Lecture 16 – Case Study

1. Read the Problem Statement 3.6.1 on the next page from "Numerical Methods with Chemical Engineering Applications" by Dorfman and Dautidis.

2. Find the extension of a λ-DNA molecule subjected to a force of 30 pN at room temperature. Use the following procedure to do so.

   (a) Identify the class of problem (linear, nonlinear, system, etc.) and decide on a method to use.

   (b) On a piece of paper, convert the equation to the standard mathematical form: $\boldsymbol{A} \cdot \boldsymbol{x} = \boldsymbol{b}$ or $\boldsymbol{f}(\boldsymbol{x}) = \boldsymbol{0}$.

   (c) Convert the problem to consistent units.

   (d) (If nonlinear) Determine a smart guess and justify your reason for making this guess.

   (e) Solve the problem using your tool of choice.

3.6 Case Study: Extension of a Tethered Polymer by a Force

3.6.1 Problem Statement

Polymer chains form random coils in solution to maximize their configurational entropy. As a result, we need to apply an external force to a polymer to stretch it out. This idea is illustrated in Fig. 3.12. In the simplest model, we can assume that the chain follows ideal random walk (Gaussian) statistics. As a result, the force F required to extend the chain to a distance X is

$$F = k_s X \tag{3.6.1}$$

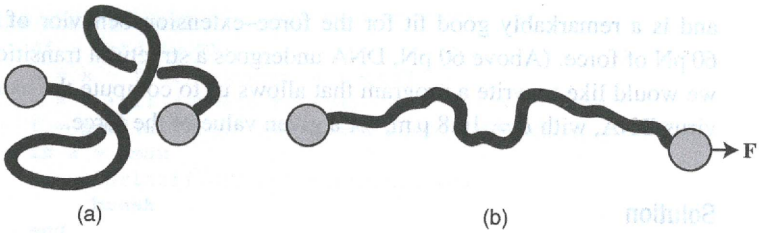

Figure 3.12 Illustration of the force–extension of a polymer chain.

You may recognize this as a Hookean spring with a spring constant k_s. In the case of polymers, this spring constant is related to the entropy lost by the chain extension,

$$k_s = \frac{3k_B T}{Lb} \tag{3.6.2}$$

where k_B is Boltzmann's constant (and hence the connection to entropy), T is the temperature, L is the total length of the chain, and b is the Kuhn length that represents one step of the random walk. The segment length depends on the chemistry, but the rest of this model is rather generic.

You may see a problem with the Gaussian spring model. Let's first rewrite the problem in a dimensionless form,

$$\frac{Fb}{k_B T} = \frac{3X}{L} \tag{3.6.3}$$

The maximum possible extension of the chain is $X/L = 1$. As a result, applying a force greater than

$$F^* = \frac{3k_B T}{b} \tag{3.6.4}$$

leads to the chain being extended beyond its contour length! This is physically impossible. In many cases of interest, the forces acting on the polymers are small, and the Gaussian model works just fine. However, for polymers in flow (which is important for material processing) this is an issue.

There are a number of approaches to deal with the so-called "finite elasticity" problem for polymers. Let's focus on DNA, which has a Kuhn length $b = 100$ nm in a typical biological fluid. From the Gaussian model, this means that DNA would reach its maximum extension for a force

$$F^* = \frac{3(1.38 \times 10^{-23}\text{J/mol K})(298\text{ K})}{10^{-7}\text{ m}} = 0.12\text{ pN} \tag{3.6.5}$$

which actually is a very small force in biological situations, such as DNA transcription. John Marko and Eric Siggia developed a famous formula for the actual force–extension behavior of DNA, based on a wormlike chain model, which has the form

$$\frac{Fb}{k_B T} = \frac{1}{2}\left(1 - \frac{X}{L}\right)^{-2} - \frac{1}{2} + \frac{2X}{L} \tag{3.6.6}$$

and is a remarkably good fit for the force–extension behavior of DNA up to around 60 pN of force. (Above 60 pN, DNA undergoes a structural transition.) In this problem, we would like to write a program that allows us to compute the extension of λ-DNA, a virus DNA, with $L = 16.8$ μm, for a given value of the force.