z \rangle}{\mathrm{L_c}} = -\frac{1}{\mathrm{L_c}} \frac{\partial \mathcal{F}}{\partial \mathrm{f}} \\ &= 1 - \frac{\mathrm{P_b} - \frac{\mathrm{B}}{2\,\mathrm{S}}(2\,\mathrm{lk}\,\pi\, \mathrm{P_c}' + \frac{\mathrm{B\,f}}{\mathrm{S}})}{2\,\mathrm{P_b} \sqrt{\mathrm{f\,P_b} - \frac{\left(2\,\mathrm{lk}\,\pi\,\mathrm{P_c}' + \frac{\mathrm{B\,f}}{\mathrm{S}}\right)^2}{4}}} + \frac{\mathrm{f} - 2\,\mathrm{B}\,\mathrm{lk}\,\pi}{\mathrm{S}} \end{aligned} \tag{6.15}$$

Finally it is interesting to know the expectation value of the torque that the end of the chain exerts on the 2 clamps that set the linking number. To calculate it, we add a term $-\tau 2\pi\ \mathrm{lk}$ to the free energy and minimize with respect to lk. This gives the torque at a point along the chain:

$$\langle \tau \rangle = 2\,\mathrm{lk}\,\mathrm{P_c}'\,\pi + \frac{\mathrm{B}(\mathrm{f} - 2\,\mathrm{B}\,\mathrm{lk}\,\pi)}{\mathrm{S}} - \frac{\mathrm{P_c}' \left(\mathrm{lk}\,\mathrm{P_c}'\,\pi + \frac{\mathrm{B\,f}}{2\,\mathrm{S}}\right)}{2\,\mathrm{P_b}\sqrt{\mathrm{f\,P_b} - \left(\mathrm{lk}\,\mathrm{P_c}'\,\pi + \frac{\mathrm{B\,f}}{2\,\mathrm{S}}\right)^2}} \tag{6.16}$$

6.2 Confined chain: isotropic case

We consider a linking number constrained chain of contour-length L_0, confined along the z-axis in a harmonic potential. Following Burkardt [171] we will assume the potential to be strong enough so that there are no overhangs. The Hamiltonian reads:

$$\mathcal{H} = \int_0^{\mathrm{L_c}} \mathrm{d}s \left[\frac{\mathrm{P_b}}{2} \left(\frac{\mathrm{d}^2 \mathbf{r}(s)}{\mathrm{d}s^2} \right)^2 + \frac{\mathrm{P_c}}{2} \dot{\psi}^2(s) + \frac{\mathrm{S}}{2} u(s)^2 + \mathrm{B}\, \dot{\psi}(s) u(s) + \frac{b}{2} (r_x^2(s) + r_y^2(s)) \right], \tag{6.17}$$

where s is the stretched chain contour, $s(t) = \int_0^t \mathrm{d}t'(1 + u(t'))$ and $\mathrm{L_c}$ the contour length of the stretched chain. We furthermore changed to coordinates perpendicular to the channel axis, neglecting all terms above quadratic ones in either $\mathbf{r}$ or its derivative.

Note that, unlike u, $\dot{\psi}$ is not in general a small variable, since we consider a chain under torsion. White's relation must hold, taking the ends parallel to the confinement axis. The absence of overhangs means that all fluctuating paths are writhe homotopic [1] to the confinement axis, so we can use Fuller's equation (4.14) and we can write $\mathrm{Wr} = \int_0^{\mathrm{L_c}} \mathrm{d}s \omega(s)$.

[1] This is actually not true since the paths in a path integral are not smooth to the extreme, but in a limit sense it can be used

Using the confinement axis as reference curve we have up to quadratic order:

$$\omega(s) \simeq \frac{1}{4\pi}\left(\frac{\mathrm{d}r_x(s)}{\mathrm{d}s}\frac{\mathrm{d}^2 r_y(s)}{\mathrm{d}s^2} - \frac{\mathrm{d}^2 r_x(s)}{\mathrm{d}s^2}\frac{\mathrm{d}r_y(s)}{\mathrm{d}s}\right) \tag{6.18}$$

We make the following coordinate change:

$$\phi(s) := \psi(s) - 2\pi\,\mathrm{lk} + 2\pi\omega(s) \text{ with linking number density: } \mathrm{lk} := \frac{\mathrm{Lk}}{\mathrm{L_c}} \tag{6.19}$$

with obviously $\int_0^{\mathrm{L_c}} \mathrm{d}s\phi(s) = 0$. After completing the square for $u(s)$ we find up to quadratic order:

$$\mathcal{H} = \int_0^{\mathrm{L_c}} \mathrm{d}s\left[\frac{\mathrm{P_b}}{2}\left(\frac{\mathrm{d}^2\mathbf{r}(s)}{\mathrm{d}s^2}\right)^2 + \frac{b}{2}\mathbf{r}^2(s) - \pi\,\mathrm{P_c}'\,\mathrm{lk}(\dot{r}_x\ddot{r}_y - \ddot{r}_x\dot{r}_y)\right] + 2\pi^2\,\mathrm{P_c}'\,\mathrm{lk}^2\,\mathrm{L_c} \tag{6.20}$$

To simplify the calculations we rescale the internal (contour) length and the external (channel width) length following Burkhardt:

$$\hat{s} = b^{1/4}\,\mathrm{P_b}^{-1/4}\,s \quad \hat{\mathbf{r}} = \mathrm{P_b}^{1/8}\,b^{3/8}\mathbf{r} \quad \hat{P} = \frac{\mathrm{P_c}'}{\mathrm{P_b}} \quad \hat{\mathrm{lk}} = b^{-1/4}\,\mathrm{P_b}^{1/4}\,\mathrm{lk} \quad \alpha := b^{1/4}\,\mathrm{P_b}^{3/4} \tag{6.21}$$

resulting in:

$$\mathcal{H} = \int_0^{\hat{\mathrm{L_c}}} \mathrm{d}\hat{s}\left[\frac{1}{2}\left(\frac{\mathrm{d}^2\hat{\mathbf{r}}(\hat{s})}{\mathrm{d}\hat{s}^2}\right)^2 + \frac{1}{2}\hat{\mathbf{r}}^2(\hat{s}) - \pi\hat{P}\hat{\mathrm{lk}}(\dot{\hat{r}}_x\ddot{\hat{r}}_y - \ddot{\hat{r}}_x\dot{\hat{r}}_y)\right] + 2\alpha\pi^2\hat{P}\hat{\mathrm{lk}}^2\hat{\mathrm{L_c}} \tag{6.22}$$

We go now to momentum space, taking periodic boundary conditions:

$$\mathcal{H} = \sum_{n=1}^{\infty}\left(\mathbf{a}_n^{\dagger}\hat{\mathsf{T}}_n\mathbf{a}_n\right) + \hat{\mathrm{L_c}}2\alpha\pi^2\hat{P}\hat{\mathrm{lk}}^2 \tag{6.23}$$

with

$$\hat{\mathsf{T}}_n = \begin{pmatrix} \left(\frac{2\pi n}{\hat{\mathrm{L_c}}}\right)^4 + 1 & \imath 2\pi\hat{P}\hat{\mathrm{lk}}\left(\frac{2\pi n}{\hat{\mathrm{L_c}}}\right)^3 \\ -\imath 2\pi\hat{P}\hat{\mathrm{lk}}\left(\frac{2\pi n}{\hat{\mathrm{L_c}}}\right)^3 & \left(\frac{2\pi n}{\hat{\mathrm{L_c}}}\right)^4 + 1 \end{pmatrix} \tag{6.24}$$

The eigenvalues are

$$\lambda_{n,\pm} = \left(\frac{2\pi n}{\hat{L_c}}\right)^4 + 1 \pm 2\pi \hat{P}\hat{lk}\left(\frac{2\pi n}{\hat{L_c}}\right)^3 =: \left(\frac{2\pi n}{\hat{L_c}}\right)^4 + 1 \pm \zeta\left(\frac{2\pi n}{\hat{L_c}}\right)^3 \tag{6.25}$$

There is an instability for

$$\zeta_{cr} = \frac{4}{3^{3/4}} \Rightarrow \mathrm{lk}_{cr} = \frac{2b^{1/4}\,\mathrm{P_b}^{3/4}}{3^{3/4}\pi\,\mathrm{P_c}'} \tag{6.26}$$

The partition sum is a product of Gaussian integrals

$$Z = \mathcal{N}\exp(-2\alpha\pi^2\hat{P}\hat{lk}^2\hat{L_c})\prod_{n=1}^{\infty}\frac{(\frac{2\pi n}{\hat{L_c}})^8}{\lambda_{n,+}\lambda_{n.-}} \tag{6.27}$$

In the denominator of the product we have a quartic expression in n^2. Let $\eta_i\bar{\eta}_i,, (i = 1, 2)$ be the pairs of conjugate roots then we can write the product as:

$$\begin{aligned}\prod_{n=1}^{\infty}(\cdots) &= \prod_{i=1,2}\prod_{n=1}^{\infty}\frac{1}{(1-\frac{\eta_i}{n^2})}\frac{1}{\left(1-\frac{\bar{\eta}_i}{n^2}\right)} \\ &= \prod_{i=1,2}\frac{\pi\sqrt{\eta_i}}{\sin(\pi\sqrt{\eta_i})}\frac{\pi\sqrt{\bar{\eta}_i}}{\sin(\pi\sqrt{\bar{\eta}_i})}\end{aligned} \tag{6.28}$$

The complex part of the square root of these roots give the exponential decay with increasing chain length. The roots are all of the form:

$$\eta_i = \left(\frac{\hat{L}}{2\pi}\right)^2\xi_i(\zeta) \qquad \text{and complex conjugate} \tag{6.29}$$

The functions ξ_i, choosing the branch cut appropriately, are found to be:

$$\xi_j(\zeta) = \frac{\zeta^2}{4} + \frac{(-1)^j}{4}\sqrt{g(\zeta)} + \frac{\imath}{2}\sqrt{4 - \frac{3}{4}\zeta^4 + \frac{g(\zeta)}{4} + (-1)^j\frac{8\zeta^2-\zeta^6}{4\sqrt{g(\zeta)}}} \tag{6.30}$$

with

$$g(\zeta) := \zeta^4 - \frac{16}{3} + \frac{128}{9h(\zeta)} + 2h(\zeta) \quad h(\zeta) := \left[4\zeta^4 - 2\zeta_{cr}^4 + 4\zeta^2\sqrt{\zeta^4-\zeta_{cr}^4)}\right]^{1/3} \tag{6.31}$$

Now write $\sqrt{\xi_{1,2}} = (x_{1,2} \pm \imath\, y_{1,2})$. In the long chain limit the contribution of the roots to the partition sum is:

$$\frac{\frac{\hat{\mathrm{L_c}}^2}{4}|\xi|}{\sin^2(\hat{\mathrm{L_c}}x/2)\cosh^2(\hat{\mathrm{L_c}}y/2) + \cos^2(\hat{\mathrm{L_c}}x/2)\sinh^2(\hat{\mathrm{L_c}}y/2)} \simeq \hat{\mathrm{L_c}}^2|\xi|e^{-\hat{\mathrm{L_c}}|y|} \tag{6.32}$$

Let $\xi_{1,2}$ be representatives of the two conjugate pairs and $y_{1,2}$ its imaginary parts. The partition sum is given by:

$$Z \simeq \mathcal{N}\exp(-2\alpha\pi^2\hat{P}\hat{\mathrm{lk}}^2\hat{\mathrm{L_c}})\hat{\mathrm{L_c}}^4|\xi_1\xi_2|e^{-\hat{\mathrm{L_c}}(|y_1|+|y_2|)} \tag{6.33}$$

The free energy of the confined chain per contour-length in the long chain limit is given by the lowest eigenvalue of the Hamiltonian :

$$\mathfrak{f} = -\lim_{\mathrm{L_c}\to\infty}\frac{1}{\mathrm{L_c}}\log(Z) = 2\pi^2\,\mathrm{P_c}'\,\mathrm{lk}^2 + \left(\frac{b}{\mathrm{P_b}}\right)^{1/4}(|y_1|+|y_2|) \tag{6.34}$$

The first term is the twist energy stored in the chain, the second represents the free energy

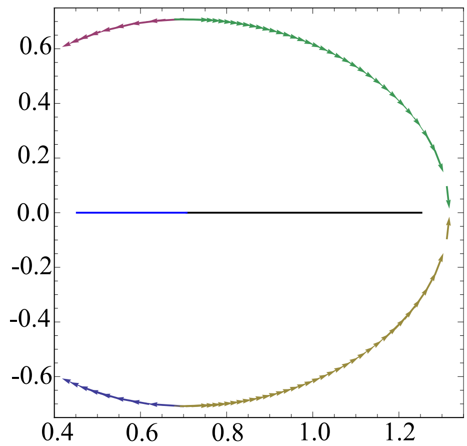

Figure 6.1: Flow of the roots $\sqrt{\xi_i}$ in the complex plane under increasing torsion. The horizontal line indicates the speed with which the roots flow as explained in the text.

of the confinement. In case the linking number density is zero, the roots are, up to a sign equal: $\xi_{1,2} = \pm\imath \Rightarrow |y_{1,2}| = 1/\sqrt{2}$ and we retrieve Burkhardt's result. The flow of the roots under increasing linking number density is depicted in Figure 6.1. Starting from $\mathrm{lk} = 0$ the root pairs move apart. Both decrease their imaginary parts, effectively decreasing the free energy of confinement. The reason is that the thermal writhe pushes the chains away from the centerline. This does not happen in a symmetric way, as is shown by the line along the x-axis, where each arrow corresponds to a fixed increase of lk. At lk_{cr} the right pair of roots becomes real indicating a singularity in the partition sum. Of course our theory breaks down before this happens. To facilitate a fast calculation of the effect of twist on the confinement free energy the following expression can be shown to give an approximation with a maximum error less than 0.7%.:

$$|y_1| + |y_2| \simeq \sqrt{2}\left[\left(\frac{3^{3/4}-1}{2\sqrt{3^{3/4}}} + \frac{\zeta}{10}\right)\sqrt{\frac{4}{3^{3/4}} - \zeta} + \frac{1}{3^{3/4}}\right] \tag{6.35}$$

Another way to calculate the free energy is the following, starting from (6.27), omitting a constant and the twist part

$$\begin{aligned}
\mathfrak{f} &= \frac{1}{\mathrm{L_c}}\sum_{n=1}^{\infty}\log\left(\frac{(p_n^4+1)^2 - \zeta^2 p_n^6}{p_n^8}\right)\\
&\simeq -\frac{b^{1/4}}{\mathrm{P_b}^{1/4}}\int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\log\left(\frac{p^8}{(p^4+1)^2 - \zeta^2 p^6}\right) \qquad \text{with } \epsilon := \frac{2\pi\,\mathrm{P_b}^{1/4}}{b^{1/4}\,\mathrm{L_c}}\\
&= -\frac{b^{1/4}}{\mathrm{P_b}^{1/4}}\left[\int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\log\left(\frac{p^8}{(p^4+1)^2}\right) - \int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\log\left(1 - \frac{\zeta^2 p^6}{(p^4+1)^2}\right)\right]
\end{aligned} \tag{6.36}$$

The first integral results in:

$$\begin{aligned}
\int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\log\left(\frac{p^8}{(p^4+1)^2}\right) =& \frac{\sqrt{2}}{\pi}\left(\arctan(1-\sqrt{2}p) - \arctan(1+\sqrt{2}p)\right)\\
&+ \frac{1}{\sqrt{2}\pi}\log\left(\frac{1-\sqrt{2}p+p^2}{1+\sqrt{2}p+p^2}\right) + \frac{p}{\pi}\log\left(\frac{p^4}{1+p^4}\right)\Bigg|_{\epsilon}^{\infty}\\
=& -\sqrt{2} - \frac{4}{\pi}\epsilon\log(\epsilon)
\end{aligned} \tag{6.37}$$

and the second, making use of the fact that $\zeta p^3 < p^4 + 1$, for $\zeta < \zeta_{cr}$, and noting that the series converges uniformly in any closed interval contained in $[0, \zeta_{cr})$, in:

$$\begin{aligned}
\int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\log\left(1 - \frac{\zeta^2 p^6}{(p^4+1)^2}\right) &= -\sum_{n=1}^{\infty}\frac{1}{n}\int_{\epsilon}^{\infty}\frac{\mathrm{d}p}{2\pi}\left(\frac{\zeta^2 p^6}{(p^4+1)^2}\right)^n\\
&= -\sum_{n=0}^{\infty}\frac{\Gamma(n/2-1/4)\Gamma(3n/2+1/4)\zeta^{2n}}{4\pi(2n)!} - \sqrt{2}
\end{aligned} \tag{6.38}$$

This can be rewritten with the help of standard gamma function identities as:

$$= -\sqrt{2}\left[1 - {}_3\mathrm{F}_2\left(-\tfrac{1}{4}, \tfrac{1}{12}, \tfrac{5}{12}; \tfrac{1}{4}, \tfrac{1}{2}; \tfrac{\zeta^4}{\zeta_{cr}^4}\right) + \frac{3\zeta^2}{32}\,{}_3\mathrm{F}_2\left(\tfrac{1}{4}, \tfrac{7}{12}, \tfrac{11}{12}; \tfrac{3}{4}, \tfrac{3}{2}; \tfrac{\zeta^4}{\zeta_{cr}^4}\right)\right] + \mathcal{O}(\epsilon^7) \tag{6.39}$$

making the bifurcation point explicit. The free energy of confinement is finally given by:

$$\mathfrak{f} = \frac{b^{1/4}}{\mathrm{P_b}^{1/4}}\sqrt{2}\left[{}_3\mathrm{F}_2\Big(-\tfrac{1}{4}, \tfrac{1}{12}, \tfrac{5}{12}; \tfrac{1}{4}, \tfrac{1}{2}; \tfrac{\zeta^4}{\zeta_{cr}^4}\Big) - \frac{3\zeta^2}{32}\, {}_3\mathrm{F}_2\Big(\tfrac{1}{4}, \tfrac{7}{12}, \tfrac{11}{12}; \tfrac{3}{4}, \tfrac{3}{2}; \tfrac{\zeta^4}{\zeta_{cr}^4}\Big)\right] \tag{6.40}$$

or defining the "small" parameter $x := \zeta/\zeta_{cr}$ and the dimensionless parameter $\gamma := \frac{2\pi\, \mathrm{P_c}'\sqrt{2}}{\zeta_{cr}\,\mathrm{P_b}}$

$$\begin{aligned} g := \frac{\mathfrak{f}}{\gamma\, \mathrm{lk}} &= \frac{1}{x}\, {}_3\mathrm{F}_2\big(-\tfrac{1}{4}, \tfrac{1}{12}, \tfrac{5}{12}; \tfrac{1}{4}, \tfrac{1}{2}; x^4\big) - \frac{x}{2\sqrt{3}}\, {}_3\mathrm{F}_2\big(\tfrac{1}{4}, \tfrac{7}{12}, \tfrac{11}{12}; \tfrac{3}{4}, \tfrac{3}{2}; x^4\big) \\ &= \frac{1}{x} - \frac{x}{2\sqrt{3}} - \frac{5x^3}{72} + \mathcal{O}(x^7) \end{aligned}$$

An estimate of the rest term can be obtained using the asymptotic expansion of the gamma function:

$$\begin{aligned} &\simeq \frac{1}{x} - \frac{x}{2\sqrt{3}} - \frac{5x^3}{72} - \frac{x^5}{4\sqrt{\pi}(1-x^2)} \\ &= \sum_{n=0}^{\infty} a_n x^{2n-1}, \text{ with } a_n := \frac{\Gamma(n/2-1/4)\Gamma(3n/2+1/4)\zeta_{cr}^{2n}}{4\pi\sqrt{2}(2n)!} \end{aligned} \tag{6.41}$$

It is somewhat unexpected that the two expressions for the free energy equation (6.34) and equation (6.40) are equivalent, but the second can be seen as the Laurent series of the first. It is useful to express the free energy in terms of the width of the fluctuations in the channel. For long chains this can be easily obtained from the free energy density (Burkhardt):

$$z := \frac{\mathrm{P_b}\,\gamma^3\,\mathrm{lk}^3}{2}\langle \mathbf{r}^2\rangle = \frac{\mathrm{P_b}\,\gamma^3\,\mathrm{lk}^3}{2} 2\frac{\partial \mathfrak{f}}{\partial b} = -x^5\frac{\partial g}{\partial x} = -\sum_{n=0}^{\infty}(2n-1)a_n x^{2n+3},$$

or in generalized Hypergeometric functions:

$$\begin{aligned} z = x^3\, {}_3\mathrm{F}_2\big(-\tfrac{1}{4}, \tfrac{1}{12}, \tfrac{5}{12}; \tfrac{1}{4}, \tfrac{1}{2}; x^4\big) + \frac{1}{2\sqrt{3}}x^5\, {}_3\mathrm{F}_2\big(\tfrac{1}{4}, \tfrac{7}{12}, \tfrac{11}{12}; \tfrac{3}{4}, \tfrac{3}{2}; x^4\big) \\ + \frac{5}{18}x^7\, {}_3\mathrm{F}_2\big(\tfrac{3}{4}, \tfrac{13}{12}, \tfrac{17}{12}; \tfrac{5}{4}, \tfrac{3}{2}; x^4\big) + \frac{77}{324\sqrt{3}}x^9\, {}_3\mathrm{F}_2\big(\tfrac{5}{4}, \tfrac{19}{12}, \tfrac{23}{12}; \tfrac{7}{4}, \tfrac{5}{2}; x^4\big) \end{aligned}$$

We now wish to invert the series (6.42). We use a standard trick to rewrite the series in a form that makes it suitable for Lagrange inversion, namely as a series where the derivative at the point of inversion is finite. We first write

$$z(x) = a_0 x^3 \left(1 - \sum_{n=1}^{\infty} (2n-1) \frac{a_n}{a_0} x^{2n}\right), \tag{6.42}$$

then consider the following series:

$$y(x) := \sqrt[3]{z(x)} = \sqrt[3]{a_0} x \left[1 + \sum_{k=1}^{\infty} \frac{1}{k!} \frac{\Gamma(-1/3+k)}{\Gamma(-1/3)} \left(\sum_{n=1}^{\infty} (2n-1) \frac{a_n}{a_0} x^{2n}\right)^k\right], \tag{6.43}$$

and finally apply Lagrange inversion on $y(x)$:

$$x(z) = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\mathrm{d}^{n-1}}{\mathrm{d}x^{n-1}} \left(\frac{x}{y(x)}\right)^n \Bigg|_{x=0} z^{n/3} \tag{6.44}$$

The first terms of the resulting series are:

$$\begin{aligned} x(z) &= z^{1/3} - \frac{z}{6\sqrt{3}} - \frac{7z^{5/3}}{216} + \mathcal{O}(x^{7/3}) \\ g(z) &= \frac{1}{z^{1/3}} - \frac{z^{1/3}}{3\sqrt{3}} + \frac{5z^{5/3}}{243\sqrt{3}} + \mathcal{O}(z^{7/3}) \end{aligned}$$

or in terms of the unscaled variables:

$$\mathfrak{f} = \frac{2^{1/3}}{\mathrm{P_b}^{1/3} \left\langle \mathbf{r}^2 \right\rangle^{1/3}} - \frac{(2\pi\ \mathrm{lk}\, \mathrm{P_c}^{'})^2}{8 \quad 2^{1/3}\, \mathrm{P_b}^2} (\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{1/3} + \mathcal{O}\Big(\frac{(2\pi\ \mathrm{lk}\, \mathrm{P_c}^{'})^5}{\mathrm{P_b}^6} (\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{5/3}\Big) \tag{6.45}$$

The demand $\zeta \ll \zeta_{cr}$ translates into $(\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{1/3} \ll \mathrm{P_b} / (2\pi\ \mathrm{P_c}^{'}\ \mathrm{lk})$. In the plectoneme the free energy of the confining potential is taken into account. When the potential causing the confinement potential is separately known, but complicated, the harmonic potential is just there to get an estimate for the cost of confining the chain and so its contribution needs to be subtracted [153] to get the confinement free energy:

$$\begin{aligned} \mathfrak{f}_{pot} =& \frac{1}{2} b \left\langle \mathbf{r}^2 \right\rangle = \frac{1}{4} \frac{2^{1/3}}{(\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{1/3}} + \frac{(2\pi\ \mathrm{lk}\, \mathrm{P_c}^{'})^2}{16 \quad 2^{1/3}\, \mathrm{P_b}^2} (\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{1/3} + \frac{3(2\pi\ \mathrm{lk}\, \mathrm{P_c}^{'})^4}{2^8\, \mathrm{P_b}^4} \mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle \\ &+ \mathcal{O}\Big(\frac{(2\pi\ \mathrm{lk}\, \mathrm{P_c}^{'})^5}{\mathrm{P_b}^6} (\mathrm{P_b} \left\langle \mathbf{r}^2 \right\rangle)^{5/3}\Big) \end{aligned}$$

and so we find

$$\mathfrak{f}_{conf} = \frac{3}{2^{5/3}} \frac{1}{(\mathrm{P_b}\,\langle \mathbf{r}^2\rangle)^{1/3}} - \frac{3(2\pi\ \mathrm{lk}\,\mathrm{P_c}')^2}{16\quad 2^{1/3}\,\mathrm{P_b}^2} (\mathrm{P_b}\,\langle \mathbf{r}^2\rangle)^{1/3} - \frac{3(2\pi\ \mathrm{lk}\,\mathrm{P_c}')^4}{2^8\,\mathrm{P_b}^4}\,\mathrm{P_b}\,\langle \mathbf{r}^2\rangle + \mathcal{O}\Big(\frac{(2\pi\ \mathrm{lk}\,\mathrm{P_c}')^5}{\mathrm{P_b}^6} (\mathrm{P_b}\,\langle \mathbf{r}^2\rangle)^{5/3}\Big) \tag{6.46}$$

We next consider the average thermal writhe, which is conjugate to the linking number in the fluctuation free energy:

$$\begin{aligned}\omega &= -\frac{1}{2\pi}\,\frac{\partial \mathfrak{f}}{\partial(2\pi\,\mathrm{P_c}'\,\mathrm{lk})}\bigg|_b \\ &= \frac{3}{2^{11/2}}\frac{\mathrm{P_c}'\,\mathrm{lk}}{\mathrm{P_b}^2}(\mathrm{P_b}\,\langle \mathbf{r}^2\rangle)^{1/3} + \frac{317}{2^{21/2}}\frac{\pi^2(\mathrm{P_c}'\,\mathrm{lk})^3}{\mathrm{P_b}^4}\,\mathrm{P_b}\,\langle \mathbf{r}^2\rangle + \mathcal{O}\left(\frac{(\mathrm{lk}\,\mathrm{P_c}')^5}{\mathrm{P_b}^6}(\mathrm{P_b}\,\langle \mathbf{r}^2\rangle)^{5/3}\right)\end{aligned} \tag{6.47}$$

Of course Whites relation gives us at the same time the average twist density.

To calculate the extension we add a term $(\lambda/2)(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}s})^2$ to the fluctuation Hamiltonian (6.20). The extension is then given by, using the results of section 6.1,:

$$\rho := \frac{\Delta z}{\mathrm{L_c}} = \left(1 + \frac{\mathrm{B}}{\mathrm{S}} 2\pi\ \mathrm{lk} - \frac{\partial \mathfrak{f}}{\partial \lambda}\bigg|_{\lambda=0}\right) \tag{6.48}$$

The resulting free energy expression changes to:

$$\begin{aligned}\mathfrak{f} &= -\frac{b^{1/4}}{\mathrm{P_b}^{1/4}} \int_0^\infty \frac{\mathrm{d}p}{2\pi} \log\left(\frac{p^8}{(p^4 + \hat{\lambda} p^2 + 1)^2 - \bar{\zeta}^2(\lambda) p^6}\right) \\ &= -\frac{b^{1/4}}{\mathrm{P_b}^{1/4}} \left[\int_0^\infty \frac{\mathrm{d}p}{2\pi} \log\left(\frac{p^8}{(p^4 + \hat{\lambda} p^2 + 1)^2}\right) + \sum_{n=1}^{\infty} \int_0^\infty \frac{\mathrm{d}p}{2\pi n} \left(\frac{\bar{\zeta}^2(\lambda) p^6}{(p^4 + \hat{\lambda} p^2 + 1)^2}\right)^n\right],\end{aligned} \tag{6.49}$$

with $\hat{\lambda} = \lambda\,\mathrm{P_b}^{-1/2}\,b^{-1/2}$ and $\bar{\zeta}(\lambda) = \frac{2\pi\,\mathrm{P_c}'\,\mathrm{lk} + \mathrm{B}\,\lambda/(\mathrm{S})}{\mathrm{P_b}^{3/4}\,b^{1/4}}$. We need $\partial_\lambda \mathfrak{f}$ at $\lambda = 0$. The first integral results in:

$$\begin{aligned}\frac{\partial}{\partial \lambda} \int_0^\infty \frac{\mathrm{d}p}{2\pi} \log\left(\frac{p^8}{(p^4 + \hat{\lambda} p^2 + 1)^2}\right)\bigg|_{\lambda=0} &= \mathrm{P_b}^{-1/2}\,b^{-1/2} \frac{\partial}{\partial \hat{\lambda}} \left(-2\sqrt{\frac{1}{2} + \frac{\hat{\lambda}}{4}}\right)\bigg|_{\hat{\lambda}=0} \\ &= -2^{-3/2}\,\mathrm{P_b}^{-1/2}\,b^{-1/2}\end{aligned} \tag{6.50}$$

while the second integral results in:

$$\frac{\partial}{\partial\lambda}\int_0^\infty \frac{\mathrm{d}p}{2\pi n}\left(\frac{\bar{\zeta}^2 p^6}{(p^4+\hat{\lambda}p^2+1)^2}\right)^n\Bigg|_{\lambda=0}$$
$$= -\frac{1}{\sqrt{b\,\mathrm{P_b}}}\int_0^\infty \frac{\mathrm{d}p}{\pi}\left(\frac{\zeta^2 p^6}{(p^4+1)^2}\right)^n \frac{p^2}{p^4+1} + \frac{\mathrm{B}\,\zeta^{2n-1}}{\mathrm{S}\,\mathrm{P_b}^{3/4}\,b^{1/4}}\int_0^\infty \frac{\mathrm{d}p}{\pi}\left(\frac{p^6}{(p^4+1)^2}\right)^n$$
$$= -\frac{\Gamma(n/2+1/4)\Gamma(3n/2+3/4)}{4\pi(2n)!(b\,\mathrm{P_b})^{1/2}}\zeta^{2n} + \frac{\mathrm{B}\,\zeta^{2n-1}\Gamma(n/2-1/4)\Gamma(3n/2+1/4)}{4\pi(2n-1)!b^{1/4}\,\mathrm{S}\,\mathrm{P_b}^{3/4}} \tag{6.51}$$

And so we find as contraction factor:

$$\rho = 1 - \frac{1}{2\sqrt{2}b^{1/4}\,\mathrm{P_b}^{3/4}} + \frac{3\,\mathrm{B}\,\zeta}{8\sqrt{2}\,\mathrm{P_b}\,\mathrm{S}} - \frac{5\zeta^2}{64\sqrt{2}b^{1/4}\,\mathrm{P_b}^{3/4}}$$
$$= 1 - \frac{2\,\mathrm{B}\,\mathrm{lk}}{\mathrm{S}} - \frac{(1-\frac{3\,\mathrm{B}\,\mathrm{P_c}'\,\pi\,\mathrm{lk}}{2\,\mathrm{S}\,\mathrm{P_b}})}{2^{4/3}\,\mathrm{P_b}}(\mathrm{P_b}\langle\mathbf{r}^2\rangle)^{1/3} - \frac{(1+\frac{3\,\mathrm{B}\,\mathrm{P_c}'\,\pi\,\mathrm{lk}}{8\,\mathrm{P_b}\,\mathrm{S}})(\mathrm{P_c}'\,\pi\,\mathrm{lk})^2}{4\,\mathrm{P_b}^3}\,\mathrm{P_b}\langle\mathbf{r}^2\rangle \tag{6.52}$$

6.3 Non isotropic confinement

We now consider a confinement in a channel, where the confining potential in the two directions have a different strength. The Hamiltonian (6.20) changes to:

$$\mathcal{H} = \int_0^{\mathrm{L_c}} \mathrm{d}s\left[\frac{\mathrm{P_b}}{2}\left(\frac{\mathrm{d}^2\mathbf{r}(s)}{\mathrm{d}s^2}\right)^2 + \frac{b_x}{2}r_x^2(s) + \frac{b_y}{2}r_y^2(s) - \pi\,\mathrm{P_c}'\,\mathrm{lk}(\dot{r}_x\ddot{r}_y - \ddot{r}_x\dot{r}_y)\right] + 2\pi^2\,\mathrm{P_c}'\,\mathrm{lk}^2\,\mathrm{L_c} \tag{6.53}$$

The rescaling is as before except that we replace b with

$$\lambda(b_x,b_y) := \frac{2\big(33(b_x^2 b_y + b_x b_y^2) + (b_x^2 + 14 b_x b_y + b_y^2)^{3/2} - b_x^3 - b_y^3\big)}{27 b_x b_y}. \tag{6.54}$$

which has the dimension of $[L^{-3}]$. With that choice the bifurcation point is at:

$$\zeta_{cr} := \frac{2\pi\,\mathrm{P_c}'\,\mathrm{lk}_{cr}}{\mathrm{P_b}^{3/4}\,\lambda^{1/4}} = 1. \tag{6.55}$$

And so we have again a suitable parameter for an expansion. The free energy corresponding to (6.36) is now given by:

$$
\begin{aligned}
\mathfrak{f} &= -\frac{\lambda^{1/4}}{{\mathrm{P_b}}^{1/4}} \int_0^\infty \frac{\mathrm{d}p}{2\pi} \log\left(\frac{p^8}{(p^4 + b_x/\lambda)(p^4 + b_y/\lambda) - \zeta^2 p^6}\right) \\
&= \frac{\lambda^{1/4}}{{\mathrm{P_b}}^{1/4}} \left(\frac{b_x^{1/4} + b_y^{1/4}}{\sqrt{2}\lambda^{1/4}}\right. \\
&\quad \left. - \frac{\lambda^{1/4}(b_x^{3/4} - b_y^{3/4})}{4\sqrt{2}(b_x - b_y)}\zeta^2 - \frac{\lambda^{3/4}(b_x^{9/4} - 9b_x^{5/4} b_y + 9 b_x b_y^{5/4} - b_y^{9/4})}{32\sqrt{2}(b_x - b_y)^3}\zeta^4 + \mathcal{O}(\zeta^6)\right)
\end{aligned}
\tag{6.56}
$$

The λ's neatly cancel. This is obvious from the way the scaling was defined but this makes the expansion more transparent. Since λ cancels we change to a new parameter $\alpha := 2\pi\, {\mathrm{P_c}}'\, \mathrm{lk}$. The critical point can be written as

$$
\left(2\pi\, {\mathrm{P_c}}'\, \mathrm{lk}_{cr}\right)^2 = \frac{4\sqrt{2}(b_x\, {\mathrm{P_b}}^3 + b_y\, {\mathrm{P_b}}^3) + 2\sqrt{(2(b_x + b_y)^2 + 24 b_x b_x)\, {\mathrm{P_b}}^6}}{3\sqrt{(b_x\, {\mathrm{P_b}}^3 + b_y\, {\mathrm{P_b}}^3) + \sqrt{((b_x\, {\mathrm{P_b}}^3 + b_y)^2 + 12 b_x b_x)\, {\mathrm{P_b}}^6}}}
\tag{6.57}
$$

To get an expression for the free energy as function of the second moment of the fluctuations we will use a multivariate extension of Lagrange inversion [174, 175]. For the choice of point of reversion and parameterization we will first try to treat both directions on equal footing.

We start by defining suitable scales and parameters. Define, with $i = x$ or y:

$$
z_i := \frac{\alpha}{{\mathrm{P_b}}^{3/4}\, b_i^{1/4}} \qquad\qquad \mathfrak{g}(z_x, z_y) := \frac{\mathrm{P_b}}{\alpha}\, \mathfrak{f}[b_x(z_x), b_y(z_y)],
\tag{6.58}
$$

with $i = x$ or y. The average fluctuation variance can now be calculated (as before) as:

$$
v_i(z_x, z_y) := 2\frac{\alpha^3}{{\mathrm{P_b}}^2} \left\langle r_i^2 \right\rangle (z_x, z_y) = -z_i^5 \partial_{z_i}\, \mathfrak{g}(z_x, z_y)
\tag{6.59}
$$

We need a formal power series $f_{x,y}$ that implicitly defines $z_{x,y}$ as a power series in $v_{x,y}$ through $z_i = v_i^{1/3} f_i(z_x, z_y)$. Note that we have taken the (reduced) variance to the power $1/3$, since this functional equation has only a solution, that is then also unique, when $f_i(0,0) \neq 0$. We define f_i as:

$$
f_i(z_x, z_y) := \frac{z_i}{v_i^{1/3}(z_x, z_y)}
\tag{6.60}
$$

The coefficient for the term $(\sqrt[3]{v_x})^n(\sqrt[3]{v_y})^m$, n, m not necessarily positive, of $\mathfrak{g}$, as a power series in $u_i := \sqrt[3]{v_i}$, is given by the Good-Lagrange formula [174, 175]

$$\begin{aligned}
&[u_{x,y}]^{n,m}\, \mathfrak{g}\big(z_x(u_x), z_y(u_y)\big) \\
&\quad =[z_{x,y}]^{n,m}\, \mathfrak{g}(z_x, z_y)\, f_x^n(z_x, z_y)\, f_y^m(z_x, z_y)\, \mathrm{Det}\left(\delta_{i,j} - \frac{z_i}{f_j(z_x, z_y)}\frac{\partial f_j(z_x, z_y)}{\partial z_i}\right) \\
&\quad =[z_{x,y}]^{n,m}\, \mathfrak{g}(z_x, z_y)\, f_x^n(z_x, z_y)\, f_y^m(z_x, z_y) \frac{1}{9}\, \mathrm{Det}\left(\frac{z_i}{v_j(z_x, z_y)}\frac{\partial v_j(z_x, z_y)}{\partial z_i}\right)
\end{aligned} \tag{6.61}$$

where $[x_{1,2}]^{n,m} F(x_{1,2})$ denotes the coefficient of the monomial $x_1^n x_2^m$ in the (formal) power series F. Of course the same would hold would we replace $\mathfrak{g}$ with some other power series. From the above we find:

$$\begin{aligned}
\mathfrak{g} =& \frac{1}{2^{2/3}}(v_x^{-1/3} + v_y^{-1/3}) - \frac{1}{6\ 2^{1/3}}(v_x^{1/3} + v_y^{1/3}) + \frac{1}{6\ 2^{1/3}}(v_x^{4/3} v_y^{-1} + v_x^{-1} v_y^{4/3}) \\
& - \frac{1}{6\ 2^{1/3}}(v_x^{5/3} v_y^{-4/3} + v_x^{-4/3} v_y^{5/3}) + \frac{1}{324\ 2^{2/3}}(v_x^{5/3} + v_y^{5/3})
\end{aligned} \tag{6.62}$$

and we clearly have a problem: there are an infinite number of terms in $(v_x^{(2n+1)/3} + v_y^{(2n+1)/3})$ with coefficients that do not decrease. To resolve this we will redefine our expansion parameters. We will distinguish two cases: either the harmonic potentials are almost equal, $b_x \approx b_y$ and $\langle r_x^2 \rangle \approx \langle r_y^2 \rangle$, or one of them is much smaller, say $b_x \ll b_y$. In the end we will see that they both lead to the same answer.

6.3.1 Almost isotropic case

In the first case we will use $z := z_x$ and $\delta_w := z_y/z_x - 1$ as parameterization of the potentials and $v := v_x$, $\Delta_w := \langle r_y^2 \rangle / \langle r_x^2 \rangle - 1$ as variance parameters. The defining power series are now:

$$f_v(z, \delta_w) := \frac{z}{v^{1/3}(z, \delta_w)} \qquad \text{and} \qquad f_{\Delta_w}(z, \delta_w) := \frac{\delta_w}{\Delta_w(z, \delta_w)} \tag{6.63}$$

resulting in the Good-Lagrange equation:

$$\begin{aligned}
&[\sqrt[3]{v}, \Delta_w]^{n,m}\, \mathfrak{g}\big(z(\sqrt[3]{v}, \Delta_w), \delta_w(\sqrt[3]{v}, \Delta_w)\big) = \\
&[z, \delta_w]^{n,m}\, \mathfrak{g}(z, \delta_w) \frac{f_v^n(z, \delta_w) f_{\Delta_w}^m(z, \delta_w) z \delta_w}{3 v(z, \delta_w) \Delta_w(z, \delta_w)}\, \mathrm{Det}\begin{pmatrix} \partial_z v(z, \delta_w) & \partial_z \Delta_w(z, \delta_w) \\ \partial_{\delta_w} v(z, \delta_w) & \partial_{\delta_w} \Delta_w(z, \delta_w) \end{pmatrix}
\end{aligned} \tag{6.64}$$

From this we find:

$$\mathfrak{g} = \left(2^{1/3} - \frac{\Delta_w}{3\,2^{2/3}} + \mathcal{O}(\Delta_w^2)\right) v^{-1/3} - \left(\frac{1}{8\,2^{1/3}} + \frac{\Delta_w}{48\,2^{1/3}} + \mathcal{O}(\Delta_w^2)\right) v^{1/3} + \mathcal{O}(v^{5/3})$$

$$\Rightarrow \mathfrak{f} = \frac{1-\Delta_w/6}{(\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3}} - \frac{\alpha^2(1+\Delta_w/6)}{8\,\mathrm{P_b}^2}(\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3} + \mathcal{O}(\alpha^4) \tag{6.65}$$

Also here we can calculate the entropic contribution to the confinement free energy, subtracting the contribution of the artificial harmonic potential (in case the confinement potential has been taken care of separately). Replacing $\mathfrak{g}$ in the Good-Lagrange equation (6.64) with the expectation value of the reduced potential energy density $\langle U\rangle = \frac{1}{2}(b_x\left\langle r_x^2\right\rangle + b_y\left\langle r_y^2\right\rangle)$ we find:

$$\begin{aligned}
&[\sqrt[3]{v}, \Delta_w]^{n,m}\,\langle U\rangle\left(z(\sqrt[3]{v},\Delta_w), \delta_w(\sqrt[3]{v},\Delta_w)\right) = \\
&\qquad \frac{\alpha^2}{2\,\mathrm{P_b}}[z,\delta_w]^{n,m}\frac{1}{2}(z^{-4}v(z,\delta_w) + [z(1+\delta_w)]^{-4}v(z,\delta_w)(1+\Delta_w(z,\delta_w)) \\
&\qquad\qquad \frac{f_v^n(z,\delta_w)f_{\Delta_w}^m(z,\delta_w)z\delta_w}{3v(z,\delta_w)\Delta_w(z,\delta_w)}\,\mathrm{Det}\begin{pmatrix}\partial_z v(z,\delta_w) & \partial_z\Delta_w(z,\delta_w)\\ \partial_{\delta_w}v(z,\delta_w) & \partial_{\delta_w}\Delta_w(z,\delta_w)\end{pmatrix} \Rightarrow
\end{aligned}$$

$$\langle U\rangle = \frac{1-\Delta_w/6}{(4\,\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3}} + \frac{\alpha^2(1+\Delta_w/6)}{16\,\mathrm{P_b}^2}(\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3} + \mathcal{O}(\alpha^6) \tag{6.66}$$

and so

$$\mathfrak{f}_{conf} = \mathfrak{f} - \langle U\rangle = \frac{(3-\Delta_w/2)}{4(\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3}} - \frac{\alpha^2(1+\Delta_w/6)}{16\,\mathrm{P_b}^2}(\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3} + \mathcal{O}(\alpha^4) \tag{6.67}$$

Note that these results lead to the right isotropic expressions since:

$$\frac{1}{\left\langle \mathbf{r}^2\right\rangle^{1/3}} = \frac{1}{(\left\langle r_x^2\right\rangle + \left\langle r_y^2\right\rangle)^{1/3}} \approx \frac{1-\Delta_w/6}{2^{1/3}\left\langle r_x^2\right\rangle^{1/3}} \tag{6.68}$$

For the extension we add again a fictitious force term as in the isotropic case, leading to

$$\begin{aligned}\rho_w &= 1 - \frac{1}{\mathrm{P_b}} \sum_{n=0}^{\infty} \int_0^{\infty} \frac{\mathrm{d}p}{2\pi} \frac{p^2(2p^4 + b_x + b_y)p^{6n}}{\big((p^4 + b_x)(p^4 + b_y)\big)^{2n+1}} \\ &= 1 - \frac{1}{4\sqrt{2}\,\mathrm{P_b}^{3/4}} \Bigg(\frac{b_x^{1/4} + b_y^{1/4}}{(b_x b_y)^{1/4}} + \frac{5\alpha^2}{4(b_x^{1/4} + b_y^{1/4})\left(\sqrt{b_x} + \sqrt{b_y}\right)\mathrm{P_b}^{3/2}} \\ &\qquad + \frac{11(b_x + b_y + 6\sqrt{b_x b_y} + 3b_x^{3/4}b_y^{1/4} + 3b_x^{1/4}b_y^{3/4})\alpha^4}{32\sqrt{2}(b_x^{3/4} + b_y^{3/4})(\sqrt{b_x} + \sqrt{b_y})^3\,\mathrm{P_b}^3} + \mathcal{O}(\alpha^6)\Bigg)\end{aligned} \tag{6.69}$$

relying again on the inversion formula. This finally results in:

$$\rho_w = 1 - \frac{(1 + \Delta_w/6)}{2\,\mathrm{P_b}} (\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3} - \frac{(1 + \Delta_w/2)\alpha^2}{8\,\mathrm{P_b}^3}\,\mathrm{P_b}\left\langle r_x^2\right\rangle \tag{6.70}$$

Finally we calculate the writhe density as function of the linking number density:

$$\omega = \frac{(3 + \Delta_w/2)\,\mathrm{P_c}'\,\mathrm{lk}}{8\,\mathrm{P_b}^2} (\mathrm{P_b}\left\langle r_x^2\right\rangle)^{1/3} + \frac{(3 + 3\Delta_w/2)\pi^2(\mathrm{P_c}'\,\mathrm{lk})^3}{8\,\mathrm{P_b}^4}\,\mathrm{P_b}\left\langle r_x^2\right\rangle \tag{6.71}$$

Next we will check the limit of high anisotropy.

6.3.2 Strong anisotropy

We assume $b_x \gg b_y \Rightarrow \left\langle r_x^2\right\rangle \ll \left\langle r_y^2\right\rangle$. We change δ_w and Δ_w to $\delta_s := z_x/z_y$ and $\Delta_s := (\left\langle r_x^2\right\rangle / \left\langle r_y^2\right\rangle)$, keeping the other two variables from the previous case. The defining power series are:

$$f_v(z, \delta_s) := \frac{z}{v^{1/3}(z, \delta_s)} \qquad \text{and} \qquad f_{\Delta_s}(z, \delta_s) := \frac{\delta_s}{\Delta_s^{1/3}(z, \delta_s)} \tag{6.72}$$

Note that this time we need $\Delta_s^{1/3}$ since to lowest order $\Delta_s \sim \delta_s^3$. As inversion formula we find:

$$\begin{aligned}&[\sqrt[3]{v}, \sqrt[3]{\Delta_s}]^{n,m}\, \mathfrak{g}\big(z(\sqrt[3]{v}, \sqrt[3]{\Delta_s}), \delta_s(\sqrt[3]{v}, \sqrt[3]{\Delta_s})\big) = \\ &\qquad [z, \delta_s]^{n,m}\, \mathfrak{g}(z, \delta_s) \frac{f_v^n(z, \delta_s) f_{\Delta_s}^m(z, \delta_s) z\delta_s}{9v(z, \delta_s)\Delta_s(z, \delta_s)}\, \mathrm{Det} \begin{pmatrix} \partial_z v(z, \delta_s) & \partial_z \Delta_s(z, \delta_s) \\ \partial_{\delta_s} v(z, \delta_s) & \partial_{\delta_s} \Delta_s(z, \delta_s) \end{pmatrix}\end{aligned} \tag{6.73}$$

resulting in:

$$\mathfrak{g} = \frac{1}{2^{2/3}}\left(1+\Delta_s^{1/3}\right)v^{-1/3} - \frac{1}{6\,2^{1/3}}\left(1-\Delta_s+\Delta_s^{4/3}+\mathcal{O}(\Delta_s^{7/3})\right)v^{1/3}$$
$$+\frac{1}{3\,2^{2/3}}\left(\frac{1}{108}-\frac{1}{36}\Delta_s+\frac{1}{3}\Delta_s^{4/3}-\frac{1}{2}\Delta_s^{5/3}+\mathcal{O}(\Delta_s^{6/3})\right)v^{5/3}+\mathcal{O}(v^{7/3}) \Rightarrow$$

We can in fact sum up all terms in Δ_s in the second term to get as compact expression:

$$\begin{aligned}\mathfrak{f} &= \frac{1+\Delta_s^{1/3}}{2(\mathrm{P_b}\langle r_x^2\rangle)^{1/3}} - \frac{(1-\Delta_s)(2\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{6\,\mathrm{P_b}^2(1-\Delta_s^{4/3})}(\mathrm{P_b}\langle r_x^2\rangle)^{1/3} \\ &= \frac{1+\Delta_s^{1/3}}{2(\mathrm{P_b}\langle r_x^2\rangle)^{1/3}} - \frac{(1+\Delta_s^{1/3}+\Delta_s^{2/3})(2\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{6\,\mathrm{P_b}^2(1+\Delta^{1/3})(1+\Delta^{2/3})}(\mathrm{P_b}\langle r_x^2\rangle)^{1/3}\end{aligned} \tag{6.74}$$

Remembering the definition of Δ_s it is immediately clear that the end result can be written in a symmetric way covering all cases in one formula. It is useful to introduce now the concept of deflection length of confinement as

$$\lambda_{x,y} := (\mathrm{P_b}\langle r_{x,y}^2\rangle)^{1/3} \qquad \bar{\lambda} = 2\frac{\lambda_x^3\lambda_y+\lambda_x^2\lambda_y^2+\lambda_x\lambda_y^3}{(\lambda_x+\lambda_y)(\lambda_x^2+\lambda_y^2)} \tag{6.75}$$

as a length scale over which the potential starts to dominate thermal motion. The factor 2 is a matter of convention. The torsion mixes the two confinement directions. The new deflection length that emerges can be seen as an effective one, dominated by the smallest dimension in case of highly anisotropic confinement, equal to the conventional one for isotropic confinement. With these definitions the final result of this chapter can be written as:

$$\mathfrak{f} = \frac{1}{2}\left(\frac{\mathrm{P_b}}{\lambda_x}+\frac{\mathrm{P_b}}{\lambda_y}\right) - \frac{1}{12}\frac{\bar{\lambda}(\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{\mathrm{P_b}^2} \tag{6.76a}$$

Not to become too repetitive we just mention the results for all other relevant quantities:

$$\langle U\rangle = \frac{1}{8}\left(\frac{\mathrm{P_b}}{\lambda_x}+\frac{\mathrm{P_b}}{\lambda_y}\right) + \frac{1}{24}\frac{\bar{\lambda}(\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{\mathrm{P_b}^2} \tag{6.76b}$$

$$\mathfrak{f}_{conf} = \frac{3}{8}\left(\frac{\mathrm{P_b}}{\lambda_x}+\frac{\mathrm{P_b}}{\lambda_y}\right) - \frac{1}{8}\frac{\bar{\lambda}(\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{\mathrm{P_b}^2} \tag{6.76c}$$

$$\rho_s = 1 - \frac{2\,\mathrm{B\,lk}}{\mathrm{S}} - \frac{1}{4}\left(\frac{\lambda_x}{\mathrm{P_b}} + \frac{\lambda_y}{\mathrm{P_b}}\right) + \frac{\bar{\lambda}\,\mathrm{B}\,\pi\,\mathrm{P_c}'\,\mathrm{lk}}{2\,\mathrm{S}\,\mathrm{P_b}^2}$$
$$- \frac{(7\lambda_x^3\lambda_y^5 - 2\lambda_x^4\lambda_y^4 + 7\lambda_x^5\lambda_y^3)(\pi\,\mathrm{P_c}'\,\mathrm{lk})^2}{12(\lambda_x + \lambda_y)(7\lambda_x^2 + \lambda_y^2)^2\,\mathrm{P_b}^3} \tag{6.76d}$$

$$\omega = \frac{\bar{\lambda}\,\mathrm{P_c}'\,\mathrm{lk}}{4\,\mathrm{P_b}^2} \tag{6.76e}$$