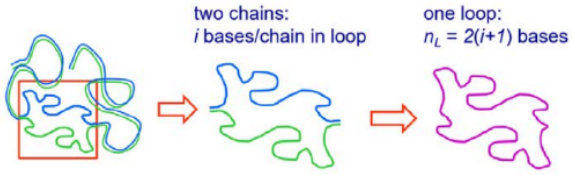
# 7.3: Polymer Loops

For certain problems, we are concerned with cyclic polymers chains:

- Bubbles/loops in DNA melting
- Polypeptide and RNA hairpins
- DNA strand separation in transcription
- Cyclic DNA, chromosomal looping, and supercoiling




In describing macromolecules in closed loop form, the primary new variable that we need to address is the loop's configurational entropy. Because of configurational constraints that tie the ends of a loop together ($R_{ee} \to 0$) the loop has lower configurational entropy than an unrestrained coil.

Let's describe how the configurational entropy of a loop $S_L$ depends on the size of the loop. We will consider the segment model with $n_L$ segments in the loop. We start with the radial probability distribution for an unconstrained random coil, which is the reference state for our calculations:

$$P(r,n) = 4\pi r^2 \left(\frac{3}{2\pi n\ell^2}\right)^{3/2} \exp\left[-\frac{3}{2}\frac{r^2}{n\ell^2}\right] \tag{7.3.1}$$

The entropy of the loop $S_L$ will reflect the constraints placed by holding the ends of the random coil together, which we describe by saying the ends of the chain must lie within a small distance $\Delta r$ of each other. Since $R_{ee} < \Delta r$, $\Delta r^2 \ll n\ell^2$, and the exponential term in eq. (7.3.1) is $\sim 1$. Then the probability of finding a random coil configuration with an end-to-end distance within a radius $\Delta r$ is

$$\begin{aligned} P_L(n_L) &\approx \int_0^{\Delta r} dr 4\pi r^2 \left(\frac{3}{2\pi n_L \ell^2}\right)^{3/2} \\ &= \left(\frac{6}{\pi}\right)^{1/2} \left(\frac{\Delta r}{\ell}\right)^3 n_L^{-3/2} \\ &\equiv b n_L^{-3/2} \end{aligned}$$

In the last line we find that the probability of finding a looped chain decreases as $P_L \propto n_L^{-3/2}$, where $b$ is the proportionality constant that emerges from integration. From the assumptions we made, $b \ll 1$, and $P_L < 1$.

To calculate the configurational entropy of the chain, we assume that the polymer (free or looped) can be quantified by $\Omega$ configurational states per segment of the chain. This reflects the fact that our segment model coarse-grains over many internal degrees of freedom of the macromolecule. Then, the entropy of a random coil of n segments is $S_C = k_B \ln \Omega^n$. To calculate the loop entropy, we correct the unrestrained chain entropy to reflect the constraints placed by holding the ends of the random coil together in the loop.

$$S_L = S_C + k_B \ln P_L$$

This expression reflects the fact that the number of configurations available to the constrained chain is taken to be $\Omega_L(n_L) = \Omega^{n_L} P_L(n_L)$, and each of these configurations are assumed to be equally probable ($S_L = k_B \ln \Omega_L$). Since $P_L < 1$, the second term is negative, lowering the loop entropy relative to the coil. We find that we can express the loop configurational entropy as

$$S_L(n_L) = k_B \left[n_L \ln \Omega - b - \frac{3}{2}\ln n_L\right]$$

Since this expression derives from the random coil, it does not account for excluded volume of the chain. However, regardless of the model used to obtain the loop entropy, we find that we can express it is the same form:

$$S_L(n_L) = k_B \left[ n_L a - b + c \ln n_L \right]$$

where $a$, $b$, and $c$ are constants. For the random coil $c = 1.50$, and for a self-avoiding random walk on a cubic lattice we find that it increases to $c = 1.77$. In 2D, a random coil results in $c = 1.0$, and a SAW gives $c = 1.44$.

## Readings


1. M. Rubinstein and R. H. Colby, *Polymer Physics*. (Oxford University Press, New York, 2003).
2. K. Dill and S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*. (Taylor & Francis Group, New York, 2010).
3. C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry Part III: The Behavior of Biological Macromolecules*. (W. H. Freeman, San Francisco, 1980).
4. R. Phillips, J. Kondev, J. Theriot and H. Garcia, *Physical Biology of the Cell*, 2nd ed. (Taylor & Francis Group, New York, 2012).
5. P. J. Flory, *Principles of Polymer Chemistry*. (Cornell University Press, Ithaca, 1953).