Assignment 6
Biophys 4322/5322

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1 Problem 1) Phillips 9.5

1.1 Part a)

Compute the electric field inside a screening close, a distance x from the polyelectrolyte using Gauss' law.

The question wants us to use Gauss' law

$$\Phi = \frac{Q_{\text{tot}}}{D\varepsilon_0} \tag{1}$$

where all the variables are the same as they are in Philips 9.3.1 which gives the electric field to be

$$E = \frac{\Phi}{A} \tag{2}$$

where A is the area of the imaginary, arbitrary enclosing surface a distance x from the polyelectrolyte surface. So then the question is really only "What's Q_{tot}?". If the chain itself has some charge Q_+ then the counterions will form a cloud around it with a total charge $Q_- = -Q_+$ in the volume $A\lambda_D$ by the definition of the Debye length λ_D. So then the charge density is

$$\rho = \frac{Q_-}{A\lambda_D} \tag{3}$$

and the total charge a distance x from the surface of the macromolecule would be

$$\begin{aligned} Q_{\text{tot}} &= Q_+ + \rho A x = Q_+ + \frac{Q_-}{A\lambda_D}Ax = Q_+ - Q_+\frac{x}{\lambda_D} \\ &= Q_+\left(1 - \frac{x}{\lambda_D}\right) \end{aligned} \tag{4}$$

and therefore the electric field is

$$\begin{aligned} E(x) &= \frac{\Phi}{A} = \frac{Q_{\text{tot}}}{AD\varepsilon_0} \\ &= \frac{Q_+}{AD\varepsilon_0}\left(1 - \frac{x}{\lambda_D}\right) \end{aligned} \tag{5}$$

1.2 Part b)

Compute the electrostatic energy of the screening cloud.

The energy is

$$
\begin{aligned}
U &= \frac{D\varepsilon_0}{2}\int_{\text{cloud}} E^2 dV = \frac{D\varepsilon_0}{2}\int_0^{\lambda_D} E^2 A dx \\
&= \frac{D\varepsilon_0}{2}\int_0^{\lambda_D}\left(\frac{Q_+}{AD\varepsilon_0}\right)^2\left(1-\frac{x}{\lambda_D}\right)^2 A dx \\
&= \frac{Q_+^2}{2AD\varepsilon_0}\int_0^{\lambda_D}\left(1-\frac{x}{\lambda_D}\right)^2 dx = \frac{Q_+^2}{2AD\varepsilon_0}\left[x-\frac{x^2}{\lambda_D}+\frac{x^3}{3\lambda_D^2}\right]_0^{\lambda_D} \\
&= \frac{Q_+^2\lambda_D}{6AD\varepsilon_0} \qquad (6)
\end{aligned}
$$

1.3 Part c)

Compute the entropy cost associated with the screening cloud. Remember both positive and negative ions.

We can do this just as the textbook did: by using chemical potential and the concentration of ions assuming a uniform cloud to handle entropic effects. The concentrations of counterions and coions are

$$
\begin{aligned}
c_+ &= c_\infty + \frac{\Delta c}{2} \\
c_- &= c_\infty - \frac{\Delta c}{2} \qquad (7)
\end{aligned}
$$

where Δc is the concentration difference, which can be related to the charge density we found in **Part a)** and the charge of a single ion ze as

$$
\Delta c = \frac{\rho}{ze} = \frac{Q}{A\lambda_D ze} \qquad (8)
$$

(we drop the subscript on Q).

Now we are ready to find the chemical potential difference of either ion

$$
\mu_\pm = \mu_0 + k_\mathrm{B}T\ln\left(\frac{c_\pm}{c_0}\right)
$$

from the chemical potential of the unperturbed state

$$
\mu_\infty = \mu_0 + k_\mathrm{B}T\ln\left(\frac{c_\infty}{c_0}\right).
$$

The differences are

$$
\begin{aligned}
\Delta\mu_\pm &= \mu_\pm - \mu_\infty \\
&= \mu_0 + k_\mathrm{B}T\ln\left(\frac{c_\pm}{c_0}\right) - \mu_0 - k_\mathrm{B}T\ln\left(\frac{c_\infty}{c_0}\right) \\
&= k_\mathrm{B}T\ln\left(\frac{c_\pm}{c_\infty}\right) = k_\mathrm{B}T\ln\left(\frac{c_\infty \pm \frac{\Delta c}{2}}{c_\infty}\right) \\
&= k_\mathrm{B}T\ln\left(1 \pm \frac{\Delta c}{2c_\infty}\right) \\
&\approx \pm k_\mathrm{B}T\frac{\Delta c}{2c_\infty} \qquad (9)
\end{aligned}
$$

Then the entropic contribution to the free energy is

$$
\begin{aligned}
G_\text{en} &= N\Delta\mu = N_+\mu_+ + N_-\mu_- \\
&\approx N_+k_\mathrm{B}T\frac{\Delta c}{2c_\infty} - N_-k_\mathrm{B}T\frac{\Delta c}{2c_\infty} = k_\mathrm{B}T\frac{\Delta c}{2c_\infty}\left(N_+ - N_-\right) \\
&= \frac{k_\mathrm{B}TQ}{2A\lambda_D zec_\infty}\left(N_+ - N_-\right). \qquad (10)
\end{aligned}
$$

Can we do anything useful with the $(N_+ - N_-)$ term? Yes. The total net charge of the sheath is $-Q$ which if each ion has charge e is $-Q = ze\left(N_+ - N_-\right)$ so we can give the free energy cost without resorting to N-variables to be

$$\begin{aligned} G_{\text{en}} &= \frac{k_{\text{B}}TQ}{2A\lambda_D zec_\infty}\left(N_+ - N_-\right) \\ &= \frac{k_{\text{B}}T}{2A\lambda_D c_\infty}\left(\frac{Q}{ze}\right)^2 . \end{aligned} \tag{11}$$

1.4 Part d)

Use Part b) and c) to compute the Debye length.

The total free energy is the electrostatic component from **Part b)** and the entropic term from **Part c)**

$$\begin{aligned} G &= G_{\text{el}} + G_{\text{en}} = U + G_{\text{en}} \\ &= \frac{Q^2\lambda_D}{6AD\varepsilon_0} + \frac{k_{\text{B}}T}{2A\lambda_D c_\infty}\left(\frac{Q}{ze}\right)^2 , \end{aligned} \tag{12}$$

which we minimize with respect to cloud width to predict the Debye length:

$$\begin{aligned} \frac{\partial G}{\partial \lambda_C} &= 0 \\ &= \frac{Q^2}{6AD\varepsilon_0} - \frac{k_{\text{B}}T}{2A\lambda_D^2 c_\infty}\left(\frac{Q}{ze}\right)^2 \\ \frac{Q^2}{6AD\varepsilon_0} &= \frac{k_{\text{B}}T}{2A\lambda_D^2 c_\infty}\left(\frac{Q}{ze}\right)^2 \\ \frac{\lambda_D^2}{6D\varepsilon_0} &= \frac{k_{\text{B}}T}{2c_\infty}\frac{1}{z^2e^2} \\ \lambda_D^2 &= \frac{3D\varepsilon_0 k_{\text{B}}T}{z^2e^2c_\infty} \\ \lambda_D &= \sqrt{\frac{3D\varepsilon_0 k_{\text{B}}T}{z^2e^2c_\infty}} \end{aligned} \tag{13}$$

This λ_D answer differs from the value given by Phillips (Eq 9.57) by a factor of $\sqrt{6}$. Not bad.

2 Problem 2) Phillips 9.7

2.1 Part a)

Find the integration constant A in the potential around a charged sphere (as a model for a protein here).

The Debye-Hückel equation in spherical coordinates is

$$\frac{d^2}{dr^2}rV(r) = \frac{rV(r)}{\lambda_D^2} \tag{14}$$

which has the general solution

$$V(r) = \frac{A}{r}e^{-r/\lambda_D} + \frac{B}{r}e^{+r/\lambda_D}. \tag{15}$$

We demand that $B = 0$ because an exponentially increasing function is non-physical. To find A we calculate the electric field from the potential to be

$$\begin{aligned} E_r\left(r\right) &= -\frac{dV}{dr} = -A\frac{d}{dr}\left(\frac{e^{-r/\lambda_D}}{r}\right) \\ &= A\left(\frac{e^{-r/\lambda_D}}{r^2} + \frac{e^{-r/\lambda_D}}{r\Lambda_D}\right) \\ &= A\frac{e^{-r/\lambda_D}}{r}\left(\frac{1}{r} + \frac{1}{\Lambda_D}\right). \end{aligned} \tag{16}$$

We also know that at the surface of the sphere $r = R$ the electric field is

$$E_r\left(R\right) = \frac{Q}{4\pi\varepsilon_0 D R^2}. \tag{17}$$

So equating Eq. (17) to Eq. (16) at $r = R$ allows us to solve for A.

$$\begin{aligned} \frac{Q}{4\pi\varepsilon_0 D R^2} &= E_r\left(R\right) \\ &= A\frac{e^{-R/\lambda_D}}{R}\left(\frac{1}{R} + \frac{1}{\Lambda_D}\right) \end{aligned} \tag{18}$$

$$\begin{aligned} A &= \frac{Q}{4\pi\varepsilon_0 D R^2}\frac{Re^{R/\lambda_D}}{\left(\frac{1}{R} + \frac{1}{\Lambda_D}\right)} \\ &= \frac{Qe^{R/\lambda_D}}{4\pi\varepsilon_0 D}\frac{1}{\left(1 + R/\Lambda_D\right)}. \end{aligned} \tag{19}$$

So then the potential is

$$\begin{aligned} V\left(r\right) &= \frac{A}{r}e^{-r/\lambda_D} + \frac{B}{r}e^{+r/\lambda_D} \\ &= \frac{Q}{4\pi\varepsilon_0 D}\left(\frac{e^{(R-r)/\lambda_D}}{1 + R/\Lambda_D}\right)\left(\frac{1}{r}\right) \end{aligned} \tag{20}$$

2.2 Part b)

State the potential in units of $k_\mathrm{B}T/e$.

To do this we should state the potential in terms of the Bjerrum length $\ell_B = e^2/4\pi\varepsilon_0 D k_\mathrm{B} T$

$$\begin{aligned} V\left(r\right) &= \frac{Q}{4\pi\varepsilon_0 D}\left(\frac{e^{(R-r)/\lambda_D}}{1 + R/\Lambda_D}\right)\left(\frac{1}{r}\right) \\ &= Q\frac{e^2}{4\pi\varepsilon_0 D k_\mathrm{B} T}\frac{k_\mathrm{B}T}{e^2}\left(\frac{e^{(R-r)/\lambda_D}}{1 + R/\Lambda_D}\right)\left(\frac{1}{r}\right) \\ &= \left[\frac{k_\mathrm{B}T}{e}\right]\left(\frac{Q}{e}\right)\left(\frac{\ell_B}{r}\right)\left(\frac{e^{(R-r)/\lambda_D}}{1 + R/\Lambda_D}\right) \end{aligned} \tag{21}$$

and **at** the surface the potential in units of $k_\mathrm{B}T/e$ is

$$V\left(R\right) = \left[\frac{k_\mathrm{B}T}{e}\right]\left(\frac{Q}{e}\right)\left(\frac{\ell_B}{R}\right)\left(\frac{1}{1 + R/\Lambda_D}\right). \tag{22}$$

2.3 Part c)

What is the concentration of Na$^+$ and Cl$^-$ ions at the surface?

We use the Boltzmann formula to find the concentration of either at any distance from the surface to be

$$c_\pm = c_\infty \exp\left(\pm\frac{eV\left(r\right)}{k_\mathrm{B}T}\right). \tag{23}$$

For $r = R$ and the values given in the question, the concentration of sodium ions is

$$c_+ = 0.27\text{M} \tag{24}$$

and chlorine is

$$c_- = 9.1\text{mM}. \tag{25}$$

2.4 Part d)

What is the concentration of Na$^+$ and Cl$^-$ ions at a distance $r = 3$Å?

We still use Eq. (23) and now find the concentration of sodium ions is

$$c_+ = 0.17\text{M} \tag{26}$$

and chlorine is

$$c_- = 15\text{mM}. \tag{27}$$

3 Problem 3) Phillips 9.9

Consider a phospholipid bilayer membrane consisting of a mixture of 90% uncharged lipid and 10% singly charged acid lipid. Assume $a = 68$Å surface area per lipid head group, and assume further that the charged lipids are uniformly distributed and immobile. The membrane is in contact with an aqueous solution of NaCl at 25°C. The salt concentration is $c_\infty = 100$mM.

3.1 Part a)

What is the charge per unit surface area?

One in ten lipids has charge $-e$ so the charge density is

$$\sigma = \frac{-e}{10a} = -0.15e/\text{nm}^2. \tag{28}$$

3.2 Part b)

What is the surface potential of the membrane?

We know that the potential is

$$V(x) = \frac{\sigma\lambda_D}{D\varepsilon_0} e^{-x/\lambda_D} \tag{29}$$

so the surface potential is

$$V_0 = V(0) = \frac{\sigma\lambda_D}{D\varepsilon_0} \tag{30}$$

If you know $D\varepsilon_0$ for water, you're ready to go but I don't. I do know that the Bjerrum length for room temperature water is $\ell_B = 0.7$nm; therefore, I'll write everything in terms of $\ell_B = e^2/4\pi\varepsilon_0 D k_\text{B} T$ (even $\lambda_D = (8\pi\ell_B c_\infty)^{-1/2}$).

$$\begin{aligned} V_0 &= \frac{\sigma\lambda_D}{D\varepsilon_0} = \sigma\lambda_D \frac{e^2}{4\pi D\varepsilon_0 k_\text{B} T}\frac{4\pi k_\text{B} T}{e^2} \\ &= \sigma\lambda_D\ell_B\frac{4\pi k_\text{B} T}{e^2} = \sigma\ell_B\sqrt{\frac{1}{8\pi\ell_B c_\infty}}\frac{4\pi k_\text{B} T}{e^2} \\ &= -31\text{mV}. \end{aligned} \tag{31}$$

3.3 Part c)

What is the electrostatic energy of binding a trivalent positive ion to the membrane (ex. spermidine) assuming binding occurs at the surface?

Since it's trivalent it has a charge $Q = ze = 3e$ so the energy is

$$U = QV(0) = 3eV_0 = 3.76k_\mathrm{B}T. \tag{32}$$

3.4 Part d)

What is the electrostatic energy of binding spermidine to the membrane assuming binding occurs just off the membrance $x = 5$Å?

To answer this it is convenient to notice that

$$V(x) = \frac{\sigma\lambda_D}{D\varepsilon_0}e^{-x/\lambda_D} = V_0 e^{-x/\lambda_D} \tag{33}$$

since we have a U at the surface *i.e.*

$$U(x) = U_0 e^{-x/\lambda_D} = 3.76k_\mathrm{B}Te^{-x/\lambda_D}. \tag{34}$$

In case you didn't find it earlier $\lambda_D = 0.97$nm through ℓ_B and c_∞. So then the energy of binding that hand-wavingly takes steric effects into account is

$$U(x) = 3.76k_\mathrm{B}Te^{-0.5/0.97} = 2.25k_\mathrm{B}T. \tag{35}$$

4 Problem 4) Phillips 9.10

4.1 Part a)

Compute the probability that a ligand is bound to a receptor and the dissociation constant.

Let's do this by building a partition function:

- The ligand can be bound with energy ϵ_b but it has to pay an entropic cost μ_l which is the chemical potential of the **ligand** in the solvent:

$$\mu_l = \mu_{l,0} + k_\mathrm{B}T\ln\left(\frac{c_l}{c_{l,0}}\right) \tag{36}$$

  where c_l is the concentration of bound ligands.

- The ligands can also be free. In this case, counterions will "bind" to the ligand and receptor with an energy ϵ_e (instead of ligand-receptor binding). The chemical potential of the **ions** (either counter- or co-ions) is

$$\mu_\pm = \mu_{\pm,0} + k_\mathrm{B}T\ln\left(\frac{c}{c_0}\right). \tag{37}$$

So then the partition function is

$$Z = \sum e^{-E_i/k_\mathrm{B}T} = e^{-(\epsilon_b-\mu_l)\beta} + e^{-(\epsilon_e-z\mu_+-z\mu_-)\beta}. \tag{38}$$

Now it's a simple matter to find that the probability of being in the bound state is

$$\begin{aligned} p_b = \frac{e^{-E_b\beta}}{Z} &= \frac{e^{-(\epsilon_b-\mu_l)\beta}}{e^{-(\epsilon_b-\mu_l)\beta} + e^{-(\epsilon_e-z\mu_+-z\mu_-)\beta}} \\ &= \frac{e^{-(\epsilon_b-\mu_l)\beta+(\epsilon_e-z\mu_+-z\mu_-)\beta}}{e^{-(\epsilon_b-\mu_l)\beta+(\epsilon_e-z\mu_+-z\mu_-)\beta}+1} \\ &= \frac{e^{-(\epsilon_b-\epsilon_e-\mu_l+z\mu_++z\mu_-)\beta}}{1+e^{-(\epsilon_b-\epsilon_e-\mu_l+z\mu_++z\mu_-)\beta}} \end{aligned} \tag{39}$$

Why did I work towards this form? Because it is easily comparable to our "probability of binding in terms of K_d" equation

$$p_b = \frac{c_l/K_d}{1+c_l/K_d}. \tag{40}$$

Immediately we see (and then substituting in the chemical potentials) that

$$\begin{aligned}
\frac{c_l}{K_d} &= \exp\left[-\left(\epsilon_b - \epsilon_e - \mu_l + z\mu_+ + z\mu_-\right)\beta\right] \\
&= \left[e^{-(\epsilon_b-\epsilon_e)}\right]\left[e^{-\mu_l\beta}\right]\left[e^{z\mu_+\beta}\right]\left[e^{z\mu_-\beta}\right] \\
&= \left[e^{-(\epsilon_b-\epsilon_e)}\right]\left[e^{\mu_{l,0}\beta}e^{-\beta k_\mathrm{B}T\ln\left(\frac{c_l}{c_{l,0}}\right)}\right]\left[e^{z\mu_{-,0}\beta}e^{\beta k_\mathrm{B}Tz\ln\left(\frac{c}{c_0}\right)}\right]\left[e^{z\mu_{+,0}\beta}e^{\beta k_\mathrm{B}Tz\ln\left(\frac{c}{c_0}\right)}\right] \\
&= \left[e^{-(\epsilon_b-\epsilon_e)}\right]\left[e^{\mu_{l,0}\beta}\left(\frac{c_l}{c_{l,0}}\right)\right]\left[e^{z\mu_{-,0}\beta}\left(\frac{c}{c_0}\right)^z\right]\left[e^{z\mu_{+,0}\beta}\left(\frac{c}{c_0}\right)^z\right] \\
&= \left[e^{-(\epsilon_b-\epsilon_e)}e^{\mu_{l,0}\beta}e^{z\mu_{-,0}\beta}e^{z\mu_{+,0}\beta}\right]\left(\frac{c_l}{c_{l,0}}\right)\left(\frac{c}{c_0}\right)^{2z} \\
&= K'_{d,0}\left(\frac{c_l}{c_{l,0}}\right)\left(\frac{c}{c_0}\right)^{2z}.
\end{aligned} \tag{41}$$

Since all those exponentials in front have no salt or ligand dependence, we collapse them into a single constant coefficient $K'_{d,0}$ (the primed is a forewarning that it will be more convenient to write this in another way soon). So then the dissociation constant is

$$\begin{aligned}
K_d &= \frac{c_{l,0}}{K'_{d,0}}\left(\frac{c_0}{c}\right)^{2z} \\
&= K_{d,0}\left(\frac{c}{c_0}\right)^{-2z}.
\end{aligned} \tag{42}$$

4.2 Part b)

Consider a model in which ligand and receptor in the unbound state are surrounded by a screening cloud of counterions, whose width is given by the Debye screening length λ_D . What is the scaling of the dissociation constant with the concentration of counterions in this case?

The bound state doesn't change but the free state does. The ligands and receptors used to be like an ideal gas but now they invest some free energy into establishing the counterion clouds around them. Phillips derived the electrostatic energy of the diffuse layer around a sphere to be

$$U = \frac{1}{2}k_\mathrm{B}T\left(\frac{Q}{e}\right)^2\frac{\ell_B\lambda_D}{R\left(R+\lambda_D\right)}, \tag{43}$$

which is Eq. 9.71 in the textbook. We have ×2 because both ligands and receptors have diffuse layers and $Q/e = z$ so the total free energy of being unbound is

$$U = k_\mathrm{B}Tz^2\frac{\ell_B\lambda_D}{R\left(R+\lambda_D\right)} \tag{44}$$

and the partition function becomes

$$Z = \sum e^{-E_i/k_\mathrm{B}T} = e^{-(\epsilon_b-\mu_l)\beta} + e^{-U\beta} \tag{45}$$

We could go through and find the probability but the question doesn't ask us to do this so instead we cheat: we know from **Part a)** that the dissociation constant will have the form

$$K_d = K'_{d,0}e^{-\beta U} \tag{46}$$

(doing the math would only tell you what the form of $K'_{d,0}$ is and we don't care). So the dissociation constant is

$$K_d = K'_{d,0} e^{-z^2 \frac{\ell_B \lambda_D}{R(R+\lambda_D)}}. \tag{47}$$

The only salt concentration is buried in $\lambda_D = \left[(3D\varepsilon_0 k_\mathrm{B}T) / \left(z^2 e^2 c\right)\right]^{1/2} \propto 1/zc^{1/2}$ so we can absorb the rest of the exponent into the constant (since there's a $k_\mathrm{B}T$ in ℓ_B as well) to get

$$K_d = K_{d,0} e^{-zc^{-1/2}}. \tag{48}$$

5 Problem 5) Phillips 10.3

Small torques exerted on a beam create a torsional strain that is linear like Hook's Law:

$$\tau = C \frac{d\theta}{dz}.$$

5.1 Part a)

Use the data shown in Figure 10.40(A) to estimate the twist modulus.

The modulus is

$$C = \frac{\tau}{d\theta/dz} \tag{49}$$

From Fig. 10.40, the torque goes from zero to about 35 pN nm in something like $\Delta_\mathrm{twist} = 0.03$ rad bp^{-1}. We know that each base pair as a length of about 0.35 nm so then

$$\frac{d\theta}{dz} \approx \frac{0.03 \frac{\mathrm{rad}}{\mathrm{bp}}}{0.35 \frac{\mathrm{nm}}{\mathrm{bp}}}$$

and the twist modulus is

$$\begin{aligned} C = \frac{\tau}{d\theta/dz} &= 35\mathrm{pNnm} \frac{0.35\mathrm{nm}}{0.03\mathrm{rad}} \\ &\approx 400 \text{ pN nm}^2. \end{aligned} \tag{50}$$

5.2 Part b)

Estimate the torque needed to wind a 14.8 kbp DNA molecule by 10 rotations and by 100 rotations.

Use the C value from above and just substitute in the values

$$\begin{aligned} \tau &= C \frac{d\theta}{dz} \\ &= 400 \text{ pN nm}^2 \left(\frac{10 \times 2\pi}{14.8 \times 1000 \times 0.35\mathrm{nm}} \right) \\ &\approx 5 \text{ pN nm} \qquad (51) \\ \tau &= 400 \text{ pN nm}^2 \left(\frac{100 \times 2\pi}{14.8 \times 1000 \times 0.35\mathrm{nm}} \right) \\ &\approx 50 \text{ pN nm} \qquad (52) \end{aligned}$$

5.3 Part c)

Write an expression for the energy stored in the twisted DNA molecule by virtue of its twist deformation. Then use the equation to estimate the energy per base pair stored in the DNA molecule of 14.8 kbp in length after the molecule has been subjected to 50 complete revolutions (*i.e.* from Part b)).

The energy from the torque on a short segment is

$$\begin{aligned} dE\left(d\theta/dz\right) &= \int \tau d\left(\frac{d\theta}{dz}\right) \\ &= \frac{C}{2}\left(\frac{d\theta}{dz}\right)^2 dz \end{aligned} \tag{53}$$

which means that the total energy stored in some length of DNA is

$$E = \int_z dE = \frac{C}{2}\int\left(\frac{d\theta}{dz}\right)^2 dz. \tag{54}$$

We have no reason not to assume that the twist is constant through the entire length of the chain so

$$\begin{aligned} E(\Delta\theta, L) &= \frac{C}{2}\int\left(\frac{d\theta}{dz}\right)^2 dz = \frac{C}{2}\int\frac{\left(d\theta\right)^2}{dz} \\ &= \frac{C}{2}\frac{\left(\Delta\theta\right)^2}{L}. \end{aligned} \tag{55}$$

We can use Eq. (55) for the example values that the question asks about:

$$\begin{aligned} E &= \frac{C}{2}\frac{\left(\Delta\theta\right)^2}{L} = \frac{400\text{ pN nm}^2}{2}\frac{\left(50\times 2\pi\right)^2}{14.8\times 1000\times 0.35\text{nm}} \\ &\approx 3800\text{ pN nm}, \end{aligned} \tag{56}$$

which is 0.26 pN nm per base pair.

5.4 Part d)

Derive an expression linking the twist fluctuations to the stiffness and use the data to estimate the twist modulus and use this result and the data to find C.

By the central limit theorem $p\left(\theta\right)$ must be Gaussian:

$$p\left(\theta\right) \sim \exp\left(\beta E\right) = \exp\left(\beta\frac{C}{2}\frac{\Delta\theta^2}{L}\right). \tag{57}$$

So then the average squared angle will be (dropping the Δ since it confuses the notation)

$$\begin{aligned} \left\langle\theta^2\right\rangle &= \frac{\int\theta^2 p\left(\theta\right)d\theta}{\int p\left(\theta\right)d\theta} = \frac{\int\theta^2 e^{\frac{\beta C\theta^2}{2L}}d\theta}{\int e^{\frac{\beta C\theta^2}{2L}}d\theta} \\ &= \frac{\int\theta^2 e^{\frac{\beta C\theta^2}{2L}}d\theta}{\sqrt{\frac{2\pi L}{\beta C}}} = \frac{\sqrt{2\pi}\left(\frac{L}{\beta C}\right)^{3/2}}{\sqrt{\frac{2\pi L}{\beta C}}} \\ &= \frac{L}{\beta C}. \end{aligned} \tag{58}$$

6 Problem 6) Phillips 10.5

Repeat the calculations of the energy of DNA packing for a spherical capsid. Contrast this result with that obtained assuming a cylinder.

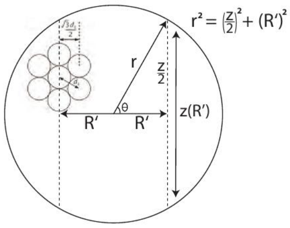

Figure 1: The variables have different names then they do in the text: $R' \to R$ and $r \to R_{\text{out}}$.

The key is to do everything that was done on pg. 378 of Phillips but for a spherical capsid. Use

$$G_{\text{bend}} = \frac{2\pi\xi k_{\text{B}}T}{\sqrt{3}d_s}\int_{R_{\text{in}}}^{R_{\text{out}}} \frac{N}{R}dR \tag{59}$$

just like in the book (Eq. 10.38) but now we need to find the number of hoops N (and eventually R_{in}) for the case of a spherical capsid. When it was a cylinder the number of hoops was $N = z/d_s$ where d_s is the spacing between DNA strands and z was the height of the cylinder. Now

$$N = \frac{z}{d_s} = \frac{2\sqrt{R_{\text{out}}^2 - R^2}}{d_s} \tag{60}$$

as can be understood from Fig. 1. The number of hoops goes into the free energy:

$$\begin{aligned}
G_{\text{bend}} &= \frac{2\pi\xi k_{\text{B}}T}{\sqrt{3}d_s}\int_{R_{\text{in}}}^{R_{\text{out}}} \frac{N}{R}dR \\
&= \frac{2\pi\xi k_{\text{B}}T}{\sqrt{3}d_s}\int_{R_{\text{in}}}^{R_{\text{out}}} \frac{2\sqrt{R_{\text{out}}^2 - R^2}}{Rd_s}dR \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\int_{R_{\text{in}}}^{R_{\text{out}}} \frac{\sqrt{R_{\text{out}}^2 - R^2}}{R}dR \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\int_{R_{\text{in}}}^{R_{\text{out}}} \left[\left(\frac{R_{\text{out}}}{R}\right)^2 - 1\right]^{1/2} dR \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\left[R_{\text{out}}\ln R - R_{\text{out}}\ln R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R^2} - R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R^2}\right)\right]_{R_{\text{in}}}^{R_{\text{out}}} \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\left\{\left[R_{\text{out}}\ln R_{\text{out}} - R_{\text{out}}\ln R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{out}}^2} - R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{out}}^2}\right)\right]\right. \\
&\quad \left. - \left[R_{\text{out}}\ln R_{\text{in}} - R_{\text{out}}\ln R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2} - R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2}\right)\right]\right\} \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\left[-R_{\text{out}}\ln R_{\text{in}} - \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2} + R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2}\right)\right].
\end{aligned} \tag{61}$$

To compare to Fig. 10.18 from Phillips, we replace R_{in} with a function of L (the length packed) and R_{out}. We can use the same equation as was used for a cylinder (Eq. 10.39)

$$\begin{aligned}
L &= \frac{2}{\sqrt{3}d_s}\int_{R_{\text{in}}}^{R_{\text{out}}} 2\pi RNdR \\
&= \frac{8\pi}{3\sqrt{3}d_s^2}\left(R_{\text{out}} - R_{\text{in}}\right)^{3/2},
\end{aligned} \tag{62}$$

which can be inverted to get the inner radius of the hoops of DNA

$$R_{\text{in}} = R_{\text{out}}\sqrt{1 - \left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}} \tag{63}$$

and be put in the bending free energy

$$
\begin{aligned}
G_{\text{bend}} &= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\left[-R_{\text{out}}\ln R_{\text{in}} - \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2} + R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{in}}^2}\right)\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}\left[-R_{\text{out}}\ln\left(R_{\text{out}}\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) - \sqrt{R_{\text{out}}^2 - R_{\text{out}}^2\left(1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}\right)}\right. \\
&\qquad \left. + R_{\text{out}}\ln\left(R_{\text{out}} + \sqrt{R_{\text{out}}^2 - R_{\text{out}}^2\left(1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}\right)}\right)\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[-\ln\left(R_{\text{out}}\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) - \sqrt{1-1+\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right. \\
&\qquad \left. + \ln\left(R_{\text{out}} + R_{\text{out}}\sqrt{1-1+\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right)\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[-\ln\left(R_{\text{out}}\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) - \left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3} + \ln\left(R_{\text{out}} + R_{\text{out}}\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right)\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\ln\left(1+\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right) - \ln\left(\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) - \left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right]. \qquad (64)
\end{aligned}
$$

Let $x = \left(\beta L d_s^2/R_{\text{out}}^3\right)^{1/3}$ and focus on the second term:

$$
\begin{aligned}
2^{nd} &= -\ln\left(\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) \\
&= -\ln\left(\sqrt{1-x^2}\right) = -\ln\left[\sqrt{(1-x)(1+x)}\right] \qquad (65)
\end{aligned}
$$

which means that the bending energy is

$$
\begin{aligned}
G_{\text{bend}} &= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\ln\left(1+\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right) - \ln\left(\sqrt{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{2/3}}\right) - \left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\ln(1+x) - \ln\left[\sqrt{(1-x)(1+x)}\right] - x\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\ln\left(\frac{1+x}{\sqrt{(1-x)(1+x)}}\right) - x\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\ln\left(\sqrt{\frac{1+x}{1-x}}\right) - x\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\frac{1}{2}\ln\left(\frac{1+x}{1-x}\right) - x\right] \\
&= \frac{4\pi\xi k_{\text{B}}T}{\sqrt{3}d_s^2}R_{\text{out}}\left[\frac{1}{2}\ln\left(\frac{1+\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}}{1-\left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}}\right) - \left(\beta\frac{Ld_s^2}{R_{\text{out}}^3}\right)^{1/3}\right] \qquad (66)
\end{aligned}
$$

So we've finished calculating the bending cost. If we want to recreate Fig. 10.18, we need also the electrostatic cost. But this doesn't really change from the cylindrical solution so we steal the answer from Phillips:

$$
G_{\text{el}} = \sqrt{3}F_0\left(c^2 + cd_s\right)Le^{-d_s/c}. \qquad (67)
$$

And then the force resisting all this packing can be found

$$f(L) = -\frac{\partial G}{\partial L} = -\left[\frac{\partial G_{\text{bend}}}{\partial L} + \frac{\partial G_{\text{el}}}{\partial L}\right]. \tag{68}$$

Do this derivative. If I have time I'll get back to it and give the graduate students a solution.