# ICFP M1 - Phase Transitions – TD n° 8 – Solution
# DNA Elasticity and Polymers Models

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1. The average position of the free end is given by

$$\begin{aligned}\langle\vec{R}\rangle &= \int \mathrm{d}\vec{u}_1 \dots \mathrm{d}\vec{u}_N \frac{1}{Z(T,\vec{f})} e^{-\beta[E(\vec{u}_1,\dots,\vec{u}_N)-\vec{f}\cdot\vec{R}]}\vec{R} \\ &= \frac{1}{Z(T,\vec{f})}\frac{1}{\beta}\vec{\nabla}Z(T,\vec{f}) = \frac{1}{\beta}\vec{\nabla}\ln(Z(T,\vec{f}))\ , \end{aligned} \tag{1}$$

   where $\vec{\nabla}$ is the gradient with respect to $\vec{f}$.

2. For any microscopic configuration $(\vec{u}_1,...,\vec{u}_N)$, the position of the free end is $\vec{R} = \sum_{i=1}^{N}\vec{u}_i$.

## 1 The freely jointed chain model

3. Assuming the same energy $E$ for all configurations $(\vec{u}_1,...,\vec{u}_N)$ will neglect
   — that in reality links between adjacent molecules cannot take any arbitrary angle due the geometry of the base pairs.
   — that in reality there can be short ranged electrostatic interaction (attraction or repulsion) between adjacent base pairs or even long-ranged electrostatic interaction along the chain if the DNA bends and almost intersects with itself.

4. We will parametrize the unit vector $\vec{u}_i \in S^2$ by the spherical coordinates angles $\phi_i \in [0, 2\pi)$ and $\theta_i \in [0, \pi]$,

$$\vec{u}_i = \begin{pmatrix}\sin\theta_i\cos\phi_i \\ \sin\theta_i\sin\phi_i \\ \cos\theta_i\end{pmatrix}\ .$$

   The sum over all configurations corresponds to an integral over the unit sphere for each $\vec{u}_i$, which in spherical coordinates reads

$$\prod_{i=1}^{N}\int_0^{2\pi}\mathrm{d}\phi_i\int_0^{\pi}\mathrm{d}\theta_i\sin\theta_i\ .$$

   The partition function becomes

$$\begin{aligned} Z(T,\vec{f}) &= \left(\prod_{i=1}^{N}\int_0^{2\pi}\mathrm{d}\phi_i\int_0^{\pi}\mathrm{d}\theta_i\sin\theta_i\right)e^{-\beta(E-f\sum_{i=1}^{N}b\cos\theta_i)} \\ &= e^{-\beta E}\left(2\pi\int_0^{\pi}\mathrm{d}\theta\sin\theta e^{\beta bf\cos\theta}\right)^N \\ &= e^{-\beta E}\left(2\pi\int_0^{\pi}\mathrm{d}\theta\frac{1}{\beta bf}(-\frac{\partial}{\partial\theta})e^{\beta bf\cos\theta}\right)^N \\ &= e^{-\beta E}\left(\frac{2\pi}{\beta bf}(e^{\beta bf}-e^{-\beta bf})\right)^N \\ &= e^{-\beta E}\left(\frac{4\pi\sinh(\beta bf)}{\beta bf}\right)^N . \end{aligned}$$

The average position of the free end, $\langle\vec{R}\rangle$, is computed via equation (1). As $Z$ depends on $\vec{f}$ only through its norm the average position $\langle\vec{R}\rangle$ will be colinear to $\vec{f}$, which was a priori obvious by symmetry. Denoting $\langle\vec{R}\rangle = z(f)\vec{e}_z$ we obtain

$$\begin{aligned} z(f) &= \frac{1}{\beta}\frac{\partial}{\partial f}\ln\left(e^{-\beta E}\left(\frac{4\pi\sinh(\beta b f)}{\beta b f}\right)^N\right) \\ &= L\left(\coth(\beta b f) - \frac{1}{\beta b f}\right), \end{aligned} \tag{2}$$

where we substituted $L = bN$.

Let us study the behaviour of the solution for small and large forces. For small $x$ we can expand

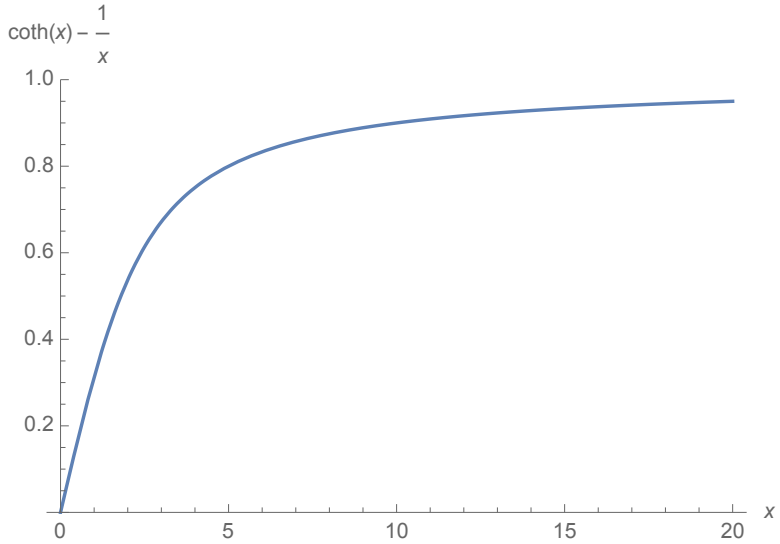
$$\begin{aligned} \coth(x) &= \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{1 + x^2/2 + \mathcal{O}(x^4)}{x(1 + x^2/3! + \mathcal{O}(x^4))} = \frac{1}{x}(1 + x^2/2 + \mathcal{O}(x^4))(1 - x^2/3! + \mathcal{O}(x^4)) \\ &= \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^4). \end{aligned}$$

Therefore, for small forces, the elongation increases linearly with the applied force, $z(f) \approx L\frac{\beta b f}{3}$. The polymer behaves like a spring with spring constant $k = \frac{3k_bT}{Lb}$. Note that in this model the polymer contracts if we increase the temperature, since the origin of its elasticity is purely entropic (and there are more possible microscopic configurations that lead to a contracted macroscopic configuration than a stretched one).

For large $x$ we rewrite $\coth(x)$ and expand in $e^{-2x}$,

$$\coth(x) = \frac{1 + e^{-2x}}{1 - e^{-2x}} = 1 + 2e^{-2x} + \mathcal{O}(e^{-4x}). \tag{3}$$

Therefore, $z(f) \approx L(1 - \frac{1}{\beta b f} + \mathcal{O}(e^{-2\beta b f}))$ and the chain is as expected almost fully stretched.




5. The caption of Figure 1 explains the procedure followed to compare the experimental (symbols) and the analytical prediction (2) of the model (solid lines).

   In the left panel $L$ was fixed to its true value $L = 32.7\ \mu$m, and the three solid curves correspond to three different values of $b$. None of them is able to reproduce satisfactorily the experimental results on the whole range of extensions, see in particular the inset that magnifies the regime of small forces and extensions; the fact that $z$ goes to $L$ in the limit of large forces has been here imposed by hand, and in this limit the solid curves are much below the experimental data.

   In the right panel both $b$ and $L$ have been treated as free parameters to fit the low force regime of the experimental data; the agreement in this regime is rather good (see the inset), nevertheless

the fitted value of $L$ is $L = 26$ $\mu$m, which is much smaller than the true one, hence with these parameters the large force part of the experimental data is completely missed.

Even if the linear regime at very small forces is captured in this model, it is unable to reproduce the experimental data on the full range of the force-elongation curve. This motivates the introduction of the more elaborate model that we shall study now, that incorporates some interactions in the polymer and leads to much better predictions.

## 2 The worm-like chain model

6. The worm-like chain model favours microscopic configurations where the direction of consecutive links does not vary a lot. The energy of a configuration is

$$E(\vec{u}_1, ..., \vec{u}_N) = \sum_{i=1}^{N-1} \frac{J}{b} (\vec{u}_{i+1} - \vec{u}_i)^2 \ .$$

7. In the limit $N \to \infty$, $b \to 0$ with $Nb = L$ fixed,

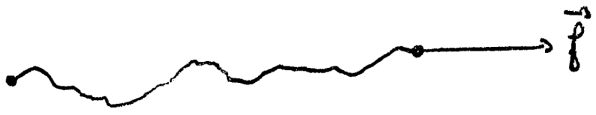
$$E = J \sum_{i=1}^{N-1} b \left( \frac{\vec{u}_{i+1} - \vec{u}_i}{b} \right)^2 \to J \int_0^L \mathrm{d}s \left( \frac{\mathrm{d}\vec{u}(s)}{\mathrm{d}s} \right)^2 = \frac{1}{\beta} \frac{A}{2} \int_0^L \mathrm{d}s \left( \frac{\mathrm{d}\vec{u}(s)}{\mathrm{d}s} \right)^2 ,$$

where the discrete index $i$ becomes a continuous parameter $\vec{u}_i \to \vec{u}(s)$. The new constant $A = 2\beta J$ has the dimension of a length, since (at zero force) the probability of any configuration $p(\{\vec{u}(s)\}) \sim e^{\frac{A}{2} \int_0^L \mathrm{d}s \left( \frac{\mathrm{d}\vec{u}(s)}{\mathrm{d}s} \right)^2}$ must be a dimensionless quantity.

$A$ can be interpreted as the length scale over which the polymer does not change direction, it is therefore called the persistence length. This can be seen by considering the specific configuration where the polymer forms a circle with radius $R$. In this case $|\mathrm{d}\vec{u}/\mathrm{d}s| \sim 1/R$ (one can explicitly write down the parametrization of the polymer as $\vec{\gamma}(s) = R(\cos(s/R), \sin(s/R))$ with $s \in [0, 2\pi R)$ and $\vec{u} = \dot{\vec{\gamma}}$) and the probability becomes $\sim e^{-\mathrm{const.} A/L}$. So if $A \gg L$, the contribution vanishes, which explains why $A$ is interpreted as the persistence length.

In the continuous limit one has $\vec{R} = \int_0^L \mathrm{d}s \, \vec{u}(s)$.

8. (a) A typical configuration of the polymer at large forces will be very stretched along the direction of $\vec{f}$ :




(b) Since $|\vec{u}(s)| = 1$, the parallel component in the decomposition $\vec{u}(s) = \vec{u}_\perp(s) + u_\parallel(s)\vec{e}_z$ can be rewritten as

$$u_\parallel(s) = \sqrt{1 - \vec{u}_\perp(s)^2} \approx 1 - \frac{1}{2} \vec{u}_\perp(s)^2,$$

where we expanded to second order in $|\vec{u}_\perp|$. The endpoint of the chain is

$$\vec{R} = \int_0^L \mathrm{d}s \ \vec{u}(s) \approx \int_0^L \mathrm{d}s \ \vec{u}_\perp(s) + \left( L - \int_0^L \mathrm{d}s \ \frac{\vec{u}_\perp(s)^2}{2} \right) \vec{e}_z. \tag{4}$$

Within this approximation one has $\frac{\mathrm{d}u_\parallel(s)}{\mathrm{d}s} \approx -\vec{u}_\perp(s) \cdot \frac{\mathrm{d}\vec{u}_\perp(s)}{\mathrm{d}s}$, hence $\left| \frac{\mathrm{d}u_\parallel(s)}{\mathrm{d}s} \right| \ll \left| \frac{\mathrm{d}\vec{u}_\perp(s)}{\mathrm{d}s} \right|$ since we assume $\vec{u}_\perp$ to be small. In the expression of the energy we can thus replace $\frac{\mathrm{d}\vec{u}(s)}{\mathrm{d}s}$ by $\frac{\mathrm{d}\vec{u}_\perp(s)}{\mathrm{d}s}$ , which gives

$$E = \frac{1}{\beta} \frac{A}{2} \int_0^L \left( \frac{\mathrm{d}\vec{u}_\perp}{\mathrm{d}s} \right)^2 \ .$$

With a force in the $z$ direction, $\vec{f} = f\vec{e}_z$, the weight for a configuration $\{\vec{u}(s)\}$ becomes

$$\exp\left(-\frac{1}{2}\int_0^L \left(A\left(\frac{\mathrm{d}\vec{u}_\perp}{\mathrm{d}s}\right)^2 + f\beta\vec{u}_\perp(s)^2\right)\mathrm{d}s\right) \ ; \tag{5}$$

we omitted the factor $e^{\beta f L}$ that does not depend on $\vec{u}$ and hence does not change the probabilities of the configurations, once normalized.

(c) Decomposing $\vec{u}_\perp$ on its two components as

$$\vec{u}_\perp(s) = \begin{pmatrix} v(s) \\ w(s) \\ 0 \end{pmatrix} \ ,$$

and inserting this form in the weight (5) we see that the contributions of $v$ and $w$ factorize, hence they become independent random variables with the same Gaussian weight

$$\exp\left(-\frac{1}{2}\int_0^L \left(A\left(\frac{\mathrm{d}v}{\mathrm{d}s}\right)^2 + f\beta v^2\right)\mathrm{d}s\right) \ ; \tag{6}$$

originally one had the constraint $|\vec{u}_\perp(s)| \leq 1$, which relates $v$ and $w$, but in the large force limit $v$ and $w$ will be small and the constraint always satisfied, we can thus treat $v$ and $w$ as independent.

Note that the partition function as a sum over all configuration now involves a path integral $\int \mathcal{D}v = \lim_{N\to\infty}\prod_{i=1}^N \int \mathrm{d}v_i$,

$$Z = \int \mathcal{D}v \exp\left(-\frac{1}{2}\int_0^L \left(A\left(\frac{\mathrm{d}v}{\mathrm{d}s}\right)^2 + f\beta v^2\right)\mathrm{d}s\right) \tag{7}$$

Using (4) one sees that the average position is colinear with the force and the elongation in the $z$ direction can be expressed as an average of $v$ :

$$\langle\vec{R}\rangle = z(f)\,\vec{e}_z \ , \qquad \text{with} \ \ z(f) = L - \int_0^L \langle v(s)^2\rangle \tag{8}$$

since $\langle\vec{u}_\perp(s)\rangle = 0$ and $\langle\vec{u}_\perp(s)^2\rangle = \langle v(s)^2\rangle + \langle w(s)^2\rangle = 2\langle v(s)^2\rangle$.

(d) By periodic continuation of $v(s)$ we can express it as a Fourier series,

$$v(s) = \sum_{q\in\mathbb{Z}} \widehat{v}_q\, e^{2i\pi\frac{s}{L}q} \quad \leftrightarrow \quad \widehat{v}_q = \frac{1}{L}\int_0^L \mathrm{d}s\, v(s)\, e^{-2i\pi\frac{s}{L}q}$$

For the bulk of the chain/polymer the representation as a Fourier series is true even if $v(0) \neq v(L)$ (and boundary effects do not affect observables in the thermodynamic limit). As $v(s)$ is real the Fourier coefficients have the property that $\hat{v}_q^* = \hat{v}_{-q}$, which implies that $\hat{v}_q\hat{v}_{-q} = |v_q|^2$. Note also that

$$\int_0^L \mathrm{d}s\ e^{2\pi i\frac{s}{L}(p+q)} = L\delta_{p,-q}$$

for $p, q \in \mathbb{Z}$. Inserting the Fourier decomposition of $v(s)$ in (6) and using these observations gives after a short computation :

$$\exp\left(-\frac{1}{2}\sum_{q\in\mathbb{Z}} |\hat{v}_q|^2\left(\beta f L + q^2\frac{4\pi^2 A}{L}\right)\right) \ . \tag{9}$$

Similarly from (8) we obtain

$$z(f) = L\left(1 - \sum_{q\in\mathbb{Z}}\langle|\hat{v}_q|^2\rangle\right) \ . \tag{10}$$

(e) Because of the constraint $\hat{v}_q^* = \hat{v}_{-q}$ the variables $\hat{v}_q$ cannot be independent for all $q \in \mathbb{Z}$. To get rid of this redundancy we shall use the variables $\hat{v}_0$, which is real, and for $q > 0$ write $\hat{v}_q = \hat{v}_q^R + i\,\hat{v}_q^I$, with $\hat{v}_q^R$ and $\hat{v}_q^I$ real. We can then deduce the value of the $\hat{v}$ with negative indices as $\hat{v}_{-q} = \hat{v}_q^R - i\,\hat{v}_q^I$ for $q > 0$. Rewriting the weight (9) in terms of these variables yields

$$\exp\left(-\frac{1}{2}\beta f L \hat{v}_0^2\right) \prod_{q>0} \exp\left(-\frac{1}{2}2\left(\beta f L + q^2 \frac{4\pi^2 A}{L}\right)(\hat{v}_q^R)^2\right) \exp\left(-\frac{1}{2}2\left(\beta f L + q^2 \frac{4\pi^2 A}{L}\right)(\hat{v}_q^I)^2\right) .$$

This shows that $\hat{v}_0$, $\{\hat{v}_q^R\}_{q>0}$, $\{\hat{v}_q^I\}_{q>0}$ are independent Gaussian random variables with zero average and the following variances :

$$\langle \hat{v}_0^2 \rangle = \frac{1}{\beta f L} , \qquad \langle (\hat{v}_q^R)^2 \rangle = \langle (\hat{v}_q^I)^2 \rangle = \frac{1}{2} \frac{1}{\beta f L + q^2 \frac{4\pi^2 A}{L}} .$$

We recall indeed that $e^{-\frac{1}{2}\alpha x^2}$ is the weight of a Gaussian random variable of variance $1/\alpha$. Expressing the sum in (10) in terms of these variables, and using the identity of the text gives

$$\begin{aligned}
\sum_{q\in\mathbb{Z}} \langle |\hat{v}_q|^2 \rangle &= \langle \hat{v}_0^2 \rangle + 2 \sum_{q>0} \langle (\hat{v}_q^R)^2 + (\hat{v}_q^I)^2 \rangle \\
&= \frac{1}{\beta f L} + 2 \sum_{q>0} \frac{1}{\beta f L + q^2 \frac{4\pi^2 A}{L}} \\
&= \sum_{q\in\mathbb{Z}} \frac{1}{\beta f L + q^2 \frac{4\pi^2 A}{L}} \\
&= \frac{1}{2\sqrt{\beta f A}} \coth\left(\sqrt{\frac{\beta f L^2}{4A}}\right) ,
\end{aligned}$$

hence the elongation reads :

$$z(f) = L\left(1 - \sum_{q\in\mathbb{Z}} \langle |\hat{v}_q|^2 \rangle\right) = L\left(1 - \frac{1}{2\sqrt{\beta f A}} \coth\left(\sqrt{\frac{\beta f L^2}{4A}}\right)\right) .$$

In the large force limit, $f \to \infty$, we have $\coth(\sqrt{\beta f L^2/4A}) \to 1$, therefore $L - z(f) \sim \frac{L}{2}\sqrt{\frac{k_B T}{A f}}$. The scaling with $f$ is thus $L - z(f) \propto \frac{1}{\sqrt{f}}$, whereas in the "freely joint chain model" (FCM) we obtained $L - z(f) \propto \frac{1}{f}$. So one needs a larger force to expand the polymer in the worm-like chain (WCM) model than in the FCM.

(f) In general, the WCM is in very good agreement with the experimental data, while the FCM differs from it in the manner described above in part (e). Note that here the figure has a log scale in contrast to the figure from question 1. There we argued that at the FCM does not reproduce experimental data at small forces. But here we consider even smaller forces, where the agreement is not too bad.

(g) • Let us first explain the origin of this correspondence. In quantum mechanics the transition amplitude for the evolution from position $x_i$ at time 0 to $x_f$ at time $t$ under a qantum mechanical Hamiltonian of the form

$$\widehat{H} = \frac{\widehat{P}^2}{2m} + V(\widehat{X})$$

can be expressed as a path integral over the exponential of the action with classical Lagrangian $\mathcal{L}$,

$$\langle x_f | e^{-i\widehat{H}t/\hbar} | x_i \rangle = \int_{x(0)=x_i}^{x(t)=x_f} \mathcal{D}x \exp\Big(\frac{i}{\hbar}\int_0^t \mathrm{d}s \underbrace{\left(\frac{m\dot{x}(s)^2}{2} - V(x(s))\right)}_{\mathcal{L}(x,\dot{x})}\Big).$$

Substituting $s \to -is$ in the integral in the exponential, defining $\beta_{\rm osc} = it$, setting $\hbar = 1$ and finally summing over all states $x_i = x_f \equiv x$, this becomes

$$Z(\beta_{\rm osc}) = \int \mathrm{d}x \ \langle x|e^{-\beta_{\rm osc}\widehat{H}}|x\rangle = \int_{x(0)=x(t)} \mathcal{D}x \ \exp\left(-\int_0^{\beta_{\rm osc}} \mathrm{d}s \left(\frac{m\dot{x}(s)^2}{2} + V(x(s))\right)\right). \tag{11}$$

We see that the partition function of the quantum mechanical system $\widehat{H}$ coupled to a thermal bath of temperature $\beta_{\rm osc}$ can also be expressed as a path integral, but with an expression in the exponential where the potential energy $V(x)$ has changed sign compared to the Lagrangian $\mathcal{L}$ of the classical system.
Now we set $V(x) = \frac{1}{2}m\omega x^2$ and compare this to (7). This shows hat the expressions are equal upon the replacement $\beta_{\rm osc} = L$, $m = A$, $\omega = \sqrt{\beta f/A}$, i.e. the thermal distribution of the quantum harmonic oscillator is the same as the distribution of the classical variable $v(s)$.

- Let us now compute explicitly the average fluctuation of the position of a quantum harmonic oscillator coupled to a heat bath with temperature $\beta_{\rm osc}$. It is defined by the Hamiltonian

$$\widehat{H} = \frac{\widehat{P}^2}{2m} + \frac{1}{2}m\omega^2\widehat{X}^2 \ .$$

Introducing the creation and annihilation operator $a^\dagger$ and $a$ according to the definitions

$$\widehat{X} = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a) \ , \qquad \widehat{P} = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a) \ ,$$

one finds that they obey the commutation rule $[a, a^\dagger] = 1$, and that the Hamiltonian can be written $\widehat{H} = \hbar\omega(a^\dagger a + \frac{1}{2})$. It is a standard exercise in quantum mechanics to show that the eigenvalues of $a^\dagger a$ are the non-negative integers, with a orthonormal basis of eigenvectors denoted $\{|n\rangle\}$ that obeys the relation $a|n\rangle = \sqrt{n}|n-1\rangle$, and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$. The average of $\widehat{X}^2$ in the quantum state $n$ reads

$$\langle n|\widehat{X}^2|n\rangle = \frac{\hbar}{2m\omega}\langle n|2a^\dagger a + 1 + (a^\dagger)^2 + a^2|n\rangle = \frac{\hbar}{m\omega}\left(n + \frac{1}{2}\right) \ .$$

The various $n$ levels being populated according to the Gibbs-Boltzmann probability, the thermal average we need to compute is thus

$$\begin{aligned}\langle X^2\rangle &= \frac{\sum_{n=0}^{\infty} e^{-\beta_{\rm osc}\hbar\omega(n+\frac{1}{2})}\frac{\hbar}{m\omega}(n+\frac{1}{2})}{\sum_{n=0}^{\infty} e^{-\beta_{\rm osc}\hbar\omega(n+\frac{1}{2})}} = -\frac{1}{m\omega^2}\frac{\partial}{\partial\beta_{\rm osc}}\ln\left(\sum_{n=0}^{\infty} e^{-\beta_{\rm osc}\hbar\omega(n+\frac{1}{2})}\right) \\ &= \frac{1}{m\omega^2}\frac{\partial}{\partial\beta_{\rm osc}}\ln\sinh\left(\frac{\beta_{\rm osc}\hbar\omega}{2}\right) = \frac{\hbar}{2m\omega}\coth\left(\frac{\beta_{\rm osc}\hbar\omega}{2}\right) \ ,\end{aligned}$$

the sum over $n$ being computable as a geometric series. Substituting $\beta_{\rm osc} = L$, $m = A$, $\omega = \sqrt{\beta f/A}$, $\hbar = 1$, one recovers the value of $\langle v(s)^2\rangle$ computed in question 8e.

9. Following the comment below equation (11) one deduces that the Lagrangian of the classical system in this case is

$$\mathcal{L}[\vec{u}, \vec{u}'] = \frac{1}{2}A\vec{u}'^2 + \beta\vec{f}\cdot\vec{u}(s).$$

With $p_i = \frac{\partial\mathcal{L}}{\partial u_i} = Au_i$ the conjugate momentum, the classical Hamiltonian is

$$H(\vec{p}, \vec{u}) = \vec{p}\cdot\vec{u}' - \mathcal{L} = \frac{\vec{p}^2}{2A} - \beta\vec{f}\cdot\vec{u} \ .$$

Following canonical quantization, $p_i$ and $u_i$ are replaced by operators $\widehat{P}_i$ and $\widehat{U}_i$ with commutation rules $[\widehat{P}_i, \widehat{U}_j] = i\delta_{i,j}$ (with $\hbar = 1$), with the constraint $\vec{U}^2 = 1$. This is fulfilled by restricting the Hilbert space of squared integrable functions on $\mathbb{R}^3$ to the functions $Y(\theta, \phi)$ defined on the unit sphere $S^2$. Then the quantum mechanical Hamiltonian (with $\vec{f} = f\vec{e}_z$) is

$$\widehat{H}(f)Y(\theta,\phi) = \left(-\frac{1}{2A}\Delta_{S^2} - \beta f\cos(\theta)\right) Y(\theta,\phi) \ .$$

10. The partition function of the polymer without constraints is obtained by integrating over the initial and final directions, uniformly over the sphere :

$$Z = \int \frac{\mathrm{d}\vec{u}_f}{4\pi}\frac{\mathrm{d}\vec{u}_i}{4\pi}\langle\vec{u}_f|e^{-L\widehat{H}}|\vec{u}_i\rangle$$

In the limit of large $L$, the operator $e^{-L\widehat{H}}$ becomes the projector on the groundstate, multiplied by $e^{-L\epsilon_0(f)}$, the contributions from the excited states being exponentially smaller, hence

$$\frac{1}{L}\ln Z \to -\epsilon_0(f) \quad \text{for } L\to\infty \ .$$

11. As before, $z(f) = \langle\vec{R}\rangle\cdot\vec{e}_z = \frac{1}{\beta}\frac{\partial}{\partial f}\ln(Z) = -\frac{L}{\beta}\frac{\partial}{\partial f}\epsilon_0(f)$. To compute this derivative we shall first derive a generic relationship known as Hellman-Feynman's theorem. Consider an Hamiltonian $\widehat{H}(f)$, depending on a parameter $f$, with an eigenvalue $\epsilon_0(f)$ and an associated normalized eigenvector $|\psi_0(f)\rangle$. As $\epsilon_0(f) = \langle\psi_0(f)|\widehat{H}(f)|\psi_0(f)\rangle$, we have

$$\begin{aligned}
\frac{\partial}{\partial f}\epsilon_0(f) &= \langle\psi_0(f)|\partial_f\widehat{H}(f)|\psi_0(f)\rangle + \langle\partial_f\psi_0(f)|\widehat{H}(f)|\psi_0(f)\rangle + \langle\psi_0(f)|\widehat{H}(f)|\partial_f\psi_0(f)\rangle \\
&= \langle\psi_0(f)|\partial_f\widehat{H}(f)|\psi_0(f)\rangle + \epsilon_0(f)\big(\langle\partial_f\psi_0(f)|\psi_0(f)\rangle + \langle\psi_0(f)|\partial_f\psi_0(f)\rangle\big) \\
&= \langle\psi_0(f)|\partial_f\widehat{H}(f)|\psi_0(f)\rangle + \epsilon_0(f)\frac{1}{2}\frac{\partial}{\partial f}||\psi_0(f)||^2 \\
&= \langle\psi_0(f)|\partial_f\widehat{H}(f)|\psi_0(f)\rangle \ .
\end{aligned}$$

In words, the derivative of the eigenvalue is the average of the derivative of the Hamiltonian in the state corresponding to the associated eigenvector. Applying this identity to the present case we obtain $z(f) = L\langle\psi_0(f)|\cos(\theta)|\psi_0(f)\rangle = \frac{L}{4\pi}\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta\sin(\theta)\psi_0(f;\theta,\phi)^*\cos(\theta)\psi_0(f;\theta,\phi)$.

12. For $f = 0$, the eigenfunctions of the Hamiltonian $\widehat{H}(f=0) = -\frac{1}{2A}\Delta_{S^2}$ are the spherical harmonics $Y_{l,m}(\theta,\phi)$ since they satisfy $\Delta_{S^2}Y_{l,m} = -l(l+1)Y_{l,m}$. For each integer $l$ they span a representation of $SO(3)$ with $m = -l, -l+1, \ldots, l-1, l$. They also form a complete basis of our Hilbert space of squared integrable functions on $S^2$. A strategy to find the actual ground state $|\psi_0(f)\rangle$ is to express $\widehat{H}(f)$ as an (infinite-dimensional) matrix in the basis $Y_{l,m}$, then truncate this matrix at some very large $l$ and finally diagonalize it with a computer. Since $\widehat{H}(f)$ is rotationally invariant around the $z$-axis the result is independent of $m$. Indeed, matrix elements of $\widehat{H}(f)$ are

$$\begin{aligned}
\langle Y_{l,m}|\widehat{H}(f)|Y_{l',m'}\rangle &= \langle Y_{l,m}| - \frac{1}{2A}\Delta_{S^2} - \beta f\cos(\theta)|Y_{l',m'}\rangle \\
&= \delta_{m,m'}\left(\frac{l(l+1)}{2A}\delta_{l,l'} - \beta f(\text{const }\delta_{l,l'+1} + \text{const }\delta_{l,l'-1})\right) .
\end{aligned}$$

The first term is the brackets is clear. To understand the second term, note that $\cos(\theta) \sim Y_{l=1,0}$. Then we have to evaluate $\langle Y_{l,m}|Y_{1,0}|Y_{l',m}\rangle$ which is by the rules of addition of angular momentum non-zero only if $l = l'+1$ or $l = l'-1$. The matrix representing $\widehat{H}(f)$ in the $Y_{l,m}$ basis is thus tridiagonal.

Alternatively, one could one could do perturbations in $f$ for the small force regime, or in $1/f$ for the large force regime and in the latter case one would recover the formalism of question 8 with the harmonic oscillator.