Module 4 : Nonlinear elasticity

Lecture 36 : Entropic Elasticity

The Lecture Contains

- Entropic Elasticity
- Highly Stretched Chain
- Elasticity of a Crosslinked Network

"Mechanics of the Cell" by David Boal, Cambridge University Press, 2002, Cambridge, UK

◀▌▌Previous   Next ▌▌▶

Entropic elasticity

As mentioned earlier, far more chain configurations have end-to-end displacement close to the mean value of r_{ee} than to the chain contour length L_c. From statistical thermodynamics, it can be shown that entropy is proportional to the logarithm of the number of configurations:

$$S = k_b \ln(P) = k_b \left[A - \frac{x^2 + y^2 + z^2}{2\sigma^2} \right] = k_b \left[A - \frac{r^2}{2\sigma^2} \right] \tag{36.1}$$

so that maximum entropy occurs for $r = \sqrt{x^2 + y^2 + z^2} = 0$ and it decreases as the chain is stretched from its equilibrium length. For free joined chains, the configurations all have vanishing energy, so that the Helmhotz free energy of a chain is defined as, $F = -TS$. Thus with increase in F, e.g. the chain is stretched, S decreases, i.e. work must be done to stretch the chain and it is elastic by virtue of its entropy. The force of retraction arising from the entropy change is

$$f = -\frac{\partial F}{\partial r} == -T\frac{\partial S}{\partial r} = \frac{k_b T}{\sigma^2} r \tag{36.2}$$

Thus the effective spring constant of the chain is be found out $k_{sp} = \frac{k_B T}{\sigma^2}$ where, $\sigma^2 = \frac{Nb^2}{3}$ for a three dimensionally oriented chain. Thus the expression for spring constant is obtained as,

$$k_{sp} = \frac{3k_B T}{Nb^2} = \frac{3k_B T}{2L_p L_c} \tag{36.3}$$

It should be noted that k_{sp} increases with temperature which can be readily verified in experiments.

Highly stretched chain

The Gaussian probability distribution is a good description of chain behavior at small displacements from equilibrium. It shows that the force required to produce an extension x in the end-to-end distance is

$$f = \left(\frac{3k_B T}{2L_p L_c}\right) x \tag{36.4}$$

which can be written as,

$$\frac{x}{L_c} = \left(\frac{2L_p}{3k_B T}\right) f \tag{36.5}$$

However if the segments of the chain are individually inextensible, the force required to extend the chain should diverge as the chain approaches its maximum extension, $\frac{x}{L_c} \to 1$. Such a divergence is not predicted by equation 36.4, signifying that the Gaussian distribution becomes increasingly inaccurate and finally invalid as the chain is stretch to its contour length. The force-extension for rigid freely jointed rods can be obtained analytically. This solution has the form,

$$\frac{x}{L_c} = \mathscr{L}\left(\frac{2L_p f}{3k_B T}\right) \tag{36.6}$$

where $\mathscr{L}(y)$ is the Langevin function given as,

$$\mathscr{L}(y) = \coth(y) - \frac{1}{y} \tag{36.7}$$

Note that x is the projection of the end-to-end displacement in the direction of the applied force. For small values of f, equation 36.6 reduces to Gaussian expression in equation 14.59. For very large value of f the Langevin function tends to 1, so that x asymptotically approaches L_c.

Although, the force-extension data derived from the freely jointed rod model gives reasonably accurate data for bio-polymers, its main drawback lies in the assumption of the chain segments being rigid. Actually, for bio-polymers like microtubules, DNA, the filaments are continuously flexible, so that they are better described by the worm-like-chain (WLC) model. The following relation describes a nearly accurate description of the WLC model which has been very useful in describing the extension of DNA,

$$\frac{L_p f_c}{k_B T} = \frac{1}{4}\frac{1}{(1 - x/L_c)^2} - \frac{1}{4} + \frac{x}{L_c} \tag{36.8}$$
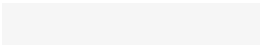
Elasticity of a crosslinked network

We have so far deduced the extensional force required to stretch a single chain by a distance x. Now, we will consider not a single chain but a network of chains in which the chains are permanently connected in certain randomly distributed joints. This kind of network occurs for rubber like materials in which the crosslinkages are introduced by vulcanization of the rubber. When the rubber material is deformed by applying some external stress, it alters the positions of these crosslinkages and thus internal state of the network. The states of the network can be represented by a system of vectors connecting neighboring crosslinking points. Let us mark the volume elements surrounding each crosslinking point as 1, 2, 3 … Then the number of vectors terminating each volume element can be represented by v_i so that the total number v of chains remain constant $v = \sum_i v_i$. Each such chain can assume number of configurations by altering the intervening portion while its end-to-end displacement vector remain unaltered. The relative number of such configurations for a chain having vector terminating to i-th cell with co-ordinates x_i, y_i, z_i are $P_i(x_i, y_i, z_i)$. Hence this quantity for v_i number of such chains is $\left[P_i(x_i, y_i, z_i) \right]^{v_i}$. Then the probability for the entire network to be found at a particular configuration is obtained by finding the product of all such probability over all the volume elements,

$$P = \prod_i \left[P_i(x_i, y_i, z_i) \right]^{v_i} \tag{36.9}$$

The entropy of the network is then found as

$$S = k_b \ln(P) = k_b \sum_i v_i \ln \left[P_i(x_i, y_i, z_i) \right] = k_b \sum_i v_i \left[A - \frac{\left(x_i^2 + y_i^2 + z_i^2 \right)}{2\sigma^2} \right] \tag{36.10}$$

Since the cross-linkages are introduced in random manner in the undeformed state of the network, the number of chains v_i terminating in the i-th volume element can be written as,

$$v_i = v P_i(x_i, y_i, z_i) dx\, dy\, dz \tag{36.11}$$

Previous   Next

Elasticity of a crosslinked network

Now say the network is elongated in the z direction by a factor λ. Then assuming that the relative positions of the network junctions change according to the macroscopic dimension of the sample, the z co-ordinate of each joint alters by a factor λ and the x and y co-ordinates alter by $\dfrac{1}{\sqrt{\lambda}}$. Thus the volume remains constant. To say it somewhat differently a junction which possess a new position z after stretching, actually was in $\dfrac{z}{\lambda}$ before stretching and its x and y co-ordinates were $x\sqrt{\lambda}$ and $y\sqrt{\lambda}$. Using these new co-ordinates, the expression for the probability P_i from equation 35.16 can be written as

$$P'_i = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-\frac{(\lambda x_i^2 + \lambda y_i^2 + z_i^2/\lambda^2)}{2\sigma^2}\right)$$
(36.12)

Then from equations 36.10 and 36.11, replacing the summation sign by integral sign, the expression for entropy is obtained as.

$$S = k_b \ln(P)$$
$$= k_b \nu \iiint_{-\infty \to \infty} \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left[-\frac{\lambda x^2 + \lambda y^2 + z^2/\lambda^2}{2\sigma^2}\right]\left[A - \frac{(x^2 + y^2 + z^2)}{2\sigma^2}\right] dx\, dy\, dz$$
(36.13)

The above integral has been estimated for change of entropy because of passing from undeformed to deformed state:

$$\Delta S = S(\lambda) - S(1) = -\frac{k_b \nu}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$
(36.14)

Then entropic contribution to the elastic force can be obtained as,

$$f = -T\frac{\partial S}{\partial L} = -\frac{T}{L_0}\frac{\partial S}{\partial \lambda} = -\frac{k_b \nu T}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$
(36.15)

Where L_0 is the initial length of the sample. Thus we obtain a new law relating force of extension and the extent of extension.

◀ Previous   Next ▶