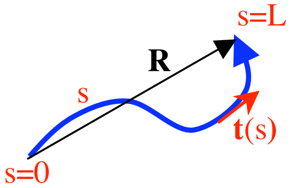
Lecture 24: Polymers: Persistence length and the worm-like chain

Problem Set 4, officially due Nov. 8 but will be accepted Wednesday, Nov. 10.
Reading for Lectures 22—24: PKT Chapter 8



Finally, a continuum version of these models:

6. Wormlike-chain model.

The blue curve represents a polymer chain which is a smooth, bendable, but inextensible rod.
The coordinate s measures distance along the contour. runs from 0 to L.
The red unit vector $\hat{t}(s)$ is the unit tangent vector at each point s.
$\hat{t}(s)ds$ is like an infinitesimal polymer segment $d\vec{a} \to \hat{t}(s)ds$.

The end-to-end length is $\vec{R} = \int_0^L ds\,\hat{t}(s)$.

In this model, this continuous polymer chair is characterized by a stiffness, so it takes energy to change the direction of the normal vector $\hat{t}(s)$. Of course, $\langle \hat{t}(s)\cdot\hat{t}(s')\rangle \to 1$ as $s \to s'$ because $\hat{t}(s)$ is a unit vector; $\langle \hat{t}(s)\cdot\hat{t}(s')\rangle \to 0$ as $|s-s'| \to \infty$ because the polymer loses track of its original direction. And, because of the stiffness, the directional correlation drops off exponentially as s' moves away from s:

$\langle \hat{t}(s)\cdot\hat{t}(s')\rangle = e^{-\frac{|s-s'|}{\xi_p}}$, where $\xi_p(T)$ is called the "persistence length" and for "long" polymers at sufficiently high $\xi_p(T) << L$.

We'll estimate $\xi_p(T)$ later. At this point what I want to do is to relate it to the Kuhn length for this model.

Thus, $\langle R^2\rangle = \left\langle \left(\int_0^L ds\,\hat{t}(s)\right)\cdot\left(\int_0^L ds'\,\hat{t}(s')\right)\right\rangle = \int_0^L ds \int_0^L ds'\, e^{-\frac{|s-s'|}{\xi_p}} = 2\xi_p L + \text{small}$, i.e. $\boxed{\ell_K = 2\xi_p}$ whenever the tangent correlations fall off exponentially with distance.

Let's do the calculation:

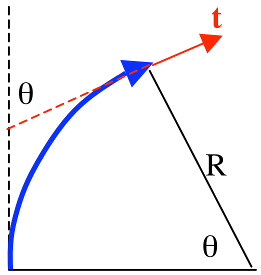
Note parallels to the discrete models 4 and 5 above.

$$\int_0^L ds \int_0^L ds'\, e^{-\frac{|s-s'|}{\xi_p}} = 2\int_0^L ds \int_0^s ds'\, e^{-\frac{(s-s')}{\xi_p}} = 2\xi_p \int_0^L ds\, e^{-\frac{s}{\xi_p}} e^{\frac{s'}{\xi_p}}\Big|_{s'=0}^{s'=s} = 2\xi_p \int_0^L ds \left(1 - e^{-\frac{s}{\xi_p}}\right) = 2\xi_p L - 2\xi_p^2\left(1 - e^{-\frac{L}{\xi_p}}\right)$$

So, $\langle R^2\rangle = 2\xi_p L + \text{small}$, as claimed. (as long as $\xi_p << L$)

Estimating ξ_p for the worm-like chain model:

It costs energy to bend a flexible elastic rod, just as it costs energy to stretch a spring.
Assume the rod is initially straight and you bend it into the arc of a circle of radius R:
The deformation of the rod material stores energy.



The density of energy (energy per unit length) is equal to $\frac{\kappa}{2R^2}$, where κ is called the "stiffness" or "rigidity modulus."

This is analogous to writing the energy of the spring as $F = -kx \Rightarrow E = \frac{kx^2}{2}$.

Thus, the energy of the whole rod is $E = \frac{\kappa}{2}\int_0^L ds \frac{1}{R^2(s)}$.

Comment: There are different ways of writing this $\frac{1}{R(s)} = \frac{d\theta}{ds} = \left|\frac{d\hat{t}}{ds}\right|$,

so sometimes this energy is written $E = \frac{\kappa}{2}\int_0^L ds \left|\frac{d\hat{t}}{ds}\cdot\frac{d\hat{t}}{ds}\right|$ (PKT).

Q: How long will the persistence length ξ_p be?

A: Qualitatively, ξ_p is the shortest distance Δs you have to go along the backbone so that the polymer has lost track of its original direction just due to thermal fluctuations:

Energy cost of angle θ change at radius R= $\varepsilon(R,\theta) = \frac{\kappa}{2R^2}\cdot\Delta s = \frac{\kappa}{2R^2}\cdot R\theta$ with θ in radians. To lose track of direction we need $\theta > 90^o$--say, $\theta = 2\ (\sim 120^o)$, so $\varepsilon = \frac{\kappa}{R} \sim k_B T$, which implies $R \equiv \xi_p \sim \frac{\kappa}{k_B T}$,

i.e., in this model the Kuhn length $\ell_K = 2\xi_p \sim \frac{2\kappa}{k_B T}$.

Note how the persistence length grows as stiffness increases or T decreases.

Message:

All kinds of short-ranged effects do change the random-walk behavior but only by changing the monomer separation a into a Kuhn length/persistence length (which may be temperature and structure dependent). The overall dependence $\langle R^2\rangle \sim L,N$ and the Guassian distribution of end-to-end distances is not changed. Picture is that the "random-coil" polymeric macrostate is a loose spaghetti-like object of spatial size $\sqrt{\langle R^2\rangle} \sim \sqrt{aL}$.

This "blob" of material is not very dense:

Its volume is $V \sim (aL)^{3/2}$ while the actual volume of material it contains is $v \sim a^2 L$, thus the fraction of space inside the blob that is filled with solid material is $f = \frac{v}{V} \sim \sqrt{\frac{a}{L}} \sim \frac{1}{\sqrt{N}}$ which is very small for a long polymer. Interactions between distant parts of the polymer chain are improbable—as if the each monomer were immersed in a "gas" of distant monomers of density $n_{gas} = \frac{N}{V} = \frac{1}{a^3\sqrt{N}}$, which is low for large N. It follows that interactions between distant monomers are relatively unimportant in the random-coil state, just as they are in the ideal gas (all gases "ideal" in the low-density limit).

What is the effect of "long-range" interactions?

A: Self-avoidance:

It turns out that, although this is not a "big" effect, as indicated above, conceptually it is a profound change (but that's not important biologically, as far as I know).

This is a "repulsive" effect, so you would expect $\langle R^2\rangle$ to increase.

Q: Is this change just an increase in the Kuhn length, as it is for short-range interactions?

A: No!

Result is $\boxed{\langle R^2\rangle \sim a_{eff}^2 N^{2\nu}.}$

Without self-avoidance, $\nu = 1/2$ (independent of the dimension of space).

With self-avoidance, however, the "critical exponent" $\nu(d)$ becomes dependent on dimension d, with $\nu(1) = 1, \nu(2) = 3/4, \boxed{\nu(3) = 0.59...,} \nu(4) = 1/2$. (Details of how this occurs are hard.)

Note that this is a large effect in low dimension, a relatively small one in 3D, and we get back the random-coil behavior in 4D.

The Gaussian distribution is also changed: $P_N(R) \sim e^{-\alpha\left(\frac{R}{N^{\nu}}\right)^{1/(1-\nu)}}$,
which agrees with previous result when $\nu = 1/2$.

B. Attractive interactions

When polymeric segments attract, then (at low-enough temperatures, at least), the chain will fold up into a tight "compact" shape. That's how nature designs proteins.

Important comment:

In biological systems, polymers exist in solution. A polymer which is "hydrophobic," i.e., which does not like to dissolve in water is forced into a compact configuration by its desire to minimize water exposure. Thus, hydrophobicity provides an important source of "effective" attraction between the monomers.

As a special case, which we will discuss more next time, proteins are amino-acid polymers. Some amino acids are hydrophobic, others are polar (hyrdrophilic). Thus, proteins are forced towards compact configurations in which the hydrophobic residues are shielded from water by being forced towards the interior and the polar residues "coat" the surface.

Of course, at high-enough temperatures, the compact shapes will generally return to the random-coil "phase." This is governed by an energy-entropy trade off.

At fixed T, the preferred configurations will be the ones with lowest Helmholtz free energy F=E-TS.

The E term is easy to estimate:

E~0 for the random-coil configurations, as given on p. 24.2.

For the compact configurations, each of the N monomers is surrounded by an environment of a small number (2—4?) other monomers close enough to interact (attractively), thus, $E \approx \varepsilon N$ with $\varepsilon < 0$. (This ignores the surface layer, which is unimportant for large N.)

The entropy of the random-coil configurations is easy to estimate from $S = k_B \ln W$, since the number of configurations is $W \sim z^N$, where z is the number of directional choices which the polymer can make at each link (e.g., z=6 for the cubic walk or z=5 for the cubic walk without immediate reversal). Thus, $S_{coil} \sim Nk_B \ln z$. The compact entropy is small.

Thus, to first approximation:

$$F_{coil} \approx -TS = -Nk_BT\ln z$$

$$F_{compact} \approx E = -|\varepsilon|N$$

You can see that, if there are attractive long-range interactions, the compact configurations will have lower free energy at low T, while the random-coil configurations will have lower free energy at large T. And, there will be a transition between these phases when $|\varepsilon| = k_BT\ln z$. This is why/how proteins denature on heating.