ENTROPY IN BIOLOGY

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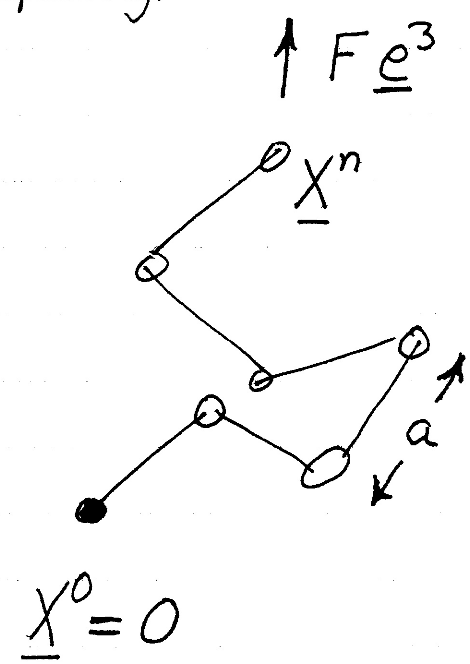
Lecture 8 Entropic Spring

- Force-extension relation of a freely-jointed chain
- Theromodynamics of the freely-jointed chain: Evaluation of the entropy as a function of the applied force
- Homework

Entropic Spring



Consider a freely jointed chain with rigid links of length a and with joints at

$$\underline{X}^0 \;\cdots\; \underline{X}^n$$

The point $\underline{X}^0$ is fixed at the origin, and a force $F\underline{e}^3$ is applied to the point $\underline{X}^n$.

The whole system is at temperature T.

Because of the applied force, the potential energy of the system is

(1) $$U = -F\underline{e}^3 \cdot \underline{X}^n$$

$$= -F\underline{e}^3 \cdot \left((\underline{X}^n - \underline{X}^{n-1}) + (\underline{X}^{n-1} - \underline{X}^{n-2}) + \cdots (\underline{X}^1 - \underline{X}^0) \right)$$

(recall that $\underline{X}^0 = 0$).

We introduce new variables

(2) $$\underline{D}^i = \underline{X}^i - \underline{X}^{i-1} \quad , \qquad i = 1 \cdots n$$

and then

(3) $$U = \sum_{i=1}^{n} -F\underline{e}^3 \cdot \underline{D}^i = \sum_{i=1}^{n} -F D_3^i$$

Because U is such a sum, it follows that the $\underline{D}^i$ at equilibrium are independent random variables, each of which has the following probability density

$$(4) \qquad \rho_D(\underline{\xi}) = \frac{e^{\frac{F\xi_3}{kT}}}{\displaystyle\int_{\|\underline{\eta}\|=a} e^{\frac{F\eta_3}{kT}}\, d\underline{\eta}}$$

In this equation $d\underline{\eta}$ is the area element on the sphere of radius a. Let $\lambda = \frac{F}{kT}$ and make the definition

$$(5) \qquad Z(\lambda) = \int_{\|\underline{\eta}\|=a} e^{\lambda\eta_3}\, d\underline{\eta}$$

$$= 2\pi a \int_{-a}^{a} e^{\lambda\eta_3}\, d\eta_3$$

For this last equality we cite Archimedes, or you can work it out using spherical polar coordinates.

From (5),

(6) $$Z(\lambda) = 4\pi a \, \frac{\sinh(\lambda a)}{\lambda}$$

$$= 4\pi a^2 \, \frac{\sinh(\lambda a)}{\lambda a}$$

From (4), $E[D_1] = E[D_2] = 0$ by symmetry, and

(7) $$E[D_3] = \frac{\displaystyle\int_{\|\underline{\xi}\|=1} e^{\lambda \xi_3} \xi_3 \, d\underline{\xi}}{\displaystyle\int_{\|\underline{\eta}\|=1} e^{\lambda \eta_3} \, d\underline{\eta}}$$

$$= \frac{d}{d\lambda} \log Z_1(\lambda) = a\left(\frac{\cosh(\lambda a)}{\sinh(\lambda a)} - \frac{1}{\lambda a}\right)$$

$$= a\left(\frac{\cosh\left(\frac{Fa}{kT}\right)}{\sinh\left(\frac{Fa}{kT}\right)} - \frac{1}{\left(\frac{Fa}{kT}\right)}\right)$$

Since equation (7) holds for all of the $\underline{D}^i$, and since the sum of the $\underline{D}^i$ is $\underline{X}^n$, we also have

(8) $$E[X_3^n] = na\left(\frac{\cosh\left(\frac{Fa}{kT}\right)}{\sinh\left(\frac{Fa}{kT}\right)} - \frac{1}{\left(\frac{Fa}{kT}\right)}\right)$$

$$= L\left(\frac{\cosh\left(\frac{FL}{nkT}\right)}{\sinh\left(\frac{FL}{nkT}\right)} - \frac{1}{\left(\frac{FL}{nkT}\right)}\right)$$

where

(9) $$L = na$$

so that L is the total length of the chain.

As $\left(\frac{FL}{nkT}\right) \to \pm\infty$, $E[X_3^n] \to \pm L$,

i.e., the chain becomes straight and aligned with the applied force, as we would expect.

For small $\left(\frac{FL}{nkT}\right)$, we have

(10) $$E[X_3^n] = L\left(\frac{1+\frac{1}{2}\left(\frac{FL}{nkT}\right)^2+\cdots}{\left(\frac{FL}{nkT}\right)+\frac{1}{6}\left(\frac{FL}{nkT}\right)^3+\cdots} - \frac{1}{\left(\frac{FL}{nkT}\right)}\right)$$

$$= \frac{L}{\left(\frac{FL}{nkT}\right)} \frac{\left(\frac{1}{2}-\frac{1}{6}\right)\left(\frac{FL}{nkT}\right)^2+\cdots}{1+\frac{1}{6}\left(\frac{FL}{nkT}\right)^2+\cdots}$$

$$= L\,\frac{1}{3}\left(\frac{FL}{nkT}\right)+\cdots$$

Ignoring higher-order terms, and solving for F, we get

(11) $$F = \frac{3nkT}{L^2} E[X_3^n]$$

This is the equation of a linear, or Hookean, spring of zero rest length.

Note the important point that the stiffness of the spring increases with increasing temperature. This is a sure sign that we are dealing with an entropic effect.

Equation (11) can also be expressed in terms of mean squared end-to-end distance of the spring at zero force. This is given by

(12) $$E[R^2]_{F=0} = na^2 = \frac{L^2}{n}$$

Since the $\underline{D}^i$ are independent random variables, and each of them has variance a^2 when $F=0$.

Thus, equation (11) can also be written

$$F = \frac{3kT}{E[R^2]_{F=0}} \, E[X_3^n] \tag{13}$$

Thermodynamics of the freely jointed chain

Now we investigate the thermodynamics of the freely jointed chain, taking as our starting point the equation of state (8). Here we write X instead of $E[X_3^n]$. This equation of state then becomes

$$X = L\left(\frac{\cosh \frac{FL}{nkT}}{\sinh \frac{FL}{nkT}} - \frac{1}{\frac{FL}{nkT}}\right) \tag{14}$$

We use (F, T) as our independent variables.

The equation of conservation of energy for reversible changes is

(15) $$dU = T\,dS + F\,dX$$

since $F\,dX$ is the work done by the external force F when X changes.

By considering changes in F with T held constant, and then changes in T with F held constant, we get

(16) $$\frac{\partial U}{\partial F} = T\frac{\partial S}{\partial F} + F\frac{\partial X}{\partial F}$$

(17) $$\frac{\partial U}{\partial T} = T\frac{\partial S}{\partial T} + F\frac{\partial X}{\partial T}$$

On physical grounds, we know that U can be at most a function of T, since the freely jointed chain has rigid links and therefore no means of storing potential energy, but we proceed here as if we do not know this, since it will be interesting to see whether this fact is somehow contained in the equation of state.

The next step is to differentiate with respect to T in (16) and with respect to F in (17):

$$\frac{\partial^2 U}{\partial F \partial T} = \frac{\partial S}{\partial F} + T\frac{\partial^2 S}{\partial F \partial T} + F\frac{\partial^2 X}{\partial F \partial T} \tag{18}$$

$$\frac{\partial^2 U}{\partial T \partial F} = T\frac{\partial^2 S}{\partial T \partial F} + \frac{\partial X}{\partial T} + F\frac{\partial^2 X}{\partial T \partial F} \tag{19}$$

It follows from this pair of equations that

$$\frac{\partial S}{\partial F} = \frac{\partial X}{\partial T} \tag{20}$$

Now we need to evaluate $\partial X/\partial T$ from (14). To facilitate this, let

$$A(\theta) = \frac{\cosh(\theta)}{\sinh(\theta)} - \frac{1}{\theta} \tag{21}$$

$$\theta = \frac{FL}{nkT} \tag{22}$$

Note that

(23) $$F \frac{\partial \theta}{\partial F} = \theta$$

(24) $$T \frac{\partial \theta}{\partial T} = -\theta$$

and therefore

(25) $$F \frac{\partial \theta}{\partial F} + T \frac{\partial \theta}{\partial T} = 0$$

In the above notation, our equation of state (14) is

(26) $$X = L A(\theta)$$

and from this we have

(27) $$\frac{\partial X}{\partial F} = L A'(\theta) \frac{\partial \theta}{\partial F}$$

(28) $$\frac{\partial X}{\partial T} = L A'(\theta) \frac{\partial \theta}{\partial T}$$

Now making use of (20) in (16), we have

(29) $$\frac{\partial U}{\partial F} = T\frac{\partial X}{\partial T} + F\frac{\partial X}{\partial F}$$

$$= LA'(\theta)\left(T\frac{\partial \theta}{\partial T} + F\frac{\partial \theta}{\partial F}\right) = 0$$

in which we have used (27) & (28), and then (25).

Thus we have indeed been able to show that U is a function only of T and not also of F. It is interesting that this is implicit in our equation of state

We would now like to determine the entropy. From equation (16)

(30) $$\frac{\partial S}{\partial F} = \frac{\partial X}{\partial T} = LA'(\theta)\,\frac{\partial \theta}{\partial T} = -\frac{L}{T}A'(\theta)\,\theta$$

Integrating over the interval $(0, F_1)$ with T constant, we get

(31) $$S(F_1,T) - S(0,T) = -\frac{L}{T}\int_0^{F_1} A'(\theta)\theta\, dF$$

But

(32) $$\frac{L\,dF}{T} = nk\, d\theta$$

so we can change variables in the integral, and rewrite (31) as follows

(33) $$S(F_1,T) - S(0,T) = -nk\int_0^{\theta_1} A'(\theta)\theta\, d\theta$$

$$= -nk\int_0^{\theta_1}\left((A(\theta)\theta)' - A(\theta)\right)d\theta$$

$$= -nk\left(A(\theta)\theta\Big|_0^{\theta_1} - \int_0^{\theta_1} A(\theta)\,d\theta\right)$$

From (21),

(34) $$\theta A(\theta) = \frac{\theta}{\tanh(\theta)} - 1$$

and this is 0 at $\theta = 0$, so

(35) $$\theta A(\theta)\Big|_0^{\theta_1} = \left(\frac{\theta_1}{\tanh(\theta_1)} - 1\right)$$

Also from (21),

(36) $$\int_0^{\theta_1} A(\theta)\,d\theta = \Big(\log(\sinh(\theta)) - \log(\theta)\Big)\Big|_0^{\theta_1}$$

$$= \log\left(\frac{\sinh(\theta)}{\theta}\right)\Big|_0^{\theta_1} = \log\left(\frac{\sinh(\theta_1)}{\theta_1}\right)$$

Putting everything together, and dropping the subscript 1, and also changing the sign on both sides of (33), we get

(37) $$S(0,T)-S(F,T) =$$

$$nk\left(\frac{\theta}{\tanh(\theta)} - 1 - \log\left(\frac{\sinh(\theta)}{\theta}\right)\right)$$

where, as before,

(38) $$\theta = \left(\frac{FL}{nkT}\right)$$

Note that the right-hand side of (37) is an even function of θ.

For small θ,

(39) $$\frac{\theta}{\tanh\theta} - 1 = \frac{\theta\left(1+\frac{1}{2}\theta^2+\cdots\right)}{\theta+\frac{1}{6}\theta^3+\cdots} - 1$$

$$= \frac{1+\frac{1}{2}\theta^2+\cdots}{1+\frac{1}{6}\theta^2+\cdots} - 1 = \frac{1}{3}\theta^2 + \cdots$$

and

$$(40) \quad \log \frac{\sinh\theta}{\theta} = \log \frac{\theta + \frac{1}{6}\theta^3 + \cdots}{\theta}$$

$$= \log\left(1 + \frac{1}{6}\theta^2 + \cdots\right) = \frac{1}{6}\theta^2 + \cdots$$

so

$$(41) \quad S(0,T) - S(F,T) = nk\left(\frac{1}{3} - \frac{1}{6}\right)\theta^2 + \cdots$$

$$= \frac{nk}{6}\left(\frac{FL}{nkT}\right)^2 + \cdots$$

This shows that the entropy is indeed maximal* at $F=0$, as we would expect.

*at least locally. It would be nice to prove that the right-hand side of (37) is positive for non-zero θ and indeed that it is increasing as a function of $|\theta|$.

As $F \to +\infty$, which is the same as $\theta \to +\infty$

(42) $$S(0,T) - S(F,T)$$

$$\sim nk\left(\theta - 1 - \log\left(\frac{e^{\theta}}{2\theta}\right)\right)$$

$$\sim nk \log(2\theta) \sim nk \log \theta$$

$$= nk \log\left(\frac{FL}{nkT}\right)$$

and this approaches $+\infty$, although only logarithmicly. Thus there is an infinite entropy difference between the zero-force state and the infinite-force state (in which the chain is stretched out straight.) Intuitively, the latter state has zero entropy, but any other state has a continuum of configurations available and therefore has infinite entropy. Nevertheless, the entropy differences between finite-force states turn out to be finite.

Homework

1) Evaluate $E[R^2]$ as a function of F, where

(43) $$R^2 = \left\| \sum_{i=1}^{n} \underline{D}^i \right\|^2 = \sum_{i,j=1}^{n} \underline{D}^i \cdot \underline{D}^j$$

2) Computationally generate some equilibrium ensembles of freely jointed chains with applied force F.

Make some 3D plots to visualize these ensembles and observe how they change character as F increases.

Use the computed ensembles to estimate $E[X_3^n]$ and $E[R^2]$, and compare your computational results for various F to the theoretical values

See next page for suggestions how to proceed.

The key ingredient for part (2) of the homework is a method for sampling from the probability density

$$\rho_{\underline{D}}(\underline{\xi}) = \frac{e^{\lambda \xi_3}}{Z(\lambda)} \tag{44}$$

where $\lambda = \frac{F}{kT}$ and $\|\underline{\xi}\| = a$.

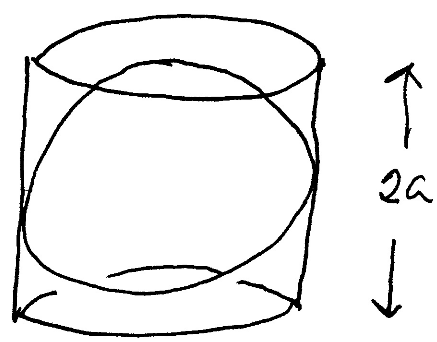
This can be done by the method of rejection, which does not require any reference at all to the normalizing factor $Z(\lambda)$.

The first thing that we need for the method of rejection in this case is a way to sample the uniform distribution on a sphere of radius a. I'll describe two simple ways to do this.

The first way uses Gaussian random variables and then normalizes the result:

```
D = randn(3, 1)
D = a * D / sqrt(D'*D)
```

The second way is more interesting. I'll call it Archimedes method. It exploits his discovery that there is an area-preserving map from a cylinder of height $2a$ and radius a to a sphere of radius a, as shown in his famous figure:



The map shrinks each horizontal circle on the cylinder to a corresponding circle <u>at the same height</u> on the sphere.

The Archimedes method is as follows

```
D(3) = a * (2* rand - 1)
theta = 2*pi * rand
r = sqrt (a^2 - D(3)^2)
D(1) = r * cos (theta)
D(2) = r * sin (theta)
```

An amazing feature of this method is that the resulting distribution on the sphere is perfectly isotropic even though the procedure is highly anisotropic. To see this visually, try generating some fairly large number of sample points and plot the result in 3D. There will be no hint of where the pole was.

Given a function rsphere(a) that generates a random point from the uniform distribution in a sphere of radius a, we can use the method of rejection to sample from the probability density (44) as follows:

```
rhonummax = exp(abs(lambda) * a)

h = rand * rhonummax

D = rsphere(a)

while (h > exp(lambda * D(3)))

    h = rand * rhonummax

    D = rsphere(a)

end
```

Remark:

Since $D(3)$ is actually uniform (see Archimedes' method, above), one could be more efficient by doing the rejection only on $D(3)$, without calling rsphere, and then, after $D(3)$ has been chosen, choose $D(1)$ and $D(2)$ as in the Archimedes' method.